Oxygen Tripod Ligands with Functionalized Pendant Arms: The Dangling Ligand Concept in Homogeneous Catalysis

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The cobalt complex $[CpCoI_2(CO)]$ reacts with the trialkyl phosphites $P(OCH_3)_2(OR)$ (R = $(C_2H_4O)_nCH_2CH{=}CH_2$, $(C_2H_4O)_nC_2H_4CN$, $(C_3H_6)_nCH{=}CH_2$, $(C_3H_6)_nCN$, $C_3H_6C(O)CH_3$; n = 1, 2) and NaI in a series of Arbuzov reactions to produce anionic complexes of the type $[CpCo\{P(O)(OCH_3)(OR)\}_3]^- \equiv L_{OMe,OR}^-$ in high yields. The products consist of two pairs of enantiomers, which have been characterized by ^1H, ^{13}C, and ^{31}P NMR and IR spectroscopy. The anions $L_{OMe,OR}^-$ have been shown to behave as tris-chelating ligands toward metal ions by using the oxygen atoms of the three P=O groups. The functional groups (olefin, nitrile, ketone) of the pendant side chains OR can act as additional intramolecular complexation sites. The rhodium complexes $[(L_{OMe,OR})Rh(CO)_2]$ have been used as catalyst precursors for hydroformylation of 1-propene, hydrogenation of cyclohexene, and cyclotrimerization of dimethyl acetylenedicarboxylate. They show considerably higher catalytic activities than the analogous complexes containing ligands L^- without functionalized pendant arms. The solubility of the ligands in water or hydrocarbons can be controlled by choosing alkyl or polyether side chains OR.

Introduction

Organometallic compounds play an increasingly important role as homogeneous catalysts and model systems for biologically active compounds. These very specific applications create a need for chemically robust systems the properties of which can be varied by functionalization and derivatization. We have published a number of papers on the syntheses and the coordination chemistry of tridentate oxygen ligands $[CpCo\{P(O)RR'\}_3]^- \equiv L_{R,R'}^-$ (R, R' = alkyl, aryl, O-alkyl, O-aryl).[1-3] Studies of the electronic spectra of their metal complexes show that the ligands occupy a high position in both the spectrochemical series and the nephelauxetic series; i.e. they are very weak and hard oxygen donor ligands.[4] These ligands are chemically remarkably inert and suitable to stabilize metal ions and organometallic fragments with transition metal centers in very different oxidation states. Hence we have been interested in the activity and selectivity of rhodium(I) complexes of various ligands $L_{R,R'}^-$ as homogeneous catalysts. In most catalytic cycles there are species involved that are coordinatively unsaturated. We have now developed a concept of stabilizing unsaturated intermediates by additional donor moieties in functionalized ligands $L_{OCH_3,OR}^-$ (R = $(C_3H_6)_nCH{=}CH_2$ (**3a,b**), $(C_3H_6)_nCN$ (**3c,d**), $C_3H_6C(O)CH_3$ (**3e**), $(C_2H_4O)_nCH_2CH{=}CH_2$ (**3f,g**), $(C_2H_4O)_nC_2H_4CN$ (**3h,i**); n = 1, 2). These pendant side chains are intended to form reversibly an intramolecular coordinate bond to the metal center. In addition, variation of the substituents R in the pendant side chains controls the solubility properties of both ligands and complexes.

Results and Discussion

Synthesis of the Ligands. The sodium salts of the ligands **3a–i** were prepared by slow addition of an acetone solution of $[CpCoI_2(CO)]$ to a solution of a functionalized tertiary phosphite $P(OCH_3)_2(OR)$ (R = $(C_3H_6)_nCH{=}CH_2$ (**2a,b**), $(C_3H_6)_nCN$ (**2c,d**), $C_3H_6C(O)CH_3$ (**2e**), $(C_2H_4O)_nCH_2CH{=}CH_2$ (**2f,g**), $(C_2H_4O)_nC_2H_4CN$ (**2h,i**); n = 1, 2) in acetone followed by addition of sodium iodide. The tertiary phosphites were synthesized by esterification of PCl_3 with functionalized alcohols **1** (see Experimental Section).

As detailed studies of the system "$[CpCoI_2(CO)]$ + $P(OMe)_3$" have shown,[5] the fast ligand substitution at the cobalt center is followed by a double Arbuzov transformation to yield $[CpCo\{P(O)(OMe)(OR)\}_2\{P(OMe)_2(OR)\}]$ with formation of methyl iodide.

$$[CpCoI_2(CO)] + 3P(OCH_3)_2(OR) \xrightarrow[-2CH_3I]{} [CpCo\{P(O)(OCH_3)(OR)\}_2\{P(OCH_3)_2(OR)\}]$$

Addition of a stoichiometric amount of sodium iodide causes a third Arbuzov rearrangement to occur.

$$[CpCo\{P(O)(OCH_3)(OR)\}_2\{P(OCH_3)_2(OR)\}] + NaI \xrightarrow[-CH_3I]{} Na[CpCo\{P(O)(OCH_3)(OR)\}_3]$$

The products Na**3a–i** were chromatographed on a silica column and isolated as yellow to red oils which are inert toward air and water. The elemental analyses indicate that they still contain $^2/_3$ mol of water that could not be removed. This is because the sodium salts form trimeric units that strongly coordinate two molecules of water.[1b] The ligands **3a–e** with aliphatic side chains are very slightly soluble in water, whereas the ligands **3f–i** containing polyether side chains are much more water-soluble. The solubility of the salts in water increases in the order: **3f** < **3g** < **3h** ≈ **3i**.

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(2) Kläui, W.; Lenders, B.; Hessner, B.; Evertz, K. *Organometallics* **1988**, *7*, 1357.

(3) For a review of the ligands L^- see e.g.: Kläui, W. *Angew. Chem.* **1990**, *102*, 661; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 627.

(4) Kläui, W.; Otto, H.; Eberspach, W.; Buchholz, E. *Chem. Ber.* **1982**, *115*, 1922.

(5) Schleman, E. V.; Brill, T. B. *J. Organomet. Chem.* **1987**, *323*, 103.

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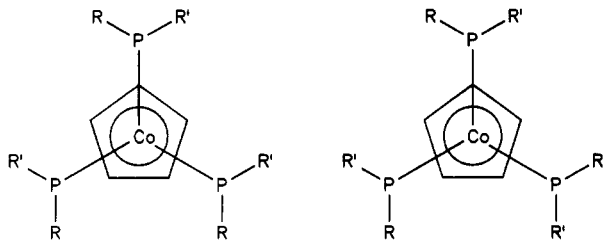


Figure 1. Newman projections of the two diastereomers 3 (*R* and *S* refer to the configurations of the three phosphorus centers).

Stereochemistry and Spectroscopic Results. The formation of the ligands 3 does not proceed with high stereoselectivity. The product 3 consists of a pair of diastereomers, each of which is an enantiomeric pair (cf. Figure 1); we did not succeed in separating the diastereomers. The formation of the *RRR/SSS* diastereomer is preferred. Accordingly, the $^{31}P\{^1H\}$ NMR spectra show a singlet resonance of the *RRR/SSS* diastereomer and a less intense multiplet resonance due to the *RRS/SSR* diastereomer.

In the 68-MHz ^{13}C NMR spectra of 3 three of the four multiplets due to the $POCH_2$ and the $POCH_3$ moieties could be discerned. The stereochemical nonuniformity of the product and the C_1 symmetry of the *RRS/SSR* isomer, however, are evident neither from the other ^{13}C NMR signals nor from the proton NMR spectra.

The IR spectra of the ligands **3a–i** show the characteristic pattern of the ligand $[CpCo\{P(O)(OCH_3)(OR)\}_3]^-$.[6] In addition, absorptions of the donor moieties of the side chain are observed, i.e. ν(C=C) at 1645 cm^{-1} (**3a,b,f,g**), ν(CN) at about 2250 cm^{-1} (**3c,d,h,i**), and ν(CO) at 1710 cm^{-1} (**3e**), respectively. The ligands **3f–i** exhibit an additional band at 1130 cm^{-1} that arises from the asymmetrical C—O—C stretching vibration.

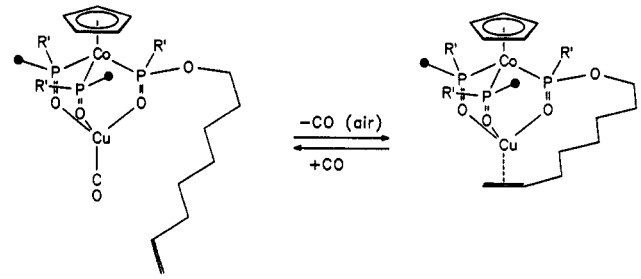
Coordination Chemistry. Complexes of the general formula $[ML_2]$ are formed from aqueous solutions of the sodium salts of 3 and divalent metal ions in quantitative yield at room temperature. The anions 3 act as tridentate ligands bonding via the three P=O moieties only, as indicated by a low-frequency shift of the P=O stretching vibration of about 40 cm^{-1}.

The complexes $[ML_2]$ are only slightly soluble in water. The polyether side chains make the ligands NaL (**3f–i**) freely soluble in water, but their hydrophilicity obviously is insufficient to keep complexes of the type $[ML_2]$ in aqueous solution.

In order to test the idea of stabilizing unsaturated intermediates by functionalized pendant side chains, we tried to prepare the copper(I) carbonyl complex [LCu(CO)], L = **3b**. We used $[Cu(NCCH_3)_4]PF_6$ in dichloromethane under 1 atm of carbon monoxide and NaL, a procedure by which we have already prepared before a series of copper carbonyl complexes of the type [L'Cu(CO)] with L' being an oxygen tripod ligand without additional side arms.[2] As judged from the ν(CO) vibration in the IR spectrum, the desired copper(I) complex formed but it behaved differently. The complexes [L'Cu(CO)] tend to disproportionate to copper metal and $[CuL'_2]$ when impure but are stable otherwise and do not lose carbon

(6) Kläui, W.; Dehnicke, K. *Chem. Ber.* **1978**, *111*, 451.

Scheme I. Decarbonylation Reaction of [LCu(CO)], L = 3b



● = $-O(CH_2)_6CH=CH_2$, R' = OCH_3

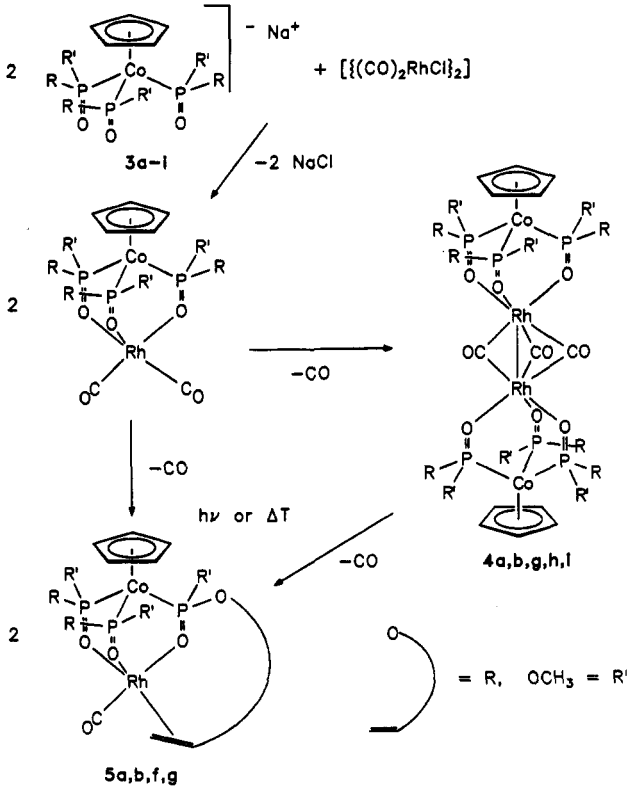
monoxide in vacuo below about 100 °C. In contrast, the complex [LCu(CO)], L = **3b**, loses the coordinated carbonyl ligand upon evaporation of the solvent but does not disproportionate. We found that the CO ligand is given off when either nitrogen or air is bubbled through the solution and that the carbonyl complex re-forms when kept under CO gas. This procedure can be repeated several times without apparent decomposition of the copper(I) complex (cf. Scheme I). Thus the complex [LCu(CO)], L = **3b**, can act as an air-stable carrier of CO. The three terminal olefin groups of the ligand L = **3b** obviously stabilize the LCu fragment rather effectively.

Rhodium(I) carbonyl compounds of the tripodal ligands were prepared by reaction of 2 equiv of the sodium salts of 3 with $[\{RhCl(CO)_2\}_2]$ to give complexes $[LRh(\mu\text{-}CO)_3RhL]$ (**4a,b,g–i**, cf. Scheme II). IR spectroscopic data (i.e. ν(CO) absorptions at about 2080 and 1995 cm^{-1}) indicate that at first products of the general formula $[LRh(CO)_2]$ (L = **3a,b,f,g–i**) are formed. Whether L acts as a bidentate or tridentate ligand in these dicarbonyl complexes is not clear. These products could not be isolated pure because they started losing carbon monoxide immediately, forming the dirhodium complexes 4. The reaction requires several weeks at room temperature for completion. It is remarkable that we were not able to isolate **4f**, though the initial formation of $[LRh(CO)_2]$ (L = **3f**) could be proved by IR spectroscopy. Further reaction yields a dark brown product that consists of several compounds containing bridging and terminal carbonyl ligands. One of these products could be identified as [LRh(CO)] (**5f**, L = **3f**), but the other products could not be characterized and the course of the reaction could not be elucidated. We have already reported on the formation of complexes 4 containing nonfunctionalized tripodal ligands. The X-ray structure of $[LRh(\mu\text{-}CO)_3RhL]$ (L^- = $[CpCo\{P(O)(OEt)_2\}_3]^-$) has been determined.[7]

The compounds of type 4 are very stable and inert toward decarbonylation or substitution reactions. Complexes **4a,b,f,g** and $[LRh(CO)_2]$ (L = **3a,b,f,g**) derived from ligands that bear additional olefin groups in the side chain can be decarbonylated thermally or photochemically to give novel complexes of general formula [LRh(CO)] (**5**). In these compounds rhodium is coordinated intramolecularly through one of the functionalized side chains. Attempts to prepare similar intramolecular complexes from $[LRh(CO)_2]$ (L = **3c,d,h,i**) derived from nitrile precursors were unsuccessful, probably because of the weaker π-acceptor character of the nitrile function.

(7) Kläui, W.; Scotti, M.; Valderrama, M.; Rojas, S.; Sheldrick, G. M.; Jones, P. G.; Schroeder, T. *Angew. Chem.* **1985**, *97*, 697; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 683.

Scheme II. Formation of Rhodium(I) Carbonyl Compounds with Functionalized Tripodal Ligands[a]



[a] Key: R' = OMe; a, R = $OC_3H_6CH{=}CH_2$; b, R = $OC_6H_{12}CH{=}CH_2$; c, R = OC_3H_6CN; d, R = $OC_6H_{12}CN$; e, R = $OC_3H_6C(O)CH_3$; f, R = $OC_2H_4OCH_2CH{=}CH_2$; g, R = $(OC_2H_4)_2OCH_2CH{=}CH_2$; h, R = $OC_2H_4OC_2H_4CN$; i, R = $O(C_2H_4O)_2C_2H_4CN$.

Table I. IR Spectroscopic Data for Rhodium(I) Compounds Containing the Functionalized Tripodal Ligands 3a,b,f-i

compd	ν(CO)/cm^{-1}	ν(P=O)/cm^{-1}
[LRh(CO)$_2$] (L = **3a**)	2083, 2004	1110
[LRh(CO)$_2$] (L = **3b**)	2080, 2000	1110
[LRh(CO)$_2$] (L = **3f**)	2084, 2044	1120
[LRh(CO)$_2$] (L = **3g**)	2073, 1998	1121
5a	1995	1140
5b	1985	1140
5f	1994	1136
5g	1995	1138
4a	1836	1110
4b	1840	1110
4g	1836	1105
4h	1837	1105
4i	1837	1105

The NMR spectra of the rhodium complexes are very similar to those of the free ligands, though the ^{13}C NMR spectra show additional resonances due to the CO ligands at about δ 205 ppm. The various carbonyl complexes can be distinguished by their IR spectra. The dicarbonyl complexes show two strong ν(CO) bands at approximately 2080 and 2000 cm^{-1}, the chelate monocarbonyl complexes **5** show one strong terminal ν(CO) band at approximately 1990 cm^{-1}, and the dirhodium complexes **4** show one strong ν(CO) band at approximately 1840 cm^{-1} due to the bridging carbonyl groups (cf. Table I).

Catalytic Studies. Several of the rhodium(I) compounds characterized above were screened for their catalytic activity in various model reactions. We were interested in the interdependence of the functionalization of the ligands and the catalytic activity and selectivity of their rhodium compounds. Table II gives the results

Table II. Hydrogenation of Cyclohexene at 60 °C[a]

catalyst	precipitation of metal	TON
4j	strong	220
4j + 5 mL of acetone	trace	660
[LRh(CO)$_2$] (L = **3e**)	trace	720
4j + 5 mL of acetonitrile	trace	20
[LRh(CO)$_2$] (L = **3c**)	trace	20
[LRh(CO)$_2$] (L = **3d**)	trace	20

[a] Conditions: t = 2 h, p_{H_2} = 40 bar, molar ratio catalyst:cyclohexene = 1:1000, catalyst dissolved in 10 mL of CH_2Cl_2, turnover determined by gas chromatography.

Table III. Catalytic Hydroformylation of Propene at 120 °C[a]

catalyst	TON	ratio n/i
4j	30	0.7
4j + 2.7 mmol of PPh_3	50	1.7
[LRh(CO)$_2$] (L = **3a**)	280	0.6
[LRh(CO)$_2$] (L = **3a**) + 2.7 mmol of PPh_3	390	2.6
[LRh(CO)$_2$] (L = **3c**)	340	0.7
[LRh(CO)$_2$ (L = **3c**) + 2.7 mmol of PPh_3	690	2.2

[a] Conditions: t = 16 h, 0.1 mmol catalyst dissolved in 10 mL of THF. The turnover and product distribution were determined by gas chromatography.

obtained for hydrogenation of cyclohexene with several rhodium complexes containing tripodal ligands. We found two compounds (i.e. LRh(CO)$_2$ (L = **3e**) and $L_{OMe}Rh(CO)_3RhL_{OMe}$ (**4j**) (L_{OMe}^- = [CpCo{P(O)(OCH$_3$)$_2$}$_3$]$^-$)) that are effective catalysts, but with the latter compound a black precipitate of rhodium metal was formed, indicating that the catalytic activity of **4j** may be the result of a heterogeneous reaction. There is no such precipitation of metal when acetone is added to the solution. This solvent obviously stabilizes the catalytically active intermediates just as well as the keto group does in [LRh(CO)$_2$] (L = **3e**). From the close correspondence between those results we conclude that in both cases the particular activity and stability of the catalyst are due to the coordinative bonding of a keto group to the rhodium center.

The use of [LRh(CO)$_2$] (L = **3c**, **3d**) or **4j** with additional acetonitrile as catalysts for hydrogenation of cyclohexene gives poor results. There is obviously a blocking of the catalysis arising from coordination of a nitrile moiety to the metal center. The low activity that was observed is likely to be the result of a heterogeneous hydrogenation catalyzed by the traces of precipitated metallic particles.

Rhodium complexes containing functionalized and nonfunctionalized tripodal ligands were found to be active hydroformylation catalysts. The results of our model reaction (hydroformylation of propene) are shown in Table III.

Not all rhodium complexes are effective catalysts for hydroformylation. Complexes containing nonfunctionalized tripodal ligands show rather low activity whereas functionalization of the ligands increases the activity by a factor of 10. It is remarkable that there is no difference between the ligands with additional olefin groups and those with additional nitrile moieties. All catalytic hydroformylation reactions that we carried out show that normally the formation of the branched product is preferred. This product distribution can be reversed by addition of triphenylphosphine to the catalyst solution. We attempted to isolate a product of defined composition from the reaction of **4j** with phosphines but without success. We do not know the composition of the catalytically active species.

Table IV. Catalytic Cyclotrimerization of Dimethyl Acetylenedicarboxylate at 120 °C[a]

catalyst	ton	catalyst	ton
[LRh] (L = **3f**)	55	**5a**	23
[LRh] (L = **3g**)	60	$[L_{OMe}Rh(CO)_2]$	<10
5f	57		

[a] Conditions: ratio catalyst:acetylene = 1:100, t = 24 h, no solvent, turnover determined by ^1H NMR spectroscopy.

There has been a lot of recent interest in cyclotrimerization reactions of alkynes[8a] and cyclocotrimerization reactions of alkynes with other unsaturated compounds[8b] catalyzed by (η^5-cyclopentadienyl)cobalt and -rhodium complexes; reactions of this type have been used to synthesize polycyclic and heterocyclic compounds. Bönnemann[8b] has shown that the catalytic activity of the $(C_5R_5)M$ fragment can be influenced by variation of the substituents R, i.e. the donor strength of the cyclopentadienyl ligand. We investigated the effect of ligands with additional donor moieties on the activity of complexes [LRh(CO)] (L = tripodal ligand) and compared them to the activity of $[L_{OMe}Rh(CO)_2]$, which had to be generated in situ from NaL_{OMe} and $[\{RhCl(CO)_2\}_2]$. We selected the cyclotrimerization of dimethyl acetylenedicarboxylate at 120 °C as a model reaction, presuming that under these conditions [LRh(CO)] and [LRh] are the catalytically active species. The results are summarized in Table IV. The compounds with functionalized tripodal ligands showed much higher activity than $[L_{OMe}Rh(CO)_2]$ which decarbonylates slowly to yield **4j**. Obviously, the catalyst remains active only if there are donor groups in the side chain to stabilize the compounds [LRh(CO)] and [LRh].

Concluding Remarks. Our results show that the concept of "dangling ligands" can be used to generate and control the catalytic activity of transition metal complexes.[9] The chelate effect of the tripod ligands is very high and the three P=O oxygen donor centers have electronic properties to those of fluoride and oxide. They will tend to stabilize high oxidation states of the coordinated metal ion. In catalytic processes involving oxidative addition/reductive elimination reactions, the efficiency of our ligand system will therefore depend on how well the dangling ligands can stabilize the lower oxidation state without coordinatively blocking the metal center.

Experimental Section

General Procedures. All reactions were carried out under dry nitrogen using freshly distilled dry solvents. All preparations and manipulations were carried out using standard Schlenk techniques although all ligands were air-stable.

IR spectra were recorded on a Perkin-Elmer 580 spectrophotometer and a FT-IR 1720 X spectrometer, respectively. ^1H and ^{31}P NMR spectra were taken on a WP 80 SY spectrometer operating at 80.1 and 32.4 MHz, respectively.

The chemical shifts of the ^{31}P NMR signals are relative to external 85% H_3PO_4. Elemental analyses were performed on a Carlo Erba 1106 elemental analyzer. GC analyses were obtained on a Carlo-Erba 2150 gas chromatographic analyzer with flame ionization detector (30-m × 0.5-mm OV 101 column, Spectra Physics SP 4100 integrator) and a Siemens Sicromat 3 gas chromatographic analyzer (50-m × 0.25-mm OV 1 column, Spectra Physics SP 4290 integrator), respectively.

Literature methods were used for the preparation of $HOC_3H_6CH{=}CH_2$,[10] $HOC_6H_{12}CH{=}CH_2$,[11] HOC_3H_6CN,[12-14] $HOC_6H_{12}CN$,[12-14] $HO(C_2H_4O)_nC_3H_5$ (n = 1, 2),[15] $HOC_2H_4OC_2H_4CN$,[16] $P(OCH_3)_2Cl$,[17] $[CpCo(CO)_2]$,[18] NaL_{OMe},[2] $[CpCoI_2(CO)]$,[19] $[\{RhCl(CO)_2\}_2]$,[20] and $[L_{OMe}Rh(\mu\text{-}CO)_3RhL_{OMe}]$ (**4j**).[7] $HO(C_2H_4O)_2C_2H_4CN$ was prepared according to the preparation for $HO(C_2H_4O)_2CH_2CH{=}CH_2$. All other starting materials were commercially available.

Preparation of the Phosphites $P(OCH_3)_2(OR)$. Pyridine (15.8 g, 200 mmol) and an equimolar amount of the alcohol HOR are dissolved in 200 mL of diethyl ether in a 500-mL round-bottomed flask fitted with a reflux condenser and a dropping funnel. The mixture is cooled to 0–5 °C on an ice bath. Dropwise addition of a solution of $P(OCH_3)_2Cl$ (25.7 g, 200 mmol) in 100 mL of diethyl ether during 2 h produces a white precipitate of pyridinium hydrochloride. After removal of the ice bath the mixture is allowed to warm to room temperature and stirred for 20 h to complete the reaction. The precipitate is filtered off through Celite and washed with several portions of diethyl ether. After removal of the solvent in vacuo, the crude product is fractionated under the mildest possible conditions.

2a ($R = C_3H_6CH{=}CH_2$): bp 69–71 °C/20 mbar: yield 18.7 g (105 mmol, 53%); ^1H NMR ($CDCl_3$) δ 1.5–1.8 (m, $^3J_{HH}$ = 6.2 Hz, 2H), 1.9–2.3 (m, $^3J_{HH}$ = 6.2 Hz, 2H), 3.43 (d, $^3J_{HP}$ = 10.4, 6H), 3.74 (td, $^3J_{HH}$ = 6.4 Hz, $^3J_{HP}$ = 7.7 Hz, 2H), 4.9 (dm, $^3J_{HH_{cis}}$ = 9.9 Hz, 1H), 5.0 (dm, $^3J_{HH_{trans}}$ = 17.0 Hz, 1H), 5.8 (tdd, $^3J_{HH}$ = 6.4 Hz, $^3J_{HH_{cis}}$ = 9.9 Hz, $^3J_{HH_{trans}}$ = 17.0 Hz, 1H) ppm; IR (film) ν(C=C) 1640 (m) cm^{-1}.

2b ($R = C_6H_{12}CH{=}CH_2$): bp 109–113 °C/20 mbar; yield 23.5 g (106 mmol, 53%); ^1H NMR ($CDCl_3$) δ 1.36–1.78 (m, 8H), 1.93–2.21 (m, 2H), 3.5 (d, $^3J_{HP}$ = 10.5 Hz, 6H), 3.75 (td, $^3J_{HH}$ = 6.4 Hz, $^3J_{HP}$ = 7.9 Hz, 2H), 4.86 (dm, $^3J_{HH_{cis}}$ = 9.9 Hz, 1H), 5.03 (dm, $^3J_{HH_{trans}}$ = 17.2 Hz, 1H), 5.08 (tdd, $^3J_{HH}$ = 6.6 Hz, $^3J_{HH_{cis}}$ = 9.9 Hz, $^3J_{HH_{trans}}$ = 17.2 Hz, 1H) ppm; IR (film) ν(C=C) 1640 (m) cm^{-1}.

2c ($R = C_3H_6CN$): bp 84 °C/2.7 mbar; yield 12.0 g (68.5 mmol, 34%); ^1H NMR ($CDCl_3$) δ 1.87–2.13 (tt, $^3J_{HH}$ = 6.2 Hz, 2H), 2.50 (t, $^3J_{HH}$ = 7.0 Hz, 2H), 3.53 (d, $^3J_{HP}$ = 10.7 Hz, 6H), 3.91 (dt, $^3J_{HH}$ = 5.6 Hz, $^3J_{HP}$ = 7.0 Hz, 2H) ppm; IR (film) ν(CN) 2244 (m), ν(P–O) 1040–1000 (s) cm^{-1}.

2d ($R = C_6H_{12}CN$): bp 82–84 °C/0.11 mbar; yield 24.0 g (109.4 mmol, 55%); ^1H NMR ($CDCl_3$) δ 1.00–2.00 (m, 8H), 2.26 (t, $^3J_{HH}$ = 6.3 Hz, 2H), 3.41 (d, $^3J_{HP}$ = 10.5 Hz, 6H), 3.71 (dt, $^3J_{HP}$ = 7.7 Hz, $^3J_{HH}$ = 6.1 Hz, 2H) ppm; IR (film) ν(CN) 2244 (m) cm^{-1}.

2e ($R = C_3H_6C(O)CH_3$: bp 105 °C/20 mbar; yield 8.3 g (42.4 mmol, 21%); ^1H NMR ($CDCl_3$) δ 1.83 (tt, $^3J_{HH}$ = 7.4 Hz, 2H), 2.07 (s, 3H), 2.48 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 3.42 (d, $^3J_{HH}$ = 6.2 Hz, $^3J_{HP}$ = 7.6 Hz, 2H) ppm; IR (film) ν(C=O) 1712 (vs) cm^{-1}.

2f ($R = C_2H_4OCH_2CH{=}CH_2$): bp 75 °C/6 mbar, yield 22.6 g (115.5 mmol, 58%); ^1H NMR ($CDCl_3$) δ 3.45 (d, $^3J_{HP}$ = 10.7 Hz, 6H), 3.46–3.60 (m, 2H), 3.73–3.90 (m, 2H), 3.96 (ddd, $^3J_{HH}$ = 5.4 Hz, $^4J_{HH_{cis}}$ = $^4J_{HH_{trans}}$ = 1.3 Hz, 2H), 5.00–5.33 (m, 2H), 5.85 (ddt, $^3J_{HH}$ = 5.4 Hz, $^3J_{HH_{cis}}$ = 9.9 Hz, $^3J_{HH_{trans}}$ = 17.3 Hz, 1H) ppm; ^{31}P NMR ($CDCl_3$) δ 138.2 (tsept, $^3J_{POCH_2}$ = 8.1 Hz, $^3J_{POCH_3}$ = 10.7 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 48.92 (dq, $^1J_{CH}$ = 145.2 Hz, $^2J_{CP}$ = 9.9 Hz), 61.40 (dt, $^1J_{CH}$ = 143.8 Hz, $^2J_{CP}$ = 10.0 Hz), 69.84 (dt, $^1J_{CH}$ = 143.3 Hz, $^3J_{CP}$ = 3.5 Hz), 72.00 (t, $^1J_{CH}$ = 141.0 Hz), 116.80 (dd, $^1J_{CH_{cis}}$ = $^1J_{CH_{trans}}$ = 159.3 Hz), 134.65 (d, $^1J_{CH}$ = 154.3 Hz) ppm; IR (film) ν(C=C) 1648 (w) cm^{-1}.

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2g (R = $(C_2H_4O)_2CH_2CH{=}CH_2$): bp 68 °C/0.002 mbar, yield 25.0 g (104.5 mmol, 52%); ^{1}H NMR ($CDCl_3$) δ 3.44 (d, $^3J_{HP}$ = 10.6 Hz, 6H), 3.52–3.70 (m, 6H), 3.77–3.93 (m, 2H), 3.94 (ddd, $^3J_{HH}$ = 5.4 Hz, $^4J_{HH_{cis}}$ = $^4J_{HH_{trans}}$ = 1.4 Hz, 2H), 5.00–5.31 (m, 2H), 5.85 (ddt, $^3J_{HH}$ = 5.4 Hz, $^3J_{HH_{cis}}$ = 9.9 Hz, $^3J_{HH_{trans}}$ = 17.3 Hz, 1H) ppm; ^{31}P NMR ($CDCl_3$) δ 138.0 (tsept, $^3J_{POCH_3}$ = 10.6 Hz, $^3J_{POCH_2}$ = 8.0 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 48.89 (dq, $^1J_{CH}$ = 145.1 Hz, $^2J_{CP}$ = 9.5 Hz), 61.34 (dt, $^1J_{CH}$ = 142.9 Hz, $^2J_{CP}$ = 11.0 Hz), 69.40 (t, $^1J_{CH}$ = 141.7 Hz), 70.57 (t, $^1J_{CH}$ = 142.1 Hz), 71.01 (dt, $^1J_{CH}$ = 140.3 Hz, $^3J_{CP}$ = 3.9 Hz), 72.08 (t, $^1J_{CH}$ = 142.1 Hz), 116.76 (dd, $^1J_{CH_{cis}}$ = $^1J_{CH_{trans}}$ = 156.9 Hz), 134.75 (d, $^1J_{CH}$ = 154.5 Hz) ppm; IR (film) ν(C=C) 1648 (m) cm^{-1}. Anal. Calcd for $C_9H_{19}O_7P$: C, 45.37; H, 8.03. Found: C, 45.07; H, 8.21.

2h (R = $C_2H_4OC_2H_4CN$): bp 81 °C/0.55 mbar, yield 13.4 g (64.3 mmol, 32%); ^{1}H NMR ($CDCl_3$) δ 2.57 (t, $^3J_{HH}$ = 6.3 Hz, 2H), 3.48 (d, $^3J_{HP}$ = 10.6 Hz, 6H), 3.62 (t, $^3J_{HH}$ = 6.3 Hz, 2H), 3.64–4.05 (m, 4H) ppm; ^{31}P NMR ($CDCl_3$) δ 138.1 (tsept, $^3J_{POCH_2}$ = 7.7 Hz, $^3J_{POCH_3}$ = 10.7 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 18.72 (t, $^1J_{CH}$ = 135.5 Hz), 49.00 (dq, $^1J_{CH}$ = 145.2 Hz, $^2J_{CP}$ = 10.2 Hz), 61.20 (dt, $^1J_{CH}$ = 143.2 Hz, $^2J_{CP}$ = 10.5 Hz), 65.79 (t, $^1J_{CH}$ = 145.9 Hz), 71.09 (dt, $^1J_{CH}$ = 140.5 Hz, $^3J_{CP}$ = 4.4 Hz), 117.59 (s) ppm; IR (film) ν(CN) 2251 (m) cm^{-1}. Anal. Calcd for $C_7H_{14}NO_4P$: C, 40.58; H, 6.81; N, 6.76. Found: C, 40.09; H, 6.96; N, 6.73.

2i (R = $(C_2H_4O)_2C_2H_4CN$): bp 110 °C/0.05 mbar, yield 14.3 g (56.6 mmol, 28%); ^{1}H NMR ($CDCl_3$) δ 2.55 (t, $^3J_{HH}$ = 6.4 Hz, 2H), 3.41 (d, $^3J_{HP}$ = 10.6 Hz, 6H), 3.61 (m, 4H), 3.67 (t, $^3J_{HH}$ = 6.4 Hz, 2H), 3.65–4.01 (m, 4H) ppm, ^{31}P NMR ($CDCl_3$) δ 138.0 (tsept, $^3J_{POCH_2}$ = 8.0 Hz, $^3J_{POCH_3}$ = 10.7 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 18.67 (t, $^1J_{CH}$ = 135.5 Hz), 48.95 (dq, $^1J_{CH}$ = 145.0 Hz, $^2J_{CP}$ = 10.2 Hz), 61.42 (dt, $^1J_{CH}$ = 143.2 Hz, $^2J_{CP}$ = 10.9 Hz), 65.92 (t, $^1J_{CH}$ = 145.9 Hz), 70.53 (t, $^1J_{CH}$ = 141.3 Hz), 70.68 (t, $^1J_{CH}$ = 141.6 Hz), 71.13 (dt, $^1J_{CH}$ = 140.2 Hz, $^3J_{CP}$ = 4.8 Hz), 117.67 (s) ppm; IR (film): ν(CN) 2251 (m) cm^{-1}. Anal. Calcd for $C_9H_{18}NO_5P$: C, 43.02; H, 7.22; N, 5.57. Found: C, 42.76; H, 7.37; N, 5.46.

Synthesis of the Ligands Na3. To a solution of 30 mmol of the tertiary phosphite $P(OCH_3)_2(OR)$ in 20 mL of acetone is added dropwise during 1.5 h a solution of 4.06 g (10 mmol) of $[CpCoI_2(CO)]$ in 80 mL of acetone. The cloudy solution immediately turns yellowish-brown, and gas evolves. The mixture is stirred for 9 h at room temperature to complete the reaction. After addition of 1.50 g (10 mmol) of NaI and further stirring for 20 h, the solvent is removed in vacuo. The residue is extracted with dichloromethane and the NaI filtered off. The dichloromethane is evaporated under reduced pressure. Chromatography of the crude product on silica gel gives two yellow bands (dichloromethane/acetone 1:1 and acetone/methanol 1:1). The second band contains the product. After removal of the solvent the product is isolated as a yellow or red oil.

Na3a: yield 4.8 g (7.6 mmol, 76%); ^{1}H NMR ($CDCl_3$) δ 1.51–1.84 (tt, $^3J_{HH}$ = 6.5 Hz, 6H), 2.03–2.29 (dt, $^3J_{HH}$ = 6.6 Hz, 6H), 3.58 (virt q, $^3J_{HP}$ = 10.4 Hz, 9H), 3.92 (m, 6H), 4.95 (dm, $^3J_{HH_{cis}}$ = 9.9 Hz, 3H), 4.98 (dm, $^3J_{HH_{trans}}$ = 17.4 Hz, 3H), 5.0 (s, 5H), 5.82 (tdd, $^3J_{HH}$ = 6.3 Hz, $^3J_{HH_{cis}}$ = 6.3 Hz, $^3J_{HH_{trans}}$ = 17.4 Hz, 3H) ppm; ^{31}P{^{1}H} NMR ($CDCl_3$, −50 °C) δ 106.8 (m) ppm; IR (film) ν(C=C) 1640 (m), ν(P=O) 1165 (vs), δ(C=CH, Cp) 830 (s), δ(P=O) 575 (s) cm^{-1}. Anal. Calcd for $C_{23}H_{41}CoNaO_9P_3{\cdot}^2/_3H_2O$: C, 42.60; H, 6.58. Found: C, 42.62; H, 6.65.

Na3b: yield 5.4 g (7.0 mmol, 70%); ^{1}H NMR ($CDCl_3$) δ 1.37–1.85 (m, 24H), 1.94–2.09 (m, 6H), 3.59 (virt q, $^3J_{HP}$ = 10.4 Hz, 9H), 3.89 (m, 6H), 4.94 (dm, $^3J_{HH_{cis}}$ = 9.9 Hz, 3H), 4.98 (dm, $^3J_{HH_{trans}}$ = 17.3 Hz, 3H), 5.01 (s, 5H), 5.86 (tdd, $^3J_{HH}$ = 6.5 Hz, $^3J_{HH_{cis}}$ = 9.9 Hz, $^3J_{HH_{trans}}$ = 17.3 Hz, 3H) ppm, ^{31}P{^{1}H} NMR ($CDCl_3$, −50 °C) δ 106.9 (m) ppm; IR (film) ν(C=C) 1640 (m), ν(P=O) 1165 (vs), δ(C=CH, Cp) 830 (m), δ(P=O) 575 (s) cm^{-1}. Anal. Calcd for $C_{32}H_{59}CoNaO_9P_3{\cdot}^2/_3H_2O$: C, 49.61; H, 7.85. Found: C, 49.70; H, 7.70.

Na3c: yield 6.2 g (9.8 mmol, 98%); ^{1}H NMR ($CDCl_3$) δ 1.96 (tt, $^3J_{HH}$ = 6.5 Hz, 6H), 2.58 (t, $^3J_{HH}$ = 6.8 Hz, 6H), 3.60 (virt q, $^3J_{HP}$ = 10.5 Hz, 9H), 3.7–4.2 (m, 6H), 5.06 (s, 5H) ppm; ^{31}P{^{1}H} NMR ($CDCl_3$, −50 °C) δ 107.8 (m) ppm; IR (film) ν(CN) 2245 (m), ν(P=O) 1160–1135 (vs), ν(P—O) 1140–1105 (vs), δ(C=CH, Cp) 830 (m), δ(P=O) 570 (s) cm^{-1}.

Na3d: yield 7.3 g (9.6 mmol, 96%); ^{1}H NMR ($CDCl_3$) δ 1.0–2.0 (m, 24H), 2.36 (t, $^3J_{HH}$ = 6.3 Hz, 6H), 3.57 (virt q, $^3J_{HP}$ = 9.9 Hz, 9H), 3.67–4.0 (m, 6H), 5.01 (s, 5H) ppm; ^{31}P{^{1}H} NMR ($CDCl_3$, −50 °C) δ 108.4 (m) ppm; IR (film) ν(CN) 2245 (m), ν(P=O) 1160 (vs), ν(P—O) 1050–1010 (vs), δ(C=CH, Cp) 830 (m), δ(P=O) 570 (s) cm^{-1}.

Na3e: yield 4.9 g (6.2 mmol, 62%); ^{1}H NMR ($CDCl_3$) δ 1.86 (tt, $^3J_{HH}$ = 6.7 Hz, 6H), 2.17 (s, 9H), 2.57 (t, $^3J_{HH}$ = 7.1 Hz, 6H), 3.56 (virt q, $^3J_{HP}$ = 9.8 Hz, 9H), 3.90 (m, 6H), 5.00 (s, 5H); ^{31}P{^{1}H} NMR ($CDCl_3$, −50 °C) δ 107.1 (m) ppm; IR (film) ν(CO) 1712 (vs), ν(P=O) 1165 (vs), 1140 (s), ν(P—O) 1050–1000 (vs), δ(C=CH, Cp) 830 (m), δ(P=O) 570 (s) cm^{-1}.

Na3f: yield 6.0 g (86.7 mmol, 87%); ^{1}H NMR ($CDCl_3$) δ 3.50 (m, 15H), 3.8–4.2 (m, br, 12H), 5.04 (s, 5H), 5.08–5.32 (m, 6H), 5.68–6.15 (ddt, $^3J_{HH}$ = 5.2 Hz, $^3J_{HH_{cis}}$ = 10.0 Hz, $^3J_{HH_{trans}}$ = 17.3 Hz, 3H) ppm; ^{31}P{^{1}H} NMR ($CDCl_3$, −50 °C) δ 105.1–114.8 (m) ppm; ^{13}C NMR ($CDCl_3$) δ 49.49, 50.03, 50.65 (3 × q, $^1J_{CH}$ = 145.3 Hz, 145.0 Hz, 144.5 Hz), 61.80, 62.35, 62.75 (3 × t, $^1J_{CH}$ = 145.1 Hz, 143.1 Hz, 144.9 Hz), 70.34 (t, $^1J_{CH}$ = 141.9 Hz), 71.95 (t, $^1J_{CH}$ = 139.5 Hz), 89.35 (d, $^1J_{CH}$ = 180.9 Hz), 116.8 (dd, $^1J_{CH_{cis}}$ = $^1J_{CH_{trans}}$ = 156.4 Hz), 135.27 (d, $^1J_{CH}$ = 154.8) ppm; IR (film) ν(C=C) 1648 (w), ν(P=O) 1168 (vs), δ(P=O) 571 (s) cm^{-1}. Anal. Calcd for $C_{23}H_{41}CoNaO_{12}P_3{\cdot}^2/_3H_2O$: C, 39.67; H, 5.67. Found: C, 39.20; H, 5.71.

Na3g: yield 7.45 g (9.0 mmol, 90%); ^{1}H NMR (acetone-d_6) δ 3.52–3.71 (m, 27H), 4.00 (ddd, $^3J_{HH}$ = 5.2 Hz, $^4J_{HH_{cis}}$ = $^4J_{HH_{trans}}$ = 1.4 Hz, 6H), 3.95–4.33 (m, br, 6H), 5.02 (s, 5H), 5.02–5.38 (m, 6H), 5.93 (ddt, $^3J_{HH}$ = 5.1 Hz, $^3J_{HH_{cis}}$ = 10.1 Hz, $^3J_{HH_{trans}}$ = 17.3 Hz, 3H) ppm; ^{31}P{^{1}H} NMR (acetone-d_6, −60 °C) δ 109.7–113.2 (m) ppm; ^{13}C NMR ($CDCl_3$) δ 49.83, 50.28, 50.67 (3 × q, $^1J_{CH}$ = 143.5 Hz, 144.1 Hz, 145.0 Hz), 61.95, 62.36, 62.72 (3 × t, $^1J_{CH}$ = 145.4 Hz, 145.0 Hz, 146.0 Hz), 69.59 (t, $^1J_{CH}$ = 141.7 Hz), 70.34 (t, $^1J_{CH}$ = 140.5), 71.73 (t, $^1J_{CH}$ = 144.1 Hz), 72.17 (t, $^1J_{CH}$ = 137.8 Hz), 89.55 (d, $^1J_{CH}$ = 180.8 Hz), 116.94 (dd, $^1J_{CH_{cis}}$ = $^1J_{CH_{trans}}$ = 156.1 Hz), 134.9 (d, $^1J_{CH}$ = 155.4 Hz) ppm; IR (film) ν(C=C) 1647 (w), ν(P=O) 1172 (vs), δ(P=O) 576 (s) cm^{-1}. Anal. Calcd for $C_{29}H_{53}CoNaO_{15}P_3{\cdot}^2/_3H_2O$: C, 42.04; H, 6.56. Found: C, 42.12; H, 6.69.

Na3h: yield 5.1 g (6.9 mmol, 69%); ^{1}H NMR ($CDCl_3$) δ 2.69 (t, $^3J_{HH}$ = 6.5 Hz, 6H), 3.62 (m, br, 15H), 3.74 (t, $^3J_{HH}$ = 6.5 Hz, 6H), 4.04 (m, br, 6H), 5.03 (s, 5H) ppm; ^{31}P{^{1}H} NMR ($CDCl_3$, −50 °C) δ 107.9–112.1 (m) ppm; ^{13}C NMR ($CDCl_3$) δ 18.61 (t, $^1J_{CH}$ = 136.4 Hz), 50.05, 50.52, 51.01 (3 × q, $^1J_{CH}$ = 144.4 Hz, 145.0 Hz, 145.3 Hz), 61.85, 62.36, 62.66 (3 × t, $^1J_{CH}$ = 144.2 Hz, 144.6 Hz, 144.0 Hz), 65.68 (t, $^1J_{CH}$ = 146.3 Hz), 71.48 (t, $^1J_{CH}$ = 141.8 Hz), 89.34 (dt, $^1J_{CH}$ = 181.1 Hz, $^2J_{CH}$ = 6.3 Hz), 118.19 (s) ppm; IR (film) ν(CN) 2250 (m), ν(P=O) 1163 (vs), δ(P=O) 572 (vs) cm^{-1}. Anal. Calcd for $C_{23}H_{38}N_3NaCoO_{12}P_3{\cdot}^2/_3H_2O$: C, 37.56; H, 5.34; N, 5.71. Found: C, 37.71; H, 5.12; N, 5.53.

Na3i: yield 7.1 g (8.2 mmol, 82%); ^{1}H NMR ($CDCl_3$) δ 2.60 (t, $^3J_{HH}$ = 6.4 Hz, 6H), 3.57–3.66 (m, br, 27H), 3.69 (t, $^3J_{HH}$ = 6.4 Hz, 6H), 4.03 (m, br, 6H), 5.02 (s, 5H) ppm; ^{31}P{^{1}H} NMR ($CDCl_3$, −50 °C) δ 107.2–111.0 (m) ppm; ^{13}C NMR ($CDCl_3$) δ 18.66 (t, $^1J_{CH}$ = 135.6 Hz), 49.87, 50.24, 50.65 (3 × q, $^1J_{CH}$ = 145.0 Hz, 146.7 Hz, 145.8 Hz), 61.80, 62.20, 62.51 (3 × t, $^1J_{CH}$ = 144.1 Hz, 145.6 Hz, 144.8 Hz), 65.84 (t, $^1J_{CH}$ = 148.0 Hz), 70.11 (t, $^1J_{CH}$ = 141.3 Hz), 70.66 (t, $^1J_{CH}$ = 143.0 Hz), 71.69 (t, $^1J_{CH}$ = 136.7 Hz), 89.35 (d, $^1J_{CH}$ = 181.1 Hz), 117.82 (s) ppm; IR (film) ν(CN) 2250 (w), ν(P=O) 1157 (vs), δ(P=O) 576 (vs) cm^{-1}. Anal. Calcd for $C_{29}H_{50}N_3NaCoO_{15}P_3{\cdot}^2/_3H_2O$: C, 40.15; H, 6.00; N, 4.84. Found: C, 40.38; H, 6.05; N, 4.78.

Preparation of $[ML_2]$ (L = 3, M = Ni^{2+}, Ba^{2+}). To a solution of 0.5 mmol of the sodium salt of the ligand **3** in 30 mL of water is added dropwise during 1 h a solution of 0.25 mmol of a barium or nickel salt (chloride or sulfate) in 10 mL of water. After 16 h of stirring at room temperature, most of the product has precipitated as yellow oil. The solvent is removed in vacuo and the residue exrtracted with several portions of pentane. The solution is filtered and then evaporated to dryness to yield the analytically pure product.

$[NiL_2]$ (L = 3f): yield 335 mg (0.24 mmol, 98%) of yellow oil; IR (film) ν(C=C) 1647 (w), ν(P=O) 1124 (vs), δ(P=O) 597 (s)

cm^{-1}. Anal. Calcd for $C_{46}H_{82}Co_2NiO_{24}P_6$: C, 39.99; H, 5.98. Found: C, 39.90; H, 5.90.

[NiL_2] (L = 3g): yield 0.40 g (0.24 mmol, 96%) of yellow oil; IR (film) ν(C=C) 1647 (w), ν(P=O) 1125 (vs), δ(P=O) 576 cm^{-1}. Anal. Calcd for $C_{58}H_{106}Co_2NiO_{30}P_6$: C, 42.32; H, 6.49. Found: C, 41.96; H, 6.40.

[BaL_2] (L = 3g): yield 0.42 g (0.24 mmol, 96%) of yellowish-red oil; ^1H NMR ($CDCl_3$) δ 3.49–3.69 (m, 54H), 4.00 (d, $^3J_{HH}$ = 5.4 Hz, 12H), 3.97–4.10 (m, br, 12H), 5.03 (s, 10H), 5.07–5.37 (m, 12H), 5.91 (ddt, $^3J_{HH}$ = 5.4 Hz, $^3J_{HH_{cis}}$ = 9.9 Hz, $^3J_{HH_{trans}}$ = 17.3 Hz) ppm; IR (film) ν(C=C) 1648 (w), ν(P=O) 1143 (vs), δ(P=O) 576 (s) cm^{-1}. Anal. Calcd for $C_{58}H_{106}BaCo_2O_{30}P_6$: C, 40.39; H, 6.19. Found: C, 40.39; H, 6.26.

[NiL_2] (L = 3h): yield 353 mg (0.24 mmol, 96%) of green oil; IR (film) ν(CN) 2250 (m), ν(P=O) 1125 (vs), δ(P=O) 597 cm^{-1}. Anal. Calcd for $C_{46}H_{76}N_6Co_2NiO_{24}P_6 \cdot 2H_2O$: C, 36.94; H, 5.39; N, 5.62. Found: C, 36.68; H, 5.12; N, 5.45.

Preparation of 4a,b. To a solution of 194 mg (0.5 mmol) of [{$RhCl(CO)_2$}$_2$] in 50 mL of dichloromethane is added 1.0 mmol of the sodium salt of **3a** or **3b**. The mixture is heated until the reaction is complete (monitor by IR spectroscopy). The solution is then cooled to room temperature and the volume of solvent reduced in vacuo. The solution is chromatographed on silica gel to give the product as a yellow band (dichloromethane/acetone 2:1). After removal of the volatiles the product is isolated as yellow wax.

4a: ^1H NMR ($CDCl_3$) δ 1.51–1.84 (tt, $^3J_{HH}$ = 6.5 Hz, 12H), 2.03–2.29 (dt, $^3J_{HH}$ = 6.6 Hz, 12H), 3.68 (virt q, $^3J_{HP}$ = 10 Hz, 18H), 4.0 (m, 12H), 4.95 (dm, $^3J_{HH_{cis}}$ = 9.9 Hz, 12H), 4.98 (dm, $^3J_{HH_{trans}}$ = 17.4 Hz, 6H), 4.99 (s, 10H), 5.82 (tdd, $^3J_{HH}$ = 6.3 Hz, $^3J_{HH_{cis}}$ = 9.9 Hz, $^3J_{HH_{trans}}$ = 17.4 Hz, 6H) ppm; IR (film) ν(CO) 1836 (vs), ν(C=C) 1640 (w), ν(P=O) 1110 (vs), δ(C=CH, Cp) 830 (m), δ(P=O) 590 (s) cm^{-1}.

4b: yield 700 mg (0.40 mmol, 79%); ^1H NMR ($CDCl_3$) δ 1.37–1.85 (m, 48H), 1.94–2.09 (m, 12H), 3.66 (virt q, $^3J_{HP}$ = 10.5 Hz, 18H), 3.97 (m, 12H), 4.94 (dm, $^3J_{HH_{cis}}$ = 9.9 Hz, 6H), 4.98 (dm, $^3J_{HH_{trans}}$ = 17.3 Hz, 6H), 4.98 (s, 5H), 5.86 (tdd, $^3J_{HH}$ = 6.5 Hz, $^3J_{HH_{cis}}$ = 9.9 Hz, $^3J_{HH_{trans}}$ = 17.3 Hz, 6H) ppm; IR (film) ν(CO) 1840 (vs), ν(C=C) 1640 (w), ν(P=O) 1110 (vs), δ(C=CH, Cp) 830 (m), δ(P=O) 590 (s) cm^{-1}.

Preparation of 4g–i. A 97-mg (0.25-mmol) sample of [{$RhCl(CO)_2$}$_2$] and 0.5 mmol of the sodium salt of the ligand **3** are dissolved in dichloromethane (60 mL), and the solution is stirred at room temperature until the reaction is complete. This takes about 12 days (IR monitoring). After evaporation of the solvent the residue is dried in vacuo and then extracted with dichloromethane (20 mL). To remove the remaining NaCl, the solution is washed with 20 mL of water. After separation of the phases the dichloromethane is evaporated to obtain the pure product.

4g: yield 423 mg (0.23 mmol, 90%) of yellowish-orange oil; ^1H NMR ($CDCl_3$) δ 3.62–3.72 (m, 54H), 4.00 (d, $^3J_{HH}$ = 5.4 Hz, 12H), 4.04–4.22 (m, br, 12H), 5.04 (s, 10H), 5.21–5.33 (m, 12H), 5.91 (ddt, $^3J_{HH}$ = 5.4 Hz, $^3J_{HH_{cis}}$ = 10.0 Hz, $^3J_{HH_{trans}}$ = 17.3 Hz, 6H) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$, –50 °C); δ = 112.5–119.1 (m) ppm; IR (CH_2Cl_2) ν(CO) 1836 (vs), ν(P=O) 1105 (vs) cm^{-1}. Anal. Calcd for $C_{61}H_{106}Co_2O_{33}P_6Rh_2$: C, 39.03; H, 5.69. Found: C, 39.39, H, 5.99.

4h: yield 418 mg (0.24 mmol, 97%) of yellow glass; ^1H NMR ($CDCl_3$) δ 2.63 (t, $^3J_{HH}$ = 6.2 Hz, 12H), 3.59–3.79 (m, 42H), 4.14 (m, br, 12H), 5.05 (s, 10H) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$, –50 °C) δ 112.1–115.9 (m) ppm; ^{13}C NMR ($CDCl_3$) δ 18.82 (t, $^1J_{CH}$ = 135.5 Hz), 51.05, 51.52, 52.14 (3 × q, $^1J_{CH}$ = 144.2 Hz, 146.1 Hz, 145.8 Hz), 62.60, 63.05, 63.39 (3 × t, $^1J_{CH}$ = 146.0 Hz, 147.2 Hz, 145.4 Hz), 65.30 (t, $^1J_{CH}$ = 147.5 Hz), 71.07 (t, $^1J_{CH}$ = 141.5 Hz), 89.38 (d, $^1J_{CH}$ = 181.8 Hz), 118.11 (s), 204.52 (t, $^1J_{CRh}$ = 30.7 Hz) ppm. Anal. Calcd for $C_{49}H_{76}Co_2N_6O_{27}P_6Rh_2$: C, 34.81; H, 4.53; N, 4.97. Found: C, 34.48; H, 4.60; N, 4.86.

4i: yield 473 mg (0.24 mmol, 97%) of dark brown oil; ^1H NMR ($CDCl_3$) δ 2.61 (t, $^3J_{HH}$ = 6.3 Hz, 12H), 3.66 (m, br, 54H), 3.71 (t, $^3J_{HH}$ = 6.3 Hz, 12H), 4.12 (m, br, 12H), 5.05 (s, 10H) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$, –50 °C) δ 112.1–115.6 (m) ppm; IR (CH_2Cl_2) ν(CN) 2256 (w), ν(CO) 1837 (vs), ν(P=O) 1105 (vs), δ(P=O) 589 (m) cm^{-1}. Anal. Calcd for $C_{61}H_{100}Co_2N_6O_{33}P_6Rh_2$: C, 37.48; H, 5.16; N, 4.30. Found: C, 37.71; H, 5.17; N, 4.25.

Preparation of [LRh(CO)] (5a,f,g) and [LRh] (L = 3f,g). A 0.6-mmol sample of the sodium salt of **3** and 190 mg (0.3 mmol) of [{$RhCl(CO)_2$}$_2$] are dissolved in toluene (20 mL). The solution is heated to 110 °C and refluxed for 45 h. After evaporation of the solvent the residue is extrracted twice with 10 mL of dichloromethane. The solution is filtered, and the volatiles are removed in vacuo. Chromatography on silica gel gives a yellow band (dichloromethane/acetone 1:1) that consists of byproducts and a reddish-brown band (acetone/methanol 2:1) that after evaporation of the solvent gives the product as a brown oil. If the initial mixture is exposed to prolonged heating, there is a third band that is eluted with acetone/methanol (1:1). It contains the completely decarbonylated product [LRh].

Catalytic Hydrogenation. In a typical run a solution of 0.1 mmol of the catalyst and 0.1 mol of cyclohexene in 10 mL of dichloromethane were introduced in a 100-mL stainless steel autoclave. Hydrogen was added to the desired pressure of 40 bar and the autoclave was heated to 60 °C during 2h. The conversion was determined by GC analysis.

Catalytic Hydroformylation. In a typical reaction a 100-mL stainless steel autoclave containing a solution of 0.1 mmol of the catalyst dissolved in 10 mL of tetrahydrofuran was filled with propene to a pressure of 7 bar. Carbon monoxide and hydrogen were added to a total pressure of 47 and 67 bar, respectively. The autoclave was heated to 120 °C during 16 h. The organic products were distilled from the catalyst. Turnover and product distribution were determined by GC analysis.

Catalytic Cyclotrimerization. In a typical reaction 2.13 g (15 mmol) of dimethyl acetylenedicarboxylate and 0.15 mmol of the catalyst were dissolved in 5 mL of toluene and the solution was heated to reflux. The reaction was monitored by ^1H NMR spectroscopy. ^1H NMR (toluene-d_8): δ 3.50 (s) (educt), 3.70 (s) (product) ppm.

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