Phosphine Ligands Bearing Donor Sites for the Binding of Lewis Acids: Synthesis, Characterization, and Application in Homogeneous Catalysis

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Novel phosphine ligands bearing additional donor sites in the backbone for the binding of Lewis acids were obtained by the condensation of functionalized anilines and (3-formylphenyl)diphenylphosphine. The corresponding Rh(I) complexes obtained by reaction with $[(CO)_2Rh(\mu\text{-}Cl)]_2$ were characterized by means of spectroscopy and show unexpected changes in the ^{31}P NMR spectra in the presence of Lewis acids such as KPF_6 and $Zn(OTf)_2$ (OTf = triflate = trifluoromethanesulfonate). They are catalytically active in the hydroaminomethylation of 1-pentene and styrene.

Introduction

The development of homogeneous catalysis in general and, in particular, the development of ligands used in catalytic reactions can be regarded as evolutionary processes. With simple compounds such as triphenylphosphine as the starting materials, more and more complex systems were obtained by specific functionalization of the ligand core. This strategy allowed the adaptation of well-known catalysts to new types of reactions, to new reaction conditions, and to new ecological and economic requirements. Electronic and steric variation of the ligand donor sites enables the "fine-tuning" of homogeneous catalysts, an intrinsic advantage of homogeneous over heterogeneous catalysis. In this manner, yields and selectivities of a number of homogeneously catalyzed reactions have been improved considerably during the last years, which especially enriched fine chemical synthesis with important methods. Parallel to this, a series of "new" solvents such as water, supercritical carbon dioxide, ionic liquids, and fluorinated hydrocarbons was established for catalytic reactions. These solvents have only rarely been used in organic synthesis before. All these innovations were only possible by further improvement of known ligand systems.[1−3] As an example, we have been working on the introduction of long alkyl chains into ligands applied to coordination to high-valent transition-metal sites, which allowed the application of these catalysts in nonpolar solvents: e.g. for catalytic olefin epoxidation.[4,5]

A comparison of ligands for homogeneous catalysis with the complexity (and selectivity) of metalloproteins[6,7] shows that the efforts discussed above can only be considered as first steps in the right direction. However, the search for complexes that will better model the active sites of metalloproteins will run into essential problems: the structure of proteins is determined by a multitude of weak chemical interactions, which are difficult to completely quantify by the modern methods of structure determination (NMR, X-ray). Additionally, the expenses for the synthesis of more and more complex ligands will increase and will become a critical factor, at least for industrially relevant systems.

To solve these problems, we are not looking for new model complexes for metallo proteins but are trying to implement new functionalities in known ligand systems, which allow us to transfer some of the principles realized by nature in enzymes to homogeneous catalysis. One of the things we are interested in is the increase in rigidity of a given ligand backbone by reversible (e. g. coordinative or hydrogen bonds) or irreversible but self-organizing covalent interactions. The desired ligands should show lowered mobility but should also be synthesized in just a few steps. Additionally, these ligands should possess extra binding sites for either substrates or reagents, which will enhance the activity or selectivity of the catalyst without interacting directly with the active site.

Results and Discussion

Ligand Synthesis. On the way to phosphine ligands bearing functions for self-organization and recognition

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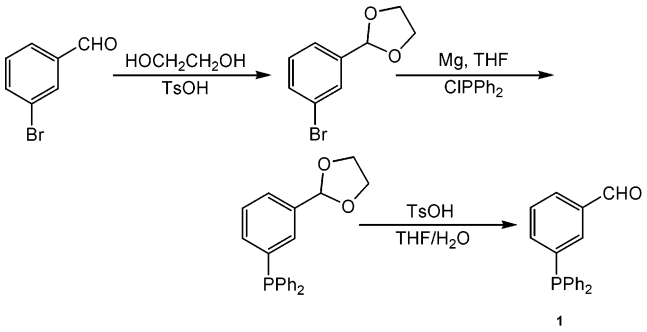
Scheme 1



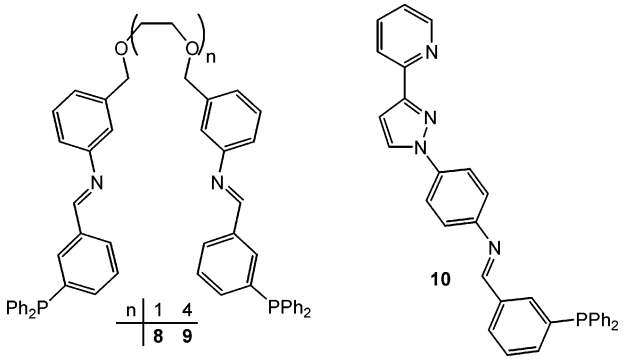
of Lewis acids, we were looking for a kind of "construction kit" allowing the implementation of different functions at a triphenylphosphine type ligand motif. It turned out to be favorable to use an imine group as a linker between the phosphine site and the functionalized site. This strategy requires an aldehyde group attached at one of the phenyl rings of PPh_3. A molecular mechanics study showed that linkage via a meta substitution is crucial for the later interaction of two ligands at the back side of the metal center.

(3-Formylphenyl)diphenylphosphine (**1**) was obtained in up to 50 g yield, with 3-bromobenzaldehyde as starting material, in excellent yields by a modified published procedure (Scheme 1).[8] It is a highly viscous colorless oil exhibiting a resonance at −4.48 ppm in the ^{31}P NMR spectrum.

Substituted anilines were chosen as the second component for the formation of the imine linker. They are accessible by two different strategies, which allow us to bind the functionalized moieties either directly or by an additional short CH_2 linker to the PPh_3 site. It is possible to build up these molecules by starting from 3-nitrobenzyl chloride or via a nucleophilic aromatic substitution with 4-fluoronitrobenzene. In both cases the remaining nitro group can be reduced to the desired amino function.

Following the first strategy allows the linkage of two PPh_3 units via polyether chains of different lengths, as shown in Scheme 2. Glycols such as ethylene and tetraethylene glycol are substituted with 3-nitrobenzyl units when treated with 3-nitrobenzyl chloride (molar ratio 1:2) either after deprotonation of the OH group with NaH or under strongly basic conditions (NaOH) in a biphasic system (CH_2Cl_2/H_2O) with (NBu_4)Cl as a phase-transfer catalyst. The resulting bis(nitrophenyl) compounds **2** and **3** are smoothly reduced by 10% Pd-C/$NH_4(HCO_2)$ in dry MeOH to give the corresponding anilines **4** and **5** in excellent yields. The pyrazolylpyridine-substituted aniline **7** was obtained by a nucleophilic aromatic substitution of 4-fluoronitrobenzene with pyrazolylpyridine, leading to the nitro derivative **6**, which could be reduced to the aniline **7** under the same conditions as described above.

Chart 1

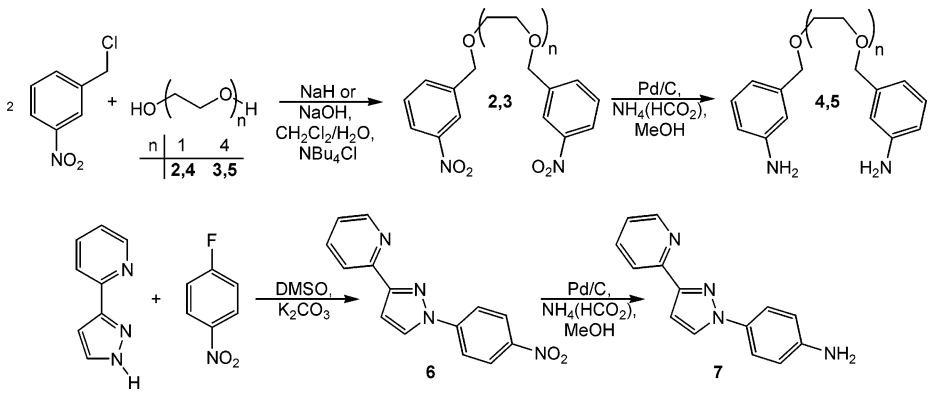


The condensation of the aldehyde **1** with the aromatic amines **4**, **5**, and **7** yielded the phosphine-substituted Schiff bases **8**−**10** (Chart 1), respectively.[9,10] The reaction was carried out under reflux conditions in dry EtOH. After the crystallization from MeOH (except for **9**, which is an oil), the Schiff bases were obtained in almost quantitative yields in all cases.

The imine groups formed could be clearly identified by their NMR resonances (^1H NMR δ 8.4 ppm, s; ^{13}C NMR δ 160.5−160.3) and their infrared absorptions at 1620−1626 cm^{-1}. All imine ligands show ^{31}P resonances at about −6.6 ppm, which are slightly shifted toward higher field compared to the signal for **1**. In the mass spectra (ESI-TOF, KSCN), each of the three compounds exhibited an $[M + K]^+$ peak with moderate to high relative intensities. Additional peaks typical for phosphine oxides $[M + O + K]^+$ for **8** and **10** and $[M + 2O + K]^+$ for **8** were observed, which are due to oxidation under the conditions of the ESI-TOF-MS, since ^{31}P NMR clearly excludes any phosphine oxide from being formed during the synthesis.

Rhodium Complexes. The rhodium complexes **11** and **12** bearing the chelating bis-phosphine ligands **8** and **9** were prepared by slowly dropping diluted solutions of $[(CO)_2Rh(\mu\text{-}Cl)]_2$ and the appropriate ligand simultaneously into large volumes of benzene, which prevents the formation of polymeric aggregates (Chart 2).

Scheme 2



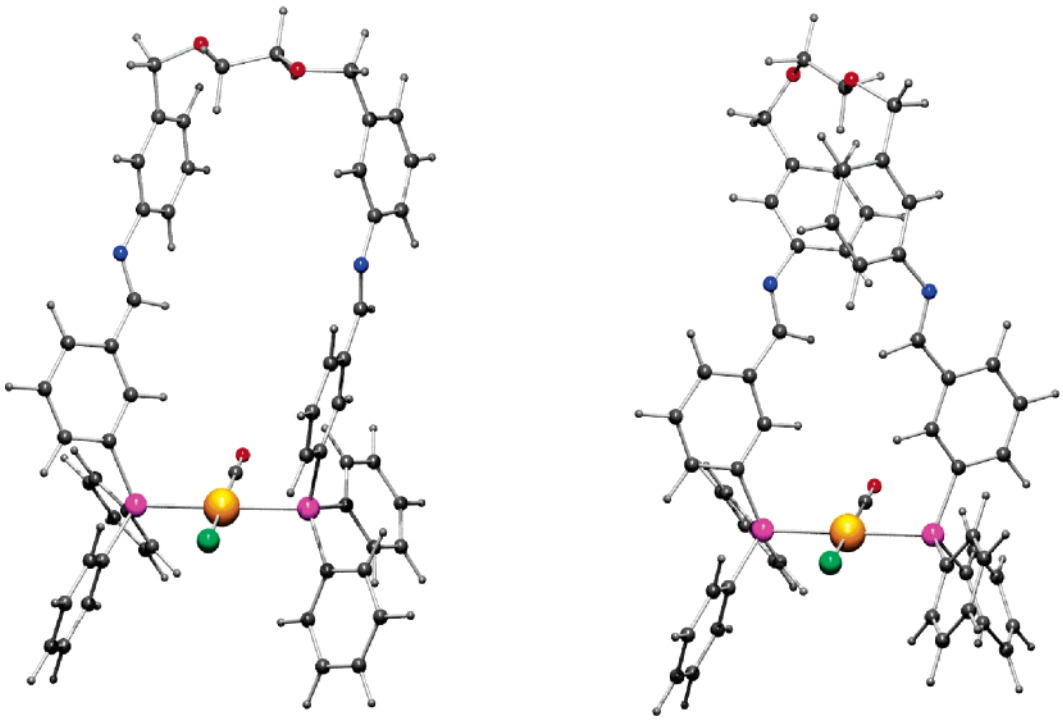
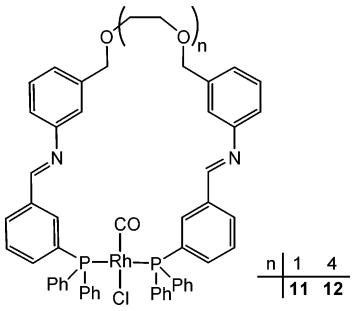


Figure 1. Visualization of the syn (left) and anti (right) conformers of the rhodium complex **11**, with structure generation by molecular mechanics calculations.[12]

Chart 2



After 1 h of stirring at room temperature, the complexes were obtained as microcrystalline solids in high yield (80−90%), which could be purified by slow diffusion of Et_2O into a CH_2Cl_2 solution. The infrared spectra show single CO absorptions at 1971 cm^{-1} for **11** and 1969 cm^{-1} for **12**, proving that the chelating ligands coordinate the rhodium center in a trans configuration.[11] There are just a few reports on cis-configured complexes of the type (P−P)Rh(CO)Cl obtained from short-chain chelating bis-phosphine ligands P−P, exhibiting typical CO absorptions at about 2010 cm^{-1}.[11]

Interestingly, the ^{31}P NMR spectra of both complexes show two doublets with chemical shifts of 28.2 and 28.3 ppm (ratio: 3:1) and $^1J_{RhP}$ values of 127.1 and 126.8 Hz for **11** and with chemical shifts of 28.7 and 28.6 ppm (ratio 4:1) and $^1J_{RhP}$ values of 128.4 and 127.6 Hz for **12**. This indicates that two different compounds with similar molecular structures are formed. Stereochemical considerations suggest two conformers differing in the relative orientation of the ligand backbone (shown in Figure 1 for **11**). Owing to the polyether linkage, the rotations around the two critical P−C_{Ph} bonds are hindered (at least on the time scale of the ^{31}P NMR), allowing the observation of two conformers with a syn or an anti orientation of the imine groups.

In the ^{13}C NMR spectrum of **12**, the CO resonance was observed as a doublet of triplets due to coupling to ^{31}P and ^{103}Rh (δ 187.5 ppm, $^1J_{RhC}$ = 74.2 Hz, $^2J_{PC}$ = 16.4 Hz). The ^{13}C NMR resonances of the ligand phenyl groups bound to phosphorus are split into two sets of signals, owing to the presence of the two conformers, which could not be separated up to now. Due to its poorer solubility, the resonance of the carbonyl ligand could not be detected in the ^{13}C NMR spectrum of **11**. Since the ether chain is shorter, two resonances are observed for each chemically inequivalent carbon atom of this compound.

In the ESI-TOF mass spectrum of complex **12**, recorded in the presence of KSCN, a peak with *m/e* 1176.0829 is in good agreement with the calculated value *m/e* 1176.2208 for a species resulting from an exchange of Cl^- with SCN^-, followed by the addition of K^+.

For the synthesis of **13**, 4 equiv of **10** dissolved in benzene was added dropwise to a solution of $[(CO)_2Rh(\mu\text{-}Cl)]_2$ in benzene, giving the desired complex in 81% yield (Chart 3).

A CO stretching frequency of 1961 cm^{-1}, which is comparable to that of $Rh(CO)Cl(PPh_3)_2$ at 1960 cm^{-1},[13] confirms the trans orientation of the phosphine ligands at the rhodium center. In this molecule, free rotation around the critical P−C_{Ph} bonds is possible and is fast with respect to the time scale of ^{31}P NMR spectroscopy,

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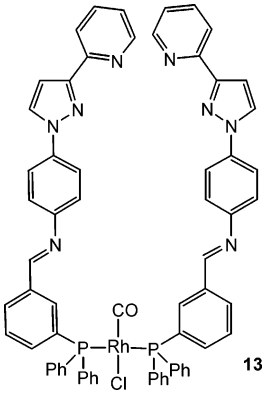
Chart 3



preventing the formation of conformers as in the case of **11** and **12**. Therefore, only one doublet is observed in the ^{31}P NMR spectrum of **13** (δ 28.4 ppm, $^{1}J_{RhP} = 127.8$ Hz). Consequently, the ^{13}C NMR and the ^{1}H NMR spectra only show one set of signals: e.g. the proton of the imine group as a singlet at 8.43 ppm. Owing to its poor solubility in most organic solvents, the ^{13}C NMR resonance of the carbonyl group of **13** could not be detected.

The data of ESI-TOF mass spectroscopic investigations at phosphine ligands **8** and **9** and the corresponding rhodium complexes obtained in the presence of KSCN gave the first hint of an interaction between the Lewis acid K^+ and the polyether chains of the bridging moieties. These interactions can also be observed in solution by means of ^{31}P NMR spectroscopy. While the ^{31}P resonances of complex **11** are only slightly shifted by the addition of 1−4 equiv of KPF_6, there is a fundamental change in the ^{31}P NMR spectrum of complex **12**, the compound with the long polyether bridge: even after the addition of 1 equiv of KPF_6 the signals of the syn and anti conformers start to coalesce. This means that the exchange between the conformers, which is slow with respect to the ^{31}P NMR time scale in the absence of KPF_6, is accelerated in the presence of the Lewis acid. In contrast to the behavior of **11** and **12**, the exchange between the syn and anti conformers is rapid for complex **13**, since the donor sites are not covalently connected. The addition of zinc trifluoromethylsulfonate ($Zn(OTf)_2$) in this case leads to a splitting of the ^{31}P NMR resonance into two signals (Figure 2), which we again assigned to syn and anti conformers. A slight change of the chemical shift is also observed.

Catalysis. The rhodium complexes **11**−**13** were tested as catalysts for two different hydroaminomethylation reactions:[14] On one hand, the reaction of 1-pentene and piperidine (Scheme 3) was used as a model system for the hydroaminomethylation of aliphatic olefins; on the other hand, the reaction of styrene and piperidine (Scheme 4) was tested as an example for the hydroaminomethylation of aromatic olefins. Selected examples of our study are summarized in Tables 1 and 2.

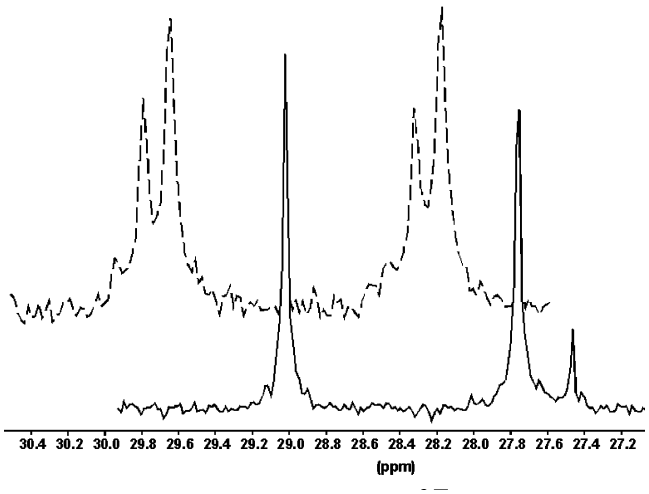
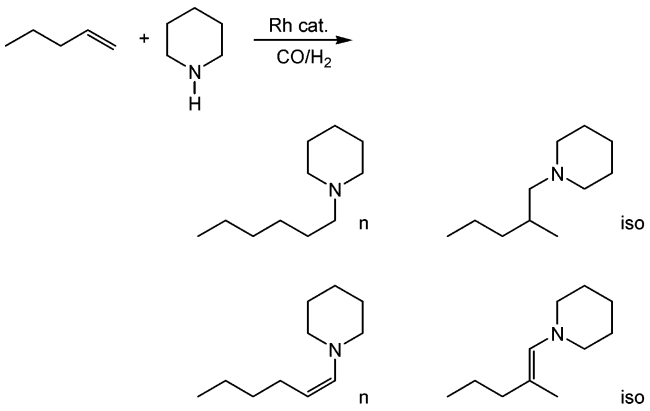
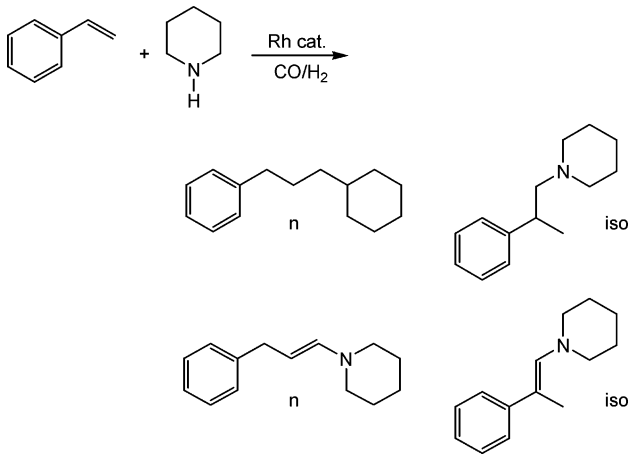


Figure 2. ^{31}P NMR spectra of complex **13** in the absence of $Zn(OTf)_2$ (—) and after the addition of 2.3 equiv of $Zn(OTf)_2$ (- - -).

Scheme 3



Scheme 4



At the beginning of the investigations we applied reaction conditions similar to our recently published procedure using rhodium carbene catalysts.[15] However, soon we realized that decreasing the partial pressure

(12) MM calculations were carried out with the MM2 module implemented in the program package CHEM3D (version 4.0). Since the parameters for the description of the binding situation at the rhodium center were not known, the structure of the fragment *trans*-$P_2RhCl(CO)$ was generated from X-ray data. The structure of this fragment was then preserved during the energy optimization.

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Table 1. Results of the Rh-Catalyzed Hydroaminomethylation of 1-Pentene with Piperidine[a]

				selectivity (%)		n:iso	
catalyst	Lewis acid	P_{CO} (bar)	conversn (%)	amine	enamine	amine	enamine
11		10	93	66	31	89:11	71:29
11		5	88	80	8	90:10	17:83
12		10	93	57	37	88:12	78:22
13		10	92	60	33	87:13	64:36
11	KPF_6	5	95	94	6	87:13	0:100
12	KPF_6	10	91	54	36	83:17	64:36
13	$Zn(OTf)_2$	10	92	76	20	89:11	40:60
$Rh(CO)_2(acac) + PPh_3$		5	90	84	15	93:7	49:51
$Rh(CO)_2(acac) + PPh_3$	KPF_6	5	96	93	6	92:8	0:100
$Rh(CO)_2(acac) + PPh_3$	$Zn(OTf)_2$	5	85	70	24	90:10	45:55
$Rh(CO)_2(acac)$		5	95	96		60:40	
$Rh(CO)_2(acac)$	KPF_6	5	98	98		62:38	
$Rh(CO)_2(acac)$	$Zn(OTf)_2$	5	97	95		58:42	

[a] Reaction conditions: 1-pentene (10 mmol), piperidine (10 mmol), solvent THF (30 mL), catalyst 0.1 mol %, Lewis acid 0.4 mol %, P_{H_2} = 50 bar, T = 95 °C, t = 12 h. Conversion and selectivity were determined by gas chromatography with bis(methoxyethyl) ether as the internal standard.

Table 2. Results of the Rh-Catalyzed Hydroaminomethylation of Styrene with Piperidine[a]

				selectivity (%)		n:iso	
catalyst	Lewis acid	P_{CO} (bar)	conversn (%)	amine	enamine	amine	enamine
11		5	90	35	63	67:33	63:37
11	KPF_6	5	94	43	53	65:35	59:41
$Rh(CO)_2(acac) + PPh_3$		5	92	51	45	41:59	65:35

[a] Reaction conditions: styrene (10 mmol), piperidine (10 mmol), solvent THF (30 mL), catalyst 0.1 mol %, Lewis acid 0.4 mol %, P_{H_2} = 50 bar, T = 95 °C, t = 12 h. Conversion and selectivity were determined by gas chromatography with bis(methoxyethyl) ether as the internal standard.

of CO to 5 bar led to significantly higher amine selectivity. Thus, most of the reactions were run at 5 bar of CO pressure.[16,17]

In general, the conversions and selectivities obtained by the rhodium(I) complexes **11**−**13** with the standard systems $Rh(CO)_2(acac)$ and $Rh(CO)_2(acac) + PPh_3$, respectively, are comparable, when an identical CO pressure is applied. Simple $Rh(CO)_2(acac)$ gives almost 100% selectivity for the formation of the amine with 1-pentene, while the addition of triphenylphosphine reduces the selectivity to about 70−90%. The addition of the Lewis acids KPF_6 and $Zn(OTf)_2$ to standard systems makes only slight differences in conversion or selectivity. However, an interesting effect was observed for compound **11** in the hydroaminomethylation of 1-pentene: the amine selectivity rises from 80% to 94% after the addition of a 4-fold molar excess of KPF_6. Parallel to this, the iso enamine is found as the only conformer. This is also observed for the catalytic system $Rh(CO)_2(acac) + PPh_3$.

Conclusion

New triphenylphosphine ligands containing functional sites in the backbone were synthesized and coordinated to the Rh(CO)Cl fragment. The resulting complexes were investigated by means of ^{31}P NMR spectroscopy and show significant changes in the ^{31}P NMR spectra, depending on the presence or absence of Lewis acids, which proves the existence of secondary interactions between the ligands and the Lewis acids. However, these interactions are relevant not only in terms of spectroscopy features but also for catalysis.

We are now going to investigate systems that carry binding motives for certain substrates in the ligand backbone. This should open up a way for substrate recognition in homogeneous catalysis.

Experimental Section

General Remarks. The synthesis of compounds containing phosphorus was carried out under an inert-gas atmosphere of argon and with dried solvents. $[(CO)_2Rh(\mu\text{-}Cl)]_2$ (Strem 45-0450) was obtained commercially. All other starting materials were obtained from Aldrich and used without further purification. Elemental analyses were carried out at the Institute of Chemistry (TU Chemnitz). Infrared spectra were recorded with a Perkin-Elmer FT-IR 1000 spectrometer. NMR spectra were recorded with a Bruker Avance 250 spectrometer. ESI-TOF mass spectra were obtained with a Mariner ESI-TOF mass spectrometer (Applied Biosystems) operating in the positive-ion mode. Samples for ESI-TOF mass spectroscopy were dissolved in THF, and traces of KSCN were added. The NMR resonances were assigned, as far as possible, according to Chart 4.

2-(3-Bromophenyl)-1,3-dioxolane. A 27.9 g amount (151 mmol) of 3-bromobenzaldehyde and 13.8 g (222 mmol) of ethylene glycol were dissolved in 120 mL of benzene. After the addition of 45 mg of 4-toluenesulfonic acid, the mixture was refluxed in a Dean−Stark apparatus until no more water was produced. The reaction mixture was washed with $NaHCO_3$ solution, and the organic layer was then separated and dried over anhydrous $MgSO_4$. After the evaporation of benzene and distillation under vacuum, 2-(3-bromophenyl)-1,3-dioxolane was obtained as a colorless liquid. Yield: 27.1 g, 78%. Anal. Calcd for $C_9H_9BrO_2$: C, 47.18; H, 3.97. Found: C, 46.77; H, 3.91. IR (neat, cm^{-1}): 3066 w, 2961 m, 2887 s, 1722 m, 1574 m, 1473 m, 1429 s, 1382 s, 1260 s, 1210 s, 1087 s, 1026 m, 957 s, 885 m, 786 m, 750 m, 695 m, 558 w, 503 w, 414 s. ^1H NMR (250.1 MHz, 25 °C, $CDCl_3$): δ 7.68 (t, $^4J_{HH}$ = 1.4 Hz, 1H, 2-H), 7.52 (dt, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, 6-H), 7.43 (dt, $^3J_{HH}$ = 7.7 Hz, 1H, 4-H), 7.26 (t, 1H, 5-H), 5.80 (s, 1H, C*H*$(OCH_2)_2$), 4.14−3.99 (m, 4H, CH$(OCH_2)_2$). $^{13}C\{^1H\}$ NMR (62.9 MHz, 25

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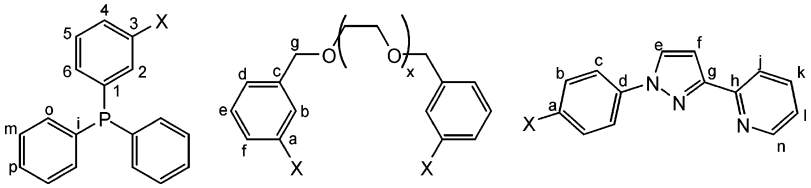
Chart 4



°C, $CDCl_3$): δ 141.0 (C-3), 133.0 (C-5), 130.4 (C-2), 130.0 (C-6), 125.7 (C-4), 122.85 (C-1), 103.1 ($CH(OCH_2)_2$), 65.7 ($CH(OCH_2)_2$).

[3-(1,3-Dioxolan-2-yl)phenyl]diphenylphosphine. A 12.5 g amount (54.6 mmol) of 2-(3-bromophenyl)-1,3-dioxolane was dropped slowly into a suspension of 1.4 g (57.6 mmol) of Mg in THF. After the formation of the Grignard reagent, a THF solution of 10.9 g (49.4 mmol) of chlorodiphenylphosphine was added dropwise to the reaction mixture at 0 °C. The mixture was stirred at 40 °C for another 2 h. Then a deoxygenated concentrated NH_4Cl solution was added dropwise at −10 °C. The mixture was extracted with benzene, and the organic phase was separated and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the residue was recrystallized from MeOH, giving a colorless crystalline solid. Yield: 9.7 g, 59%. Anal. Calcd for $C_{21}H_{19}O_2P \cdot 0.5CH_3OH$: C, 73.07; H, 6.04. Found: C, 73.79; H, 5.68. IR (KBr, cm^{-1}): 2884 m, 1573 w, 1473 m, 1427 m, 1387 m, 1308 w, 1267 w, 1218 m, 1178 m, 1077 vs, 1031 w, 979 m, 883 w, 788 s, 748 s, 692 vs, 536 w, 497 s, 420 w. ^{1}H NMR (250.1 MHz, 25 °C, $CDCl_3$): δ 7.53−7.28 (m, 14H, all aromatic protons), 5.78 (s, 1H, $CH(OCH_2)_2$), 4.18−3.97 (m, 4H, $CH(OCH_2)_2$). $^{13}C\{^1H\}$ NMR (62.9 MHz, 25 °C, $CDCl_3$): δ 138.9 (d, $^3J_{PC}$ = 7.5 Hz, C-3), 138.1 (d, $^1J_{PC}$ = 12.0 Hz, C-1), 137.6 (d, $^1J_{PC}$ = 11.2 Hz, C−i), 135.0 (d, $^2J_{PC}$ = 16.2 Hz, C-2), 134.3 (d, $^2J_{PC}$ = 19.5 Hz, C-o), 132.7 (d, $^2J_{PC}$ = 23.3 Hz, C-6), 129.3 (s, C-p), 129.2 (d, $^3J_{PC}$ = 3.8 Hz, C-5), 129.1 (d, $^3J_{PC}$ = 6.9 Hz, C-m), 127.5 (s, C-4), 104.0 ($CH(OCH_2)_2$), 65.8 ($(CH(OCH_2)_2$). $^{31}P\{^1H\}$ NMR (101.2 MHz, 25 °C, $CDCl_3$): δ −3.98.

(3-Formylphenyl)diphenylphosphine (1). A 6.5 g amount (49.4 mmol) of [3-(1,3-dioxolan-2-yl)phenyl]diphenylphosphine was dissolved in 240 mL of a 1:1 mixture of THF and water. A 0.6 g amount of 4-toluenesulfonic acid was added, and the mixture was refluxed for 4 h. After washing with Na_2CO_3, the aqueous layer was extracted with benzene. The combined organic layer was evaporated, and the residue was purified by column chromatography on silica gel. The first fraction in benzene contained the desired compound. After the removal of the solvent, **1** was obtained as a colorless oil. Yield: 8.2 g, 57%. Anal. Calcd for $C_{19}H_{15}OP \cdot 0.33H_2O$: C, 77.02; H, 5.33. Found: C, 77.31; H, 5.14. IR (neat, cm^{-1}): 3055 m, 2821 w, 2724 w, 1698 vs ($\nu_{C=O}$), 1580 s, 1477 m, 1431 m, 1378 m, 1307 w, 1274 w, 1202 s, 1166 w, 1094 m, 1024 w, 1000 w, 892 m, 861 m, 794 s, 746 s, 695 s, 647 w, 533 w, 499 s, 428 w. ^{1}H NMR (250.1 MHz, 25 °C, $CDCl_3$): δ 9.98 (s, 1H, CHO), 7.87 (tt, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.4 Hz, 2H, p-H), 7.61−7.48 (m, 2H, 4-H, 6-H), 7.45−7.33 (m, 10H, 2-H, 5-H, o-H, m-H). $^{13}C\{^1H\}$ NMR (62.9 MHz, 25 °C, $CDCl_3$): δ 192.46 (s, CHO), 139.9 (d, $^1J_{PC}$ = 14.4 Hz, C-1), 139.7 (d, $^2J_{PC}$ = 18.2 Hz, C-2), 136.9 (d, $^3J_{PC}$ = 6.2 Hz, C-3), 136.7 (d, $^1J_{PC}$ = 11.0 Hz, C-i), 135.6 (d, $^2J_{PC}$ = 20.2 Hz, C-6), 134.3 (d, $^2J_{PC}$ = 20.2 Hz, C-o), 129.8 (s, C-4), 129.7 (s, C-p), 129.7 (d, $^3J_{PC}$ = 5.8 Hz, C-5), 129.3 (d, $^3J_{PC}$ = 7.2 Hz, C-m). $^{31}P\{^1H\}$ NMR (101.2 MHz, 25 °C, $CDCl_3$): δ −4.48.

1,2-Bis-(3-nitrobenzyloxy)ethane (2). To a solution of 0.62 g of ethylene glycol (10 mmol) in 40 mL of DMF was added 0.72 g of NaH (30 mmol) at room temperature. After 1 h, to this suspension, 3.43 g of 3-nitrobenzyl chloride (20 mmol) in 10 mL of DMF was added. After another 3 h, EtOH was added, and the mixture was evaporated. The residue was extracted with CH_2Cl_2 and dried with anhydrous Na_2SO_4. The solution was then purified by column chromatography on silica gel; the first yellow fraction in CH_2Cl_2 contained **2**, which was a yellow oil after concentration. Yield: 0.75 g, 23%. Anal. Calcd for $C_{16}H_{16}N_2O_6$: C, 57.82; H, 4.86; N, 8.43. Found: C, 58.20; H, 4.86; N, 8.41. IR (neat, cm^{-1}): 3091 m, 2922 vs, 2866 vs, 1725 w, 1616 m, 1585 m, 1533 vs (ν_{NO_2}, asym), 1480 s, 1350 vs (ν_{NO_2}, sym), 1265 s, 1209 m, 1097 vs, 1001 w, 928 w, 892 m, 806 s, 733 s, 687 s, 673 s, 613 w, 498 w, 462 w, 458 w. ^{1}H NMR (250.1 MHz, 25 °C, $CDCl_3$): δ 8.20 (s, 2H, b-H), 8.10 (d, $^3J_{HH}$ = 8.1 Hz, 2H, f-H), 7.68 (d, $^3J_{HH}$ = 7.5 Hz, 2H, d-H), 7.50 (t, 2H, e-H), 4.67 (s, 4H, g-H), 3.76 (s, 4H, OCH_2CH_2O). $^{13}C\{^1H\}$ NMR (62.9 MHz, 25 °C, $CDCl_3$): δ 148.7 (C-a), 140.9 (C-c), 133.7 (C-d), 129.8 (C-e), 123.0 (C-f), 122.6 (C-b), 72.4 (C-g), 70.5 (OCH_2CH_2O).

1,15-Bis-(3-nitrophenyl)-2,5,8,11,14-pentaoxypentadecane (3). A mixture of 1.21 g (6.25 mmol) of tetraethylene glycol, 10 mL of CH_2Cl_2, 173 mg (5 mol %) of $[NBu_4]Cl$, 2.57 g (15 mmol) of 3-nitrobenzyl chloride, and a solution of 3.00 g of sodium hydroxide in 3.00 mL of water was stirred vigorously at 65 °C for 2.5 h. The mixture then was extracted with CH_2Cl_2, and the organic phase was separated and washed with H_2O until pH 7. After the organic phase was dried with anhydrous Na_2SO_4, the solvent was evaporated and the residue was purified by column chromatography on silica gel. The product is eluted with a 95/5 mixture of CH_2Cl_2 and Et_2O. Evaporation of the solvent gave **3** as a deep yellow oil. Yield: 1.88 g, 65%. Anal. Calcd for $C_{22}H_{28}N_2O_9$: C, 56.88; H, 6.09; N, 6.03. Found: C, 56.49; H, 6.09; N, 6.05. IR (neat, cm^{-1}): 3088 w, 2869 s, 1712 w, 1618 w, 1548 w, 1531 vs (ν_{NO_2}, asym), 1481m, 1348vs (ν_{NO_2}, sym), 1292 m, 1261 m, 1221 w, 1101 vs, 1044 w, 1002w, 931 w, 894 w, 846 w, 807 m, 733 s, 691 w, 673 w, 613 w, 492 w. ^{1}H NMR (250.1 MHz, 25 °C, $CDCl_3$): δ 8.21 (s, 2H, b-H), 8.12 (d, $^3J_{HH}$ = 8.1 Hz, 2H, f-H), 7.67 (d, $^3J_{HH}$ = 7.6 Hz, 2H, d-H), 7.50 (t, 2H, e-H), 4.65 (s, 4H, g-H), 3.73−3.64 (m, 16H, OCH_2CH_2O). $^{13}C\{^1H\}$ NMR (62.9 MHz, 25 °C, $CDCl_3$): δ 148.7 (C-a), 141.1 (C-c), 133.8 (C-d), 129.7 (C-e), 122.8 (C-f), 122.5 (C-b), 72.2 (C-g), 71.1, 71.0, 71.0, 70.5 (4 × OCH_2CH_2O).

General Procedure for the Synthesis of the Amines 4 and 5. A 0.25 g amount of 10% Pd-C was added under an atmosphere of argon to a stirred solution of 0.83 g (2.5 mmol) of **2** or 1.16 g (2.5 mmol) of **3** in 15 mL of dry MeOH followed by 1.45 g (23 mmol) of anhydrous $NH_4(HCO_2)$ in a single portion. The resulting mixture was stirred at room temperature for 3 h. After this, the catalyst was removed by filtration through a Celite pad and washed with 30 mL of MeOH. The filtrate was evaporated, the residue was triturated with H_2O, the product was extracted with CH_2Cl_2, and the organic phase was dried with anhydrous Na_2SO_4. Evaporation of the solvent gave **4** and **5** as dark yellow oils.

4: yield 0.63 g, 93%. Anal. Calcd for $C_{16}H_{20}N_2O_2$: C, 70.55; H, 7.42; N, 10.29. Found: C, 69.44; H, 7.26; N, 10.01. IR (neat, cm^{-1}): 3434 m, 3355 s, 3223 w (3 × ν_{NH}, st), 3036 w, 2908 m, 2861 m, 1622 vs, 1606 vs, 1591 vs, 1493 s, 1463 s, 1353 m, 1315 m, 1296 s, 1228 w, 1166 m, 1090 vs, 1050 m, 995 w, 925 w, 869 m, 785 s, 753 w, 734 w, 694 m, 530 w. ^{1}H NMR (250.1 MHz, 25 °C, $CDCl_3$): δ 7.12 (t, $^3J_{HH}$ = 7.9 Hz, 2H, e-H), 6.74−6.71 (m, 4H, b-H, f-H), 6.61−6.57 (m, 2H, d-H), 4.50 (s, 4H, g-H), 3.66 (s, 4H, OCH_2CH_2O), 3.63 (bs, 4H, NH_2). $^{13}C\{^1H\}$ NMR (62.9 MHz, 25 °C, $CDCl_3$): δ 147.1 (C-a), 140.0 (C-c), 129.7 (C-e), 118.3 (C-d), 114.8 (C-f), 114.7 (C-b), 73.6 (C-g), 69.9 (OCH_2CH_2O).

5: yield 0.95 g, 93%. Anal. Calcd for $C_{22}H_{32}N_2O_5$: C, 65.31; H, 7.99; N, 6.93. Found: C, 64.63; H, 7.80; N, 6.88. IR (neat, cm^{-1}): 3445 m, 3358 s, 3230 w (3 × ν_{NH}, st), 3037 w, 2867 vs, 1687 w, 1622 s, 1607 s, 1591 m, 1514 w, 1493 m, 1464 m, 1350 m, 1298 m, 1248 w, 1097 vs, 1036 w, 995 w, 946 w, 868 w, 785 m, 754 w, 733 w, 696 m, 649 w, 529 w. ^{1}H NMR (250.1 MHz, 25 °C, $CDCl_3$): δ 7.07 (t, $^3J_{HH}$ = 7.8 Hz, 2H, e-H), 6.68−6.65 (m, 4H, b-H, f-H), 6.54 (d, $^3J_{HH}$ = 8.8 Hz, 2H, d-H), 4.44 (s, 4H, g-H), 3.74 (bs, 4H, NH_2), 3.64−3.57 (m, 16H, OCH_2CH_2O). $^{13}C\{^1H\}$ NMR (62.9 MHz, 25 °C, $CDCl_3$): δ 147.3 (C-a), 139.9 (C-c), 129.6 (C-e), 118.0 (C-d), 114.7 (C-f), 114.7 (C-b), 73.6 (C-g), 71.0, 71.0, 71.0, 69.7 (4 × OCH_2CH_2O).

1-(4-Nitrophenyl)-3-(2-pyridyl)pyrazole (6). An 18.0 g amount (124 mmol) of 3-(2-pyridinyl)pyrazole, 26.3 g (186 mmol) of 4-fluoronitrobenzene, and 51.5 g (373 mmol) of K_2CO_3 were heated in 100 mL of DMSO for 4 h to 180 °C. The reaction mixture was poured on crushed ice. The resulting solid was filtered off, dried, and extracted in a Soxhlet apparatus with $CHCl_3$. After evaporation of the solvent, a yellow solid was obtained. Yield: 25.3 g, 77%. Anal. Calcd for $C_{14}H_{10}N_4O_2 \cdot 0.25H_2O$: C, 62.10; H, 3.91; N, 20.69. Found: C, 62.29; H, 3.76; N, 20.60. IR (KBr, cm^{-1}): 3126 w, 1593 s, 1535 m, 1518 s (ν_{NO_2}, asym), 1483 m, 1455 m, 1393 m, 1366 m, 1333 vs (ν_{NO_2}, sym), 1313 s, 1276 s, 1112 m, 1049 m, 1038 m, 957 w, 939 m, 852 s, 767 m, 749 m. ^{1}H NMR (250.1 MHz, 25 °C, $CDCl_3$): δ 8.67 (d, $^3J_{HH}$ = 4.8 Hz, 1H, n-H), 8.36 (d, $^3J_{HH}$ = 9.1 Hz, 2H, b-H), 8.13 (d, $^3J_{HH}$ = 8.0 Hz, 1H, j-H), 8.09 (d, $^3J_{HH}$ = 2.6 Hz, 1H, e-H), 7.97 (d, 2H, c-H), 7.78 (dt, $^4J_{HH}$ = 1.5 Hz, 1H, k-H), 7.29 (dd, 1H, l-H), 7.21 (d, 1H, f-H). $^{13}C\{^1H\}$ NMR (62.9 MHz, 25 °C, $CDCl_3$): δ 154.3 (C-g), 150.7 (C-h), 149.7 (C-n), 145.1, 144.1 (C-a, C−d), 137.3 (C-k), 130.8 (C-e), 125.6 (C-b), 123.8 (C-l), 120.2 (C-j), 118.7 (C-c), 108.1 (C-f).

1-(4-Aminophenyl)-3-(2-pyridyl)pyrazole (7). The preparation followed the procedure applied for the synthesis of **4** and **5**. From 9.40 g (149 mmol) of **6**, 5.83 g (81%) of **7** was obtained. Anal. Calcd for $C_{14}H_{12}N_4$: C, 71.16; H, 5.12; N, 23.71. Found: C, 70.85; H, 5.08; N, 23.42. IR (KBr, cm^{-1}): 3438 m, 3334, 3214 s (3 × ν_{NH}, st), 1634 s, 1513 vs, 1458 m, 1422 m, 1264 m, 1052 m, 828 s, 771 s, 622 m. ^{1}H NMR (250.1 MHz, 25 °C, $CDCl_3$): δ 8.64 (dd, $^3J_{HH}$ = 5.7 Hz, $^4J_{HH}$ = 0.8 Hz, 1H, n-H), 8.08 (d, $^3J_{HH}$ = 8.0 Hz, 1H, j-H), 7.83 (d, $^3J_{HH}$ = 2.4 Hz, 1H, e-H), 7.72 (dt, 1H, k-H), 7.51 (d, $^3J_{HH}$ = 8.7 Hz, 2H, c-H), 7.20 (m, 1H, l-H), 7.06 (d, 1H, f-H), 6.73 (d, 2H, b-H), 3.73 (b, 2H, NH_2). $^{13}C\{^1H\}$ NMR (62.9 MHz, 25 °C, $CDCl_3$): δ 152.6, 152.4 (C-g, C-h), 149.5 (C-n), 145.5 (C-a), 136.6 (C-k), 132.4 (C-d), 128.4 (C-e), 122.5 (C-l), 121.2 (C-c), 120.3 (C-j), 115.5 (C-b), 105.8 (C-f).

General Procedure for the Preparation of Schiff Bases 8−10. A solution of 1.45 g (5.0 mmol) of **1** and of the appropriate amine **4** (0.68 g, 2.5 mmol), **5** (1.01 g, 2.5 mmol), or **7** (1.18 g, 5.0 mmol) in 20 mL of absolute EtOH was refluxed for 8 h. The solvent was removed, and the residue was crystallized from MeOH to give the corresponding Schiff base as a light yellow solid (**8** and **10**) in almost quantitative yield. **9** was obtained as a deep yellow oil.

8. Anal. Calcd for $C_{54}H_{46}N_2O_2P_2 \cdot CH_3OH$: C, 77.81; H, 5.94; N, 3.30. Found: C, 77.58; H, 5.76; N, 3.36. IR (KBr, cm^{-1}): 3461 w, 3136 w, 3055 w, 2856 w, 1956 w, 1886 w, 1812 w, 1690 w, 1620 m ($\nu_{C=N}$), 1584 m, 1476 m, 1428 m, 1404 m, 1355 w, 1300 w, 1261 w, 1204 w, 1090 s, 1027 m, 876 w, 794 m, 741 s, 691 vs, 492 m, 450 m. ^{1}H NMR (250.1 MHz, 25 °C, $CDCl_3$): δ 8.42 (s, 2H, CH=N), 8.00 (d, $^3J_{HH}$ = 7.0 Hz, 2H, ar H), 7.86 (d, $^3J_{HH}$ = 8.0 Hz, 2H, ar H), 7.40−7.10 (m, 32H, ar H), 4.61 (s, 4H, g-H), 3.73 (s, 4H, OCH_2CH_2O). $^{13}C\{^1H\}$ NMR (62.9 MHz, 25 °C, $CDCl_3$): δ 160.5 (CH=N), 152.5 (C-a), 139.7 (C-c), 138.8 (d, $^1J_{PC}$ = 12.5 Hz, C-1), 137.2 (d, $^1J_{PC}$ = 10.6 Hz, C-i), 136.9 (d, $^3J_{PC}$ = 7.2 Hz, C-3), 136.9 (d, $^2J_{PC}$ = 16.8 Hz, C-6), 135.3 (d, $^2J_{PC}$ = 22.6 Hz, C-2), 134.3 (d, $^2J_{PC}$ = 19.7 Hz, C-o), 129.6 (s, C-4), 129.5 (d, $^3J_{PC}$ = 6.7 Hz, C-5), 129.4 (s, C-p), 129.1 (d, $^3J_{PC}$ = 6.7 Hz, C-m), 128.7 (s, C-e), 125.8 (s, C-d), 120.8 (s, C-f), 120.4 (s, C-b), 73.5 (s, C-g), 70.1 (OCH_2CH_2O). $^{31}P\{^1H\}$ NMR (101.2 MHz, 25 °C, $CDCl_3$): δ −6.56. ESI-TOF MS, *m*/*z* (%): 887.1768 (22) $[M + 2O + K]^+$, 871.1885 (58) $[M + O + K]^+$, 855.1865 (71) $[M + K]^+$.

9. Anal. Calcd for $C_{60}H_{58}N_2O_5P_2 \cdot CH_3OH$: C, 74.68; H, 6.37; N, 2.86. Found: C, 74.21; H, 6.55; N, 2.88. IR (neat, cm^{-1}): 3362 w, 3069 m, 3052 m, 2868 vs, 2244 m, 1955 w, 1887 w, 1816 w, 1699 w, 1626 s ($\nu_{C=N}$), 1602 s, 1585 s, 1568 m, 1480 s, 1435 s, 1412 w, 1350 m, 1324 w, 1305 w, 1254 w, 1211 w, 1094 vs, 997 w, 974 w, 909 s, 849 w, 798 s, 742 s, 695 s, 646 m, 618 w, 570 w, 536 w, 502 m, 488 m. ^{1}H NMR (250.1 MHz, 25 °C, $CDCl_3$): δ 8.41 (s, 2H, CH=N), 8.00 (d, $^3J_{HH}$ = 6.7 Hz, 2H, ar H), 7.88 (d, $^3J_{HH}$ = 8.0 Hz, 2H, ar H), 7.48−7.04 (m, 32H, ar H), 4.61 (s, 4H, g-H), 3.69−3.58 (m, 16H, OCH_2CH_2O). $^{13}C\{^1H\}$ NMR (62.9 MHz, 25 °C, $CDCl_3$): δ 160.4 (CH=N), 152.5 (C-a), 140.0 (C-c), 138.9 (d, $^1J_{P-C}$ = 13.0 Hz, C-1), 137.2 (d, $^1J_{P-C}$ = 11.1 Hz, C-i), 136.9 (d, $^3J_{P-C}$ = 7.3 Hz, C-3), 136.9 (d, $^2J_{P-C}$ = 14.7 Hz, C-6), 135.3 (d, $^2J_{P-C}$ = 19.7 Hz, C-2), 134.3 (d, $^2J_{P-C}$ = 19.7 Hz, C-o), 129.6 (C-4), 129.5 (d, $^3J_{P-C}$ = 7.2 Hz, C-5), 129.4 (C-p), 129.1 (d, $^3J_{P-C}$ = 7.0 Hz, C-m), 129.0 (C-e), 125.8 (C-d), 120.7 (C-f), 120.5 (C-b), 73.4 (C-g), 71.1, 71.1, 71.1, 70.0 (4 × OCH_2CH_2O). $^{31}P\{^1H\}$ NMR (101.2 MHz, 25 °C, $CDCl_3$): δ −6.61. ESI-TOF MS, *m*/*z* (%): 987.2398 (63) $[M + K]^+$, 715.1974 (100) $[M - Ph_2PC_6H_4C + H + K]^+$.

10. Anal. Calcd for $C_{33}H_{25}N_4P \cdot 0.5CH_3OH$: C, 76.70; H, 5.19; N, 10.68. Found: C, 76.12; H, 5.13; N, 10.97. IR (KBr, cm^{-1}): 1622 m ($\nu_{C=N}$), 1592 m, 1567 w, 1529 m, 1508 s, 1484 m, 1458 m, 1433 m, 1388 m, 1370 m, 1352 m, 1317 m, 1282 m, 1271 m, 1198 w, 1165 w, 1148 w, 1128 w, 1089 m, 1070 w, 1050 m, 1041 m, 1026 w, 993 w, 974 w, 960 w, 945 m, 894 w, 853 w, 841 m, 812 w, 798 m, 768 s, 748 m, 694 s, 666 w, 620 w, 542 w, 508 m, 499 m, 479 w, 460 w, 416 w. ^{1}H NMR (250.1 MHz, 25 °C, $CDCl_3$): δ 8.66 (d, $^3J_{HH}$ = 4.4 Hz, 1H, m-H), 8.43 (s, 1H, CH=N), 8.15 (d, $^3J_{HH}$ = 9.3 Hz, 1H, j-H), 7.97 (d, $^3J_{HH}$ = 2.5 Hz, 1H, e-H), 8.00−7.20 (m, 20H, ar H), 7.14 (d, 1H, f-H). $^{13}C\{^1H\}$ NMR (62.9 MHz, 25 °C, $CDCl_3$): δ 160.3 (CH=N), 153.7, 152.4 (2 × s, C-g, C-h), 150.5 (s, C-n), 149.9 (s, C-a), 138.9 (d, $^1J_{PC}$ = 13.0 Hz, C-1), 138.7 (s, C-k), 137.1 (d, $^1J_{PC}$ = 11.0 Hz, C-i), 137.0 (s, C-d), 137.0 (d, $^2J_{PC}$ = 16.3 Hz, C-6), 136.7 (d, $^3J_{PC}$ = 7.2 Hz, C-3), 135.3 (d, $^2J_{PC}$ = 23.0 Hz, C-2), 134.2 (d, $^2J_{PC}$ = 19.7 Hz, C-o), 129.5 (d, $^3J_{PC}$ = 8.5 Hz, C-5), 129.4 (s, C-p), 129.1 (d, $^3J_{PC}$ = 7.0 Hz, C-m), 128.9, 128.6 (2 × s, C-e, C-4), 123.1 (C-l), 122.4 (C-b), 120.8 (C-j), 120.3 (C-c), 107.0 (C-f). $^{31}P\{^1H\}$ NMR (101.2 MHz, 25 °C, $CDCl_3$): δ −6.56. ESI-TOF MS, *m*/*z* (%): 563.0719 (98) $[M + O + K]^+$, 547.0791 (100) $[M + K]^+$, 275.0340 (94) $[M - Ph_2PC_6H_4C + H + K]^+$.

General Procedure for the Synthesis of Rhodium Complexes 11−13. A 97.2 mg amount (0.25 mmol) of $[(CO)_2Rh(\mu\text{-}Cl)]_2$ was dissolved in 30 mL of benzene. A 408 mg amount (0.50 mmol) of **8** or 474 mg (0.50 mmol) of **9** was dissolved in another 30 mL of benzene. Over 2 h, both of these solutions were added dropwise at the same time to 300 mL of benzene. For the preparation of **13**, 508 mg (1.0 mmol) of **10** in 30 mL of benzene was added dropwise to a solution of $[(CO)_2Rh(\mu\text{-}Cl)]_2$ in 30 mL of benzene. After the addition, the reaction mixtures were stirred at room temperature for another 1 h. After the removal of the benzene in vacuo, the rhodium complexes were crystallized from CH_2Cl_2 by slow diffusion of Et_2O and thus obtained as yellow microcrystalline solids.

11: yield 442 mg, 90%. Anal. Calcd for $C_{55}H_{46}ClN_2O_3P_2Rh \cdot 0.4CH_2Cl_2$: C, 66.81; H, 4.74; N, 2.81. Found: C, 64.85; H, 4.78; N, 2.74. IR (KBr, cm^{-1}): 3046 w, 2962 w, 2901 w, 2851 w, 2691 w, 2525 w, 2366 w, 2337 w, 1971 vs (ν_{CO}), 1658 w, 1624 m ($\nu_{C=N}$), 1578 m, 1543 w, 1524 w, 1477 m, 1432 m, 1405 m, 1350 w, 1311 w, 1261 s, 1208 w, 1166 w, 1093 vs, 1024 s, 930 w, 873 w, 800 s, 744 m, 691 s, 618 w, 570 m, 502 m, 466 m, 444 m. ^{1}H NMR (250.1 MHz, 25 °C, $CDCl_3$): δ 8.43−7.07 (m, 38H, ar H, CH=N), 4.59, 4.57 (2 × s, 4H, ratio 4:1, 2 × g-H), 3.67, 3.66 (2 × s, 4H, ratio 4:1, 2 × OCH_2CH_2O). $^{13}C\{^1H\}$ NMR (62.9 MHz, 25 °C, $CDCl_3$): δ not observed (2 × CO), 160.4, 160.2 (2 × s, 2 × CH=N), 152.5, 152.3 (2 × s, 2 × C-a), 139.9, 139.8 (2 × s, 2 × C-c), 137.9, 137.6 (m, 2 × C-1, 2 ×

C-i), 136.5 (m, 2 × C-3), 135.4, 135.1 (2 × t, $^2J_{PC}$ = 13.0, $^4J_{PC}$ = 12.5 Hz, 2 × C-o), not observed (2 × C-6), 132.9, 132.7 (2 × t, $^2J_{PC}$ = 45.2, $^4J_{PC}$ = 45.6 Hz, 2 × C-2), 130.9, 130.8 (2 × s, 2 × C−p), 129.6, 129.5 (2 × s, 2 × C-4), 129.5, 129.4 (2 × s, 2 × C-e), 129.2, 129.0 (2 × t, $^3J_{PC}$ = 8.6, $^5J_{PC}$ = 13.4 Hz, 2 × C-5), 128.8 (t, $^3J_{PC}$ = $^5J_{PC}$ = 10.1 Hz, 2 × C-m), 125.9, 125.8 (2 × s, 2 × C-d), 120.6, 120.6 (2 × s, 2 × C-f), 120.5, 120.4 (2 × s, 2 × C-b), 73.6, 73.4 (2 × s, 2 × C-g), 70.0, 69.9 (2 × s, 2 × O*C*H$_2$*C*H$_2$O). ^{31}P{^{1}H} NMR (101.2 MHz, 25 °C, CDCl$_3$): δ 28.20, 28.33 (2 × d, $^1J_{RhP}$ = 127.1, $^1J_{RhP}$ = 126.8 Hz). ESI-TOF MS, *m*/*z* (%): 1044.0256 (96) [M − Cl + SCN + K]$^+$.

12: yield 510 mg, 91%. Anal. Calcd for $C_{61}H_{58}ClN_2O_6P_2Rh\cdot 0.5CH_2Cl_2$: C, 63.79; H, 5.14; N, 2.42. Found: C, 63.55; H, 5.17; N, 2.40. IR (KBr, cm^{-1}): 3048 w, 2963 w, 2857 w, 2408 w, 2127 w, 1969 s (ν_{CO}), 1625 w ($\nu_{C=N}$), 1571 w, 1478 m, 1432 m, 1348 w, 1260 m, 1209 w, 1093 s, 1026 m, 935 w, 872 w, 798 m, 745 m, 691 s, 569 m, 501 m. ^{1}H NMR (250.1 MHz, 25 °C, CDCl$_3$): δ 8.45−7.04 (m, 38H, ar H, CH═N), 4.58, 4.56 (2 × s, 4H, ratio 5:1, 2 × g-H), 3.69−3.61 (m, 16H, OC*H*$_2$C*H*$_2$O). ^{13}C{^{1}H} NMR (62.9 MHz, 25 °C, CDCl$_3$): δ 187.5 (dt, $^1J_{RhC}$ = 74.2 Hz, $^2J_{PC}$ = 16.4 Hz, 2 × CO), 160.2 (s, 2 × CH═N), 152.4 (s, 2 × C-a), 140.0, 139.9 (2 × s, 2 × C-c), 137.9 (t, $^1J_{PC}$ = $^3J_{PC}$ = 11.4 Hz, 2 × C-1), 137.4, 137.1 (2 × t, $^1J_{PC}$ = 15.0, $^3J_{PC}$ = 17.6 Hz, 2 × C-i), 136.5 (t, $^3J_{PC}$ = $^5J_{PC}$ = 8.8 Hz, 2 × C-3), 135.1 (t, $^2J_{PC}$ = $^4J_{PC}$ = 12.8 Hz, 2 × C-o), 134.3 (t, $^2J_{PC}$ = $^4J_{PC}$ = 45.2 Hz, 2 × C-6), 132.9 (t, $^2J_{PC}$ = $^4J_{PC}$ = 45.6 Hz, 2 × C-2), 130.8 (s, 2 × C-p), 129.8 (s, 2 × C-4), 129.6, 129.5 (2 × s, 2 × C-e), 129.1 (t, $^3J_{PC}$ = $^5J_{PC}$ = 9.9 Hz, 2 × C-5), 128.8 (t, $^3J_{PC}$ = $^5J_{P-C}$ = 9.9 Hz, 2 × C-m), 125.8 (s, 2 × C-d), 120.6, 120.5 (2 × s, 2 × C-f, 2 × C-b), 73.4 (s, 2 × C-g), 71.1, 69.1 (2 × s, 2 × 4 × O*C*H$_2$*C*H$_2$O). ^{31}P{^{1}H} NMR (101.2 MHz, 25 °C, CDCl$_3$): δ 28.66, 28.59 (2 × d, $^1J_{RhP}$ = 128.4, $^1J_{RhP}$ = 127.6 Hz). ESI-TOF MS, *m*/*z* (%): 1176.0829 (87) [M − Cl + SCN + K]$^+$.

13: yield 479 mg, 81%. Anal. Calcd for $C_{67}H_{50}ClN_8OP_2Rh\cdot CH_2Cl_2$: C, 64.39; H, 4.13; N, 8.83. Found: C, 64.52; H, 4.15; N, 9.14. IR (KBr, cm^{-1}): 1961 vs (ν_{CO}), 1622 m ($\nu_{C=N}$), 1588 m, 1562 w, 1528 w, 1507 s, 1482 m, 1454 w, 1432 m, 1384 w, 1366 m, 1314 w, 1262 s, 1191 w, 1164 w, 1139 w, 1093 s, 1049 s, 1024 w, 996 w, 961 w, 942 w, 890 w, 835 m, 797 s, 766 m, 746 m, 690 s, 674 w, 643 w, 618 w, 574 w, 542 w, 510 s, 468 w, 442 w, 419 w. ^{1}H NMR (250.1 MHz, 25 °C, CDCl$_3$): δ 8.66 (d, $^3J_{HH}$ = 4.7 Hz, 2H, n-H), 8.43 (s, 2H, CH═N), 8.28 (t, J_{HH} = 5.5 Hz, 2H, ar H), 8.11 (t, J_{HH} = 8.1 Hz, 4H, ar H), 7.98 (d, $^3J_{HH}$ = 2.5 Hz, 2H, e-H), 7.86−7.71 (m, 16H, ar H), 7.62−7.20 (m, 20H, ar H), 7.13 (d, 2H, f-H). ^{13}C{^{1}H} NMR (62.9 MHz, 25 °C, CDCl$_3$): δ not observed (CO), 160.0 (s, CH═N), 153.7, 152.4 (2 × s, C-h, C-g), 150.4 (s, C-n), 149.9 (s, C-a), 138.7 (s, C-j), 137.8 (t, $^1J_{PC}$ = $^3J_{PC}$ = 12.5 Hz, C-1), 137.0 (s, C-d), 136.8 (t, $^3J_{PC}$ = $^5J_{PC}$ = 8.6 Hz, C-3), 136.4 (t, $^1J_{PC}$ = $^3J_{PC}$ = 10.1 Hz, C-i), 135.1 (t, $^2J_{PC}$ = $^4J_{PC}$ = 13.0 Hz, C-o), 134.3 (t, $^2J_{PC}$ = $^4J_{PC}$ = 45.6 Hz, C-6), 132.9 (t, $^2J_{PC}$ = $^4J_{PC}$ = 44.6 Hz, C-2), 130.8(s, C-4), 129.2 (t, $^3J_{PC}$ = $^5J_{PC}$ = 5.3 Hz, C-5), 128.8 (t, $^3J_{PC}$ = $^5J_{PC}$ = 10.1 Hz, C-m), 128.7 (s, C-p), 128.6 (s, C-e), 123.1 (s, C-l), 122.4 (s, C-b), 120.7 (s, C-k), 120.3 (s, C-c), 107.0 (s, C-f). ^{31}P-{^{1}H} NMR (101.2 MHz, 25 °C, CDCl$_3$): δ 28.39 (d, $^1J_{RhP}$ = 127.8 Hz). ESI-TOF MS, *m*/*z* (%): 1244.0581 (13) [M − Cl + SCN + K]$^+$, 563.0669 (100) [$C_{33}H_{25}N_4PO$ + K]$^+$, 275.0308 (78) [$C_{33}H_{25}N_4P$ − $Ph_2PC_6H_4C$ + H + K]$^+$.

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