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Synthesis of New Calix[4]arene-Based Phosphorus Ligands and Their Application in the Rh(I) Catalyzed Hydroformylation of 1-Octene

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ABSTRACT: *The synthesis of calix[4]arene-based phosphorus diamides and phosphites is described. These oligocyclic ligands have been tested in the Rh(I)-catalyzed hydroformylation of 1-octene. Depending on the reaction conditions, yields up to 99% and* n/iso-*selectivities between 0.7 and 2.6 have been observed.* tert-*Butyl groups on the upper rim of the calix[4]arene template had a beneficial effect on the catalytic reaction. In general biuret-derived P-ligands were superior. For comparison, the corresponding "monomeric" ligands have also been synthesized and were employed in the catalytic reaction.* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:577–585, 2001

INTRODUCTION

The synthesis of trivalent phosphorus compounds based on calixarenes and their application as ligands in homogeneously metal-catalyzed reactions is a rapidly growing field of general interest [1]. In particular P-ligands derived from calix[4]arenes form metal complexes with unique coordination modes [2]. In addition, the interior of the cavity represents a space potentially able to entrap or confine reactive fragments bound to the transition metal [3]. Several calix[4]arene ligands are easily available, and their synthesis is frequently based on a few steps. By functionalization of calix[4]arenes with phosphorus groups, a broad variety of phosphorus ligands, for example, phosphines or phosphites with different hapticity, electronic, and steric properties can be produced [4]. Selective functionalization of calix[4]arenes allows the incorporation of one [5], two [6], three [7], four [8] or even more [9] identical or different [10] phosphorus groups in a single calix[4]arene template. By substitution of the opposite rim, for example by the incorporation of bulky alkyl groups, further modifications influencing the coordination behavior and catalytic properties are possible.

A particular challenge is the application of calix[4]arene-containing phosphorus ligands in the homogeneously catalyzed hydroformylation of olefins. This reaction is of pivotal importance for academic research as well as for industrial application

Dedicated to Professor Marianne Baudler on the occasion of her 80th birthday.

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[11]. More than 7 million tons, in particular *n*-aldehydes, are produced annually in the bulk and specialty chemicals business. In the search for new and more efficient hydroformylation catalysts up to now mainly Rh(I) catalysts based on monophosphines and bisphosphines or monophosphites and bisphosphites have been investigated. In general, an excess of the phosphorus ligand has to be applied to avoid its full displacement from the metal by the competing CO. Considerable evidence was accumulated that with bidentate bisphosphines the ligand bite angle is of crucial importance for the regioselectivity in the hydroformylation product [12]. Other studies revealed that ligands with electron-withdrawing groups form more active and selective catalysts [13]. Recently, we showed methoxy or hydroxy groups adjacent to the phosphorus functionality to also exert a beneficial effect on the *n*-regioselective hydroformylation of internal olefins [14].

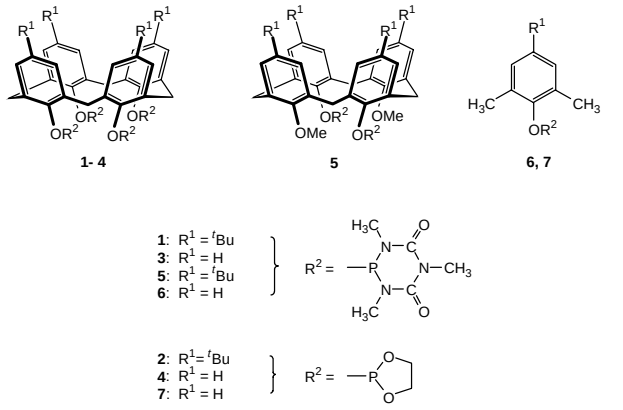
Due to the broad tunability and variability outlined above, calix[4]arene-containing phosphorus groups as ligands should have an interesting potential for selective hydroformylation reactions. Indeed, as recently shown, bidentate bisphosphites with a calix[4]arene backbone can advantageously be employed for the Rh(I)-catalyzed hydroformylation of 1-octene under low pressure affording good *n*:*iso* ratios [15]. Calix[4]arene phosphines and phosphinites, bonded to Pt(II), have also been successfully applied in hydroformylation catalysis [16]. In particular, attractive for an industrial application is the unique air-robustness of calix[4]arene monophosphites reported recently [17]. Such monophosphites are less π-acidic than most triarylphosphite ligands. Moreover, by incorporation of sulfonate groups in calix[4]arene bisphosphines, water-solubility of the hydroformylation catalyst can be achieved [18].

Herein, we describe the synthesis of electron-poor calix[4]arene based phosphorus diamides and phosphites and their application in the hydroformylation of 1-octene. In a previous article, some of us reported that the reaction of *p-tert*-butyl-calix[4]arene with 2-chloro-1,3,5-trimethyl-1,3,5-triaza-2$\sigma^3\lambda^3$-phosphorin-4,6-dione gives rise to the calix[4]arene-based tetradentate ligand **1** [19].

RESULTS AND DISCUSSION

Synthesis of the Ligands

In general, phosphoric acid diamides are stronger π-acids than triarylphosphines and more basic than triarylphosphites. Van Leeuwen et al. [20] suggested that they are electronically closely related to phosphites. However, the biuret group was considered to be a better electron acceptor than two aryloxy groups. Therefore, the comparison with analogous phosphites like the calix[4]arene-based tetraphosphite **2** (Scheme 1) seems to be of general interest. In order to study the effect of the *tert*-butyl substituents on the upper rim of the calix[4]arene fragment, we also synthesized the analogous compounds **3** and **4**. Prior protection of the hydroxy groups in the 1,3-positions as methyl ether and subsequent substitution of the remaining hydroxy groups with phosphorus-containing groups afforded the bidentate ligand **5** bearing methoxy groups as potentially hemilabile [21] ligands in close neighborhood to the *P*-ligating atoms. In order to identify catalytic effects that might be related to the cavity of the calixarene moiety, we also synthesized the "monomeric" ligands **6** and **7**.

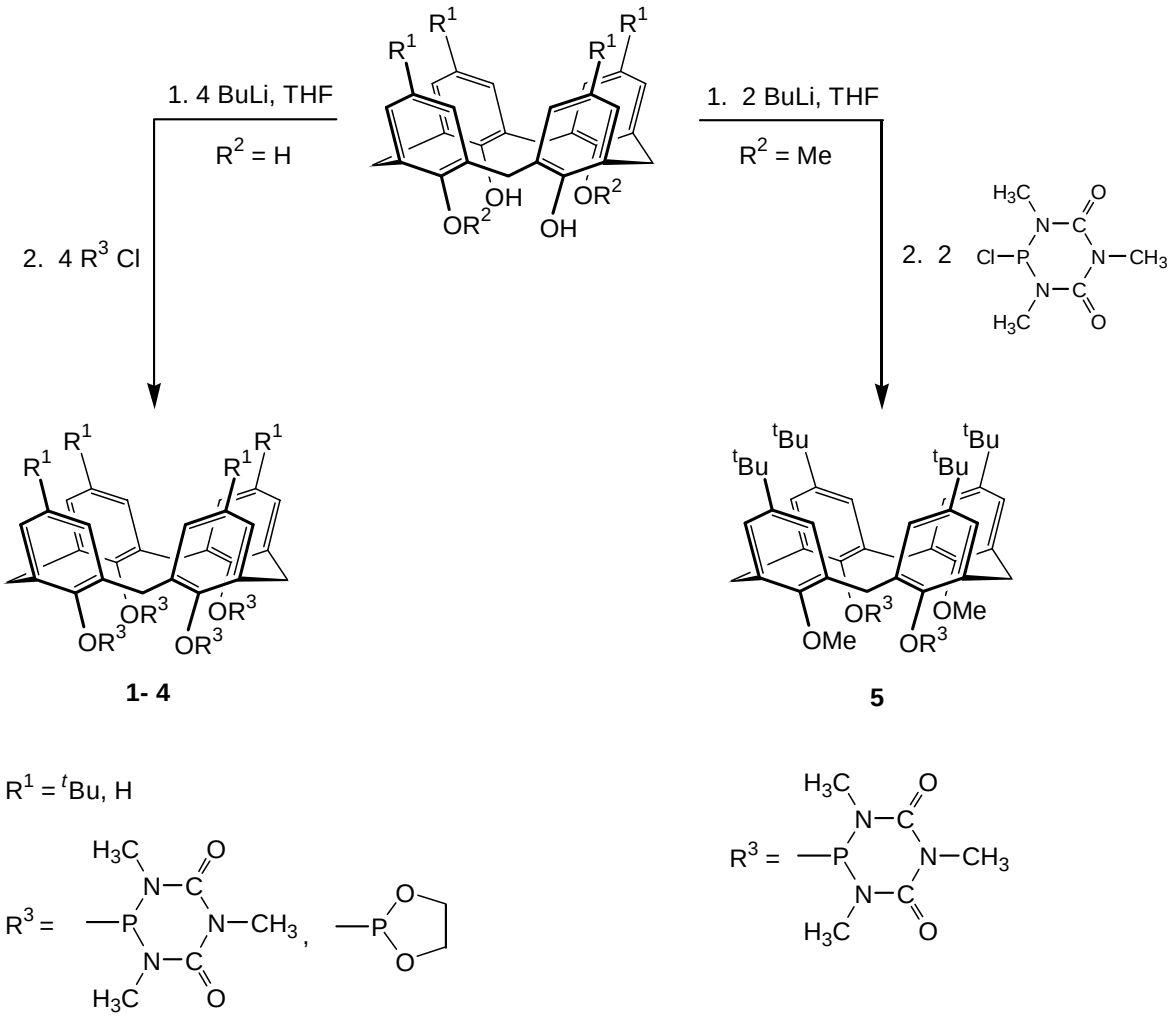


SCHEME 1 Various ligands used in the hydroformylation reactions.

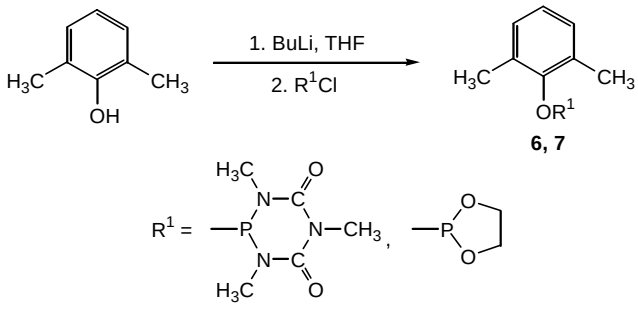
For the synthesis of calix[4]arene-containing phosphorus ligands, the required phenolates were generated by treatment of the macromolecular phenols with *n*-BuLi. Subsequent addition of four and two equivalents, respectively, of 2-chloro-1,3,5-trimethyl-1,3,5-triaza-2$\sigma^3\lambda^3$-phosphorin-4,6-dione afforded the desired derivatives **1–5** (Scheme 2).

The phosphites **2** and **4** (Scheme 2) were synthesized by the same method applying 2-chloro-1,3-dioxa-2$\sigma^3\lambda^3$-phospholane as a reagent.

The reaction of 2,6-dimethylphenol with one equivalent of *n*-BuLi and subsequent addition of one equivalent of 2-chloro-1,3,5-trimethyl-1,3,5-triaza-2$\sigma^3\lambda^3$-phosphorin-4,6-dione or 2-choro-1,3-dioxa-2$\sigma^3\lambda^3$-phospholane afforded, after vacuum distillation, the analytically pure compounds **6** and **7** (Scheme 3). These oily colorless liquids proved to be air- and moisture-sensitive. All new compounds



SCHEME 2 Synthesis of the ligands **1–5**.



SCHEME 3 Synthesis of the ligands **6** and **7**.

reported herein were characterized using mass spectrometry, NMR spectroscopy, and elemental analysis, giving results consistent with their expected structures.

The molecular structure of **3**, which was determined by X-ray crystallography, is depicted in Figure 1.

The X-ray crystal structure analysis confirmed the expected cone conformation of the calix[4]arene framework. The interplanar angles between the aromatic rings of the macrocycle and the calixarene reference plane (the average plane defined by the four bridging methylene carbon atoms) are 32.8, 72.5 and 38.5 and 72.3° (Figure 2). This cone conformation is distorted such that the distances between the centers of the opposite phenolic rings show remarkable differences. The distances between the centers of the opposite phenolic rings are 4.529 Å and 7.825 Å, respectively. As a result, two 1,3,5-triaza-$2\sigma^3\lambda^3$-phosphorin-4,6-dionyloxy groups are pointing away from the calix[4]arene cavity. The remaining two heterocycles approach each other in order to

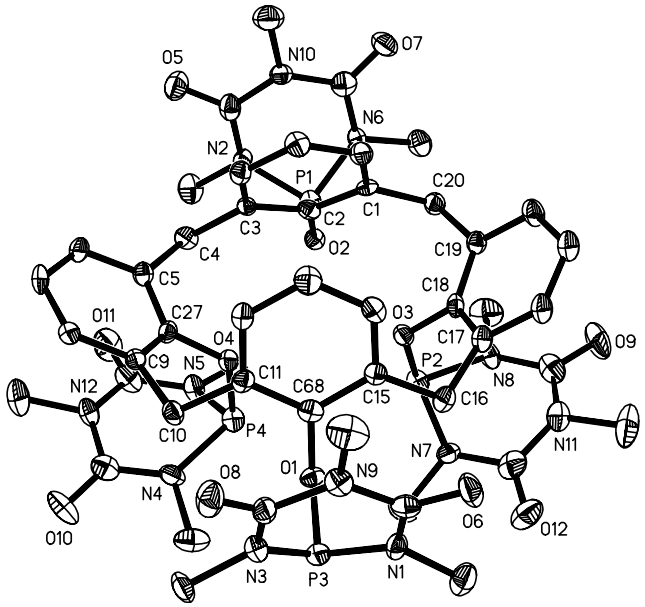


FIGURE 1 Molecular structure of **3** in the crystal. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths (pm) and angles(°): P(1)–O(2) 166.9(4), P(2)–O(3) 166.9(5), P(3)–O(1) 166.9(4), P(4)–O(4) 166.5(5), O(1)–C(68) 140.9(7), O(4)–C(27) 140.3(7), O(3)–C(18) 142.0(7), O(2)–C(2) 142.0(8); N(1)–P(3)–N(3) 96.0(3), N(7)–P(2)–N(8) 95.1(3), N(6)–P(1)–N(2) 94.8(3), N(5)–P(4)–N(4) 95.6(3), C(68)–O(1)–P(3) 121.4(3), C(27)–O(4)–P(4) 125.3(4), C(18)–O(3)–P(2) 124.0(4), C(2)–O(2)–P(1) 124.2(4), C(9)–C(10)–C(11) 110.0(5), C(17)–C(16)–C(15) 109.9(6), C(5)–C(4)–C(3) 109.8(5), C(1)–C(20)–C(19) 109.1(5).

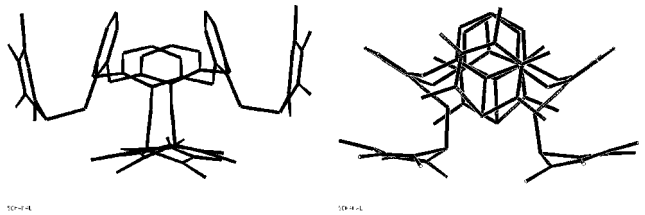


FIGURE 2 Two views (Schakal-92) of **3** showing the relative arrangement of the opposite aryl rings of the calixarene part.

minimize steric interactions between neighboring phenolic groups and heterocycles.

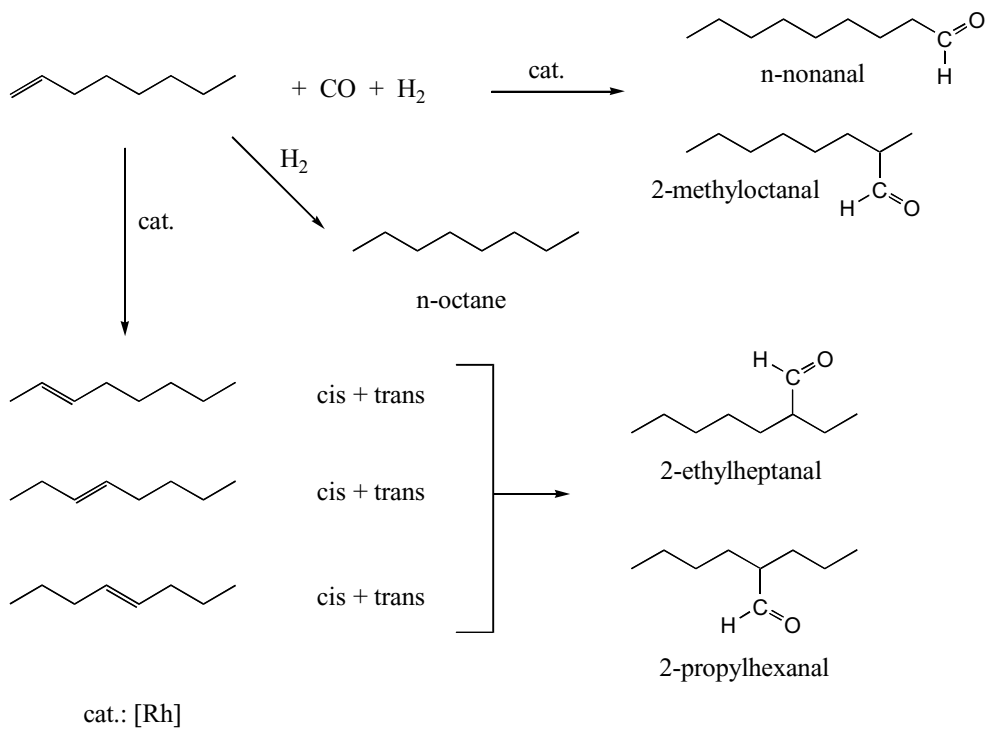
In contrast to the crystal structure of the comparable calixarene **1**, the opposite aryl rings of compound **3** are neither coplanar nor perpendicular (Figure 2) in the crystalline state (35.2° and 71.3°, respectively) [19]. Obviously, the cone conformation dominates in solution. Thus, in the ^{31}P NMR spectrum, two well separated resonances at $\delta = 92.6$ and 96.7 were observed, because of the hindered rotation about the P–O bond. The bridging methylene groups were characterized by two sets of signals in the ^{1}H and ^{13}C NMR spectra. By contrast, the 1,3-disubstituted compound **5** was characterized by a single resonance in the ^{31}P NMR spectrum. In the ^{13}C NMR spectrum one singlet for the C-atoms of the bridging methylene groups was observed. Both observations establish a normal cone conformation. The same standard cone conformation was deduced from the corresponding NMR spectra of compounds **2** and **4**.

Hydroformylation

Rhodium complexes of all new phosphorus ligands were tested in the hydroformylation of 1-octene. As illustrated in Scheme 4, depending on the extent of olefin isomerization prior to the hydroformylation, besides *n*-nonanal and 2-methyloctanal, different branched aldehydes can be formed from the corresponding internal olefins.

The hydroformylation reactions were carried out with a 1:1 mixture of CO and H_2 at a pressure of 40 or 50 bar. Precatalysts were generated prior to the hydroformylation *in situ* by mixing the relevant P-ligand with [(acac)Rh(1,5-cyclooctadiene)] in toluene. Depending on the solubility of the precatalysts, toluene, tetrahydrofuran (THF), or methylene chloride were used as solvents. In addition, the effect of varying Rh:ligand ratios was also investigated. In all trials, the ratio Rh:olefin of 1:15,700 was kept constant. Results of the catalytic reactions are summarized in Table 1.

It is obvious that all Rh(I)-complexes tested catalyze the hydroformylation of 1-octene. The reaction is sensitive to the conditions and ligands employed. In general, the increase of the P:Rh ratio enhances the *n*:*iso*-selectivity. As seen in the reactions with **1** a ligand, the change from toluene to THF as solvent can improve the regioselectivity as well as the yield. In the case of **5** and **6** the use of higher P:Rh ratios also improved the overall yield. The application of the bidentate ligand **5** bearing two additional hemilabile methoxy groups had no advantage over the use of the tetradentate ligand **1**. At a P:Rh ratio of 1:1 the presence of four *tert*-butyl groups in the *p*-position of the calix[4]arene template did not change the catalytic results (**1** versus **3**) because of the distance of these groups from the metal center. Thus, the steric influence of the butyl groups is not significant. However, at a higher P:Rh ratio, the catalyst based on **1** was superior in terms of activity. It is noteworthy that, with all ligands (except when **3** was used in a large excess), the activities were good or even excellent. The comparison of the results obtained with catalysts based on **1** and the monomeric ligand **6** indicates that the assembly of four ligating



SCHEME 4 Hydroformylation reaction of 1-octene with consideration of the prior isomerization of the substrate.

phosphorus diamide groups in the calix[4]arene structure does not disadvantageously affect the yield as well as the selectivity of the reaction. This is in contrast to related investigations of van Leeuwen and coworkers, who observed a remarkable loss of activity by replacement of monodentate by the corresponding bidentate ligands [20].

Compared to catalysts based on calix[4]arene biuret ligands, the hydroformylation with phosphites **2**, **4**, and **7** is much more sensitive to the structure of the ligands and conditions applied. In terms of activity, in general, calix[4]arene tetraphosphite-derived complexes were inferior in comparison to the related biuret catalysts. A small increase of the P:Rh ratio even blocked the catalytic reaction. In comparison to the biuret ligands slightly higher *n*-selectivities were noted. The catalyst formed by the monomeric ligand **7** was significantly more active than its calix[4]arene counterpart but displayed reduced selectivity.

CONCLUSION

A series of new calix[4]arene-containing phosphorus groups were synthesized and characterized. These compounds were tested as ligands in the Rh(I) catalyzed hydroformylation of 1-octene. All ligands could be successfully employed for this reaction. In general, moderate selectivities for the formation of the *n*-aldehyde were observed. Yield and regioselectivity of the hydroformylation were dependent on the structure of the ligand and the reaction conditions applied. Catalysts based on calix[4]arene-containing phosphorus diamide groups exhibited superior activity in comparison to the corresponding phosphites. This result confirms reports in the literature on effects obtained by the use of simpler phosphorus diamide and phosphite ligands [20]. Compared to the corresponding monomeric ligand, in several cases calix[4]arene-containing phosphorus diamide groups exhibited even higher efficiency and selectivity. The opposite tendency was noted in the series of phosphites. It seems that bulky groups like *tert*-butyl groups in the *p*-position of the ligating groups have a beneficial effect on the catalytic reaction. Thus, the loss of activity by application of high P:Rh ratios found with nonsubstitued calix[4]arene ligands was prevented by *tert*-butyl groups in the upper rim. The effect of additional MeO-groups in the lower rim of calix[4]arene-containing phosphorus diamide groups was quite small.

EXPERIMENTAL

All experiments were carried out with exclusion of air and moisture using Schlenk techniques. Solvents

TABLE 1 Hydroformylation of 1-Octene with Rh-Catalysts based on Ligands of Type **1, 2,** and **3**[a]

Ligand	T [°C]	p [bar]	Solvent	Rh:L	Yield[b] (%)	n-C9 (%)	i-C8 (%)	i-C7 (%)	i-C6 (%)	n/iso[c]
1	120	50	Toluene	1:1	92.1	42.3	34.6	12.8	10.3	0.73
1	120	50	THF	1:1	95.0	46.4	34.2	11.2	8.2	0.87
1	120	50	THF	1:10	89.4	61.7	34.8	3.0	0.5	1.61
5	100	50	THF	1:1	75.7	48.0	35.6	9.8	6.6	0.92
5	100	50	THF	1:2	88.4	50.2	35.0	9.0	5.8	1.01
5	100	50	THF	1:10	86.6	57.7	34.7	5.6	2.0	1.36
3	100	40	CH_2Cl_2	1:1	99.0	43.6	34.9	12.6	8.9	0.77
3	100	40	CH_2Cl_2	1:10	4.0	69.8	30.2	n.d.	n.d.	2.31
6	100	40	CH_2Cl_2	1:4	95.9	43.8	35.3	11.9	9.0	0.78
6	100	40	CH_2Cl_2	1:40	99.0	58.9	32.7	6.1	2.3	1.43
2	120	40	THF	1:1	39.6	68.8	28.5	2.3	0.4	2.19
2	120	40	THF	1:5	3.4	n.d.	n.d.	n.d.	n.d.	0.0
4	100	40	CH_2Cl_2	1:1	27.4	74.2	25.1	0.7	n.b.	2.58
7	100	40	CH_2Cl_2	1:4	92.4	60.7	32.9	5.3	2.1	1.54

[a]For conditions, see Experimental Section.
[b]Overall yield after 3 hours determined by VPC, with toluene as internal standard.
[c]Corresponds to the sum of all branched aldehydes formed. The amount of octane formed in this reaction is less than 1%.

were dried according to standard procedures and distilled immediately prior to use. The NMR spectra were recorded on Bruker AC 200 (200.1 MHz for ^{1}H NMR, 50.3 MHz for ^{13}C NMR, and 81.0 MHz for ^{31}P NMR spectra), Bruker DRX-400, and Bruker ARX 400 instruments (400.1 MHz for ^{1}H-NMR, 100.6 MHz for ^{13}C NMR and 162.0 MHz for ^{31}P NMR spectra); solvent $CDCl_3$; shifts are given, relative to TMS (^{1}H, ^{13}C) and 85% H_3PO_4 (^{31}P). The mass spectra were recorded on a Finnigan Mat 8430 and an AMD Intectra 402/3. Elemental analysis data were obtained on a Carlo Erba analytical gas chromatograph. The abreviation "i.v." refers to a pressure of 0.1 mm Hg.

p-tert-Butyl-calix[4]arene [22], calix[4]arene [23], *p-tert*-butyl-bis-dimethoxycalix[4]arene [24], and 2-chloro-1, 3, 5-trimethyl-1,3,5-triaza-2$\sigma^3\lambda^3$-phosphorin-4,6-dione [25] were prepared according to literature procedures.

The X-ray diffraction data of compound **3** were collected on a STOE-IPDS diffractometer using graphite-monochromated Mo Kα radiation. The structure was solved by direct methods (SHELXS-86) [26] and refined by full-matrix least-squares techniques against F^2 (SHELXL-93) [27]. XP (Siemens Analytical X-ray Instruments, Inc.) and Schakal-92 were used for structure representations.

The hydroformylation experiments were performed in a stainless steel 200 mL autoclave (Buddeberg GmbH, Mannheim, Germany), equipped with a reservoir, a pressure transducer, a thermocouple, a sampling device, and a magnetically driven stirrer. In a typical experiment, the autoclave was flushed several times with argon and afterwards charged with 5 mL of an 0.0121 M solution of [(acac)Rh(1,5-cyclooctadien)] in toluene, 51 mL of solvent, and the amount of the P-ligand indicated. Then the substrate in solution (15 mL of 1-octene) was charged into the reservoir. The autoclave was then pressurized with 30–33 bar of syngas and heated with stirring (1500 rpm) at 100 or 120°C. When the appropriate temperature was reached, the pressure was increased to 40 or 50 bar. During the whole reaction, the pressure was kept constant by means of a pressure controller (Fa. Bronkhorst, NL). Gas chromatographic analyses were performed on a Hewlett Packard 5890 Series II Plus instrument, equipped with a 50 m methyl siloxane cross-linked phase column (inner diameter 0.2 mm, film thickness 0.5 μm) and a flame ionization detector (FID).

p-tert-Butyl-tetrakis(1,3-dioxa-2$\sigma^3\lambda^3$-phospholanoxy)calix[4]arene **2** *(cone conformation)*

A hexane solution of *n*-BuLi (15.4 mL, 1.6 M, 24.64 mmol) was added to a suspension of *p-tert*-butyl-calix[4]arene (4.0 g, 6.16 mmol) in 50 mL of THF at room temperature. The resulting yellowish slurry was stirred for 2 hours. Neat 2-chloro-1,3-dioxa-2$\sigma^3\lambda^3$-phospholane (3.14 g, 24.83 mmol) was added to the suspension, using a syringe, whereupon the color changed from yellow to colorless. The reaction mixture was stirred for 4 days at room temperature and examined by ^{31}P NMR spectroscopy,

which indicated the formation of **2**. The suspension was filtered and the precipitate was dried i.v. for 4 hours. The remaining solid was redissolved in 30 mL CH_2Cl_2, and LiCl was removed by filtration through Celite. The filtrate and the CH_2Cl_2 washings of the Celite were combined before evaporation to dryness. The colorless, moisture-sensitive solid **2** was dried *i.v.* for 14 hours at room temperature. (5.03 g, 81%), m.p. 278°C; ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 0.99$ (s, 36 H, C(C$\underline{H}_3$)$_3$); 3.08 (d, 4 H, ^2J(HH) = 13.3 Hz, Ar-C$\underline{H}^1$H^2-Ar); 3.84–3.88 (m, 16 H, O–P–O–C$\underline{H}_2$), 4.67 (d, 4 H, ^2J(HH) = 13.2 Hz, Ar-CH$^1\underline{H}^2$-Ar); 6.68 (s, 8 H, Ar-$\underline{H}$); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 31.29$ (s, 12 C, C($\underline{C}$H$_3$)$_3$); 32.69 (s, 4 C, Ar-$\underline{C}$H^{1}H^2-Ar); 33.77 (s, 4 C, $\underline{C}$(CH$_3$)$_3$); 65.06 (s, 8 C, O–P–O–$\underline{C}$H$_2$); 124.89 (s, 8 C, *m*-$\underline{C}$); 125.87 (s, 4 C, *p*-$\underline{C}$); 133.32 (s, 8 C, *o*-$\underline{C}$); 145.51 (s, 4 C, *ipso*-$\underline{C}$); ^{31}P NMR (81.0 MHz, $CDCl_3$): $\delta = 124.5$ (s); ESI-MS, *m/z* (%): 1031.3 (100) [M + Na]$^+$, 647.5 (100) [M–4 $PO_2C_2H_4$]; Anal. Calcd. for $C_{52}H_{68}O_{12}P_4$ (1009.00): C, 61.90; H, 6.79. Found: C, 61.35; H, 7.14.

Tetrakis(1,3,5-trimethyl-1,3,5-triaza-2$\sigma^3\lambda^3$-phosphorin-4,6-dionyloxy)-calix[4]arene **3**

A hexane solution of *n*-BuLi (11.75 mL, 1.6 mol/L, 18.8 mmol) was added dropwise to a stirred solution of calix[4]arene (2.0 g, 4.7 mmol) in 40 mL of THF at room temperature. After the mixture had been stirred for 2 hours, 2-chloro-1,3,5-trimethyl-1,3,5-triaza-2$\sigma^3\lambda^3$-phosphorin-4,6-dione (3.95 g, 18.8 mmol) was added slowly to the yellowish reaction mixture using a cannula. The resulting suspension was stirred at room temperature for an additional 2 days. A ^{31}P NMR spectrum showed the formation of **3**. The precipitate formed was filtered off and dried *i.v.* for 4 hours at room temperature. The residue was then dissolved in 20 mL of $CHCl_3$, and LiCl was removed by filtration through Celite. The filtrate and the $CHCl_3$ washings were combined before evaporation to dryness. The colorless, moisture-sensitive solid **3** was dried *i.v.* for 12 hours at room temperature (7.60 g, 68%), m.p. 331°C; ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 2.56$ (s, 12 H, C$\underline{H}_3$NC(:O)); 3.13 (d, 2 H, ^{2}J(HH) = 14.9 Hz, Ar-C$\underline{H}_2$-Ar); 3.19 (d, 12 H, ^3J(HP) = 12.5 Hz, C$\underline{H}_3$NP); 3.21 (d, 2 H, ^2J(HH) = 14.5 Hz, Ar-C$\underline{H}_2$-Ar); 3.22 (d, 12 H, ^3J(HP) = 12.4 Hz, C$\underline{H}_3$NP); 3.95 (d, 2 H, ^2J(HH) = 14.1 Hz, Ar-C$\underline{H}_2$-Ar); 4.00 (d, 2 H, ^2J(HH) = 13.7 Hz, Ar-C$\underline{H}_2$-Ar); 6.01–7.16 (m, 12 H, Ar-$\underline{H}$); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 29.96$ (s, 4 C, $\underline{C}$H$_3$NC(:O)); 31.40 (s, 2 C, Ar-$\underline{C}$H$_2$-Ar); 31.67 (s, 2 C, Ar-$\underline{C}$H$_2$-Ar); 34.75 (d, 4 C, ^2J(CP) = 40.0 Hz, $\underline{C}$H$_3$NP); 34.85 (d, 4 C, ^2J(CP) = 39.1 Hz, $\underline{C}$H$_3$NP); 120.44–145.86 (m, 24 C, Ar-$\underline{C}$); 152.88 (d, 4 C, ^2J(CP) = 7.8 Hz, $\underline{C}$(:O)NP); 152.92 (d, 4 C, ^2J(CP) = 7.7 Hz, $\underline{C}$(:O)NP); ^{31}P NMR (81.0 MHz, $CDCl_3$): $\delta = 92.6$ (s), 96.7 (s); FAB MS, *m/z* (%): 1139 (5) [M + Na]$^+$, 1117 (13) [M + H]$^+$, 942 (8) [M–$C_5H_9N_3O_2P$]$^+$, 769 (8) [M + H − 2x $C_5H_9N_3O_2P$], 174 (100) [$C_5H_9N_3O_2P$]$^+$; ESI-MS, *m/z* (%): 1139 (100) [M + Na]$^+$; Anal. Calcd. for $C_{48}H_{56}N_{12}O_{12}P_4$ (1116.94): C, 51.62; H, 5.05; N, 15.05. Found: C, 53.50; H, 5.38; N, 12.41.

Crystal Data of **3**

Suitable crystals of **3** for the X-ray crystal structure were obtained by slow diffusion of pentane into a toluene solution of **3**. Crystal dimensions $0.5 \times 0.4 \times 0.3$ mm, colorless determination prisms, space group $P2_1/n$, monoclinic, $a = 1364.8(3)$ pm, $b = 2254.6(5)$ pm, $c = 2215.6(4)$ pm, $\beta = 92.49(3)°$, $V = 6811$ Å^3, $Z = 4$, $\rho_{calcd} = 1.262$ g cm^{-3}, 29575 reflections measured, 8747 were independent of symmetry and 3423 were observed ($I > 2\sigma(I)$), $R1 = 0.066$, $wR2$ (all data) = 0.176, 750 parameters.

Full details (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Rd., GB-Cambridge CB2 1EZ, under the number CCDC-165694. Copies may be obtained free of charge on application to the Director (Telefax: Int. +12 23 33 60 33; e-mail: deposit@ccdc.cam.ac.uk).

Tetrakis(-1,3-dioxa-2$\sigma^3\lambda^3$-phospholanoxy-)calix[4]arene **4**

A hexane solution of *n*-BuLi (29.45 mL, 1.6 M, 47.12 mmol) was added to a solution of calix[4]arene (5.0 g, 11.78 mmol) in 100 mL of THF at room temperature, and the resulting orange slurry was stirred for 2 hours. Subsequently 2-chloro-1,3-dioxa-2$\sigma^3\lambda^3$-phospholane (5.96 g 47.12 mmol) was added to the suspension with stirring at room temperature. The formation of a white precipitate was observed after a few minutes. The reaction mixture was stirred for an additional 16 hours at room temperature. Examination by ^{31}P NMR spectroscopy showed the formation of **4**. The precipitate was separated by filtration and dried *i.v.* for 4 hours at room temperature. After drying, the solid was redissolved in 40 mL of CH_2Cl_2 and filtered through Celite in order to remove LiCl. The filtrate and the CH_2Cl_2 washings were combined and evaporated to dryness. Drying of the resulting precipitate for 12 hours at room temperature gave **4** as a colorless, moisture-sensitive solid. (7.02 g, 76%), m.p. 268°C; ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 3.12$ (d, 4 H, ^2J(HH) = 13.7 Hz, Ar-C$\underline{H}^1$H^2-Ar); 3.79–3.91 (m, 16 H, O-P-O-C$\underline{H}_2$), 4.66 (d, 4 H, ^2J(HH) = 13.7 Hz, Ar-CH$^1\underline{H}^2$-Ar); 6.53–6.99 (m, 12 H, Ar-$\underline{H}$); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 32.38$ (s, 4 C, Ar-$\underline{C}$H^{1}H^2-Ar);

65.12 (s, 8 C, O–P–O–$\underline{C}H_2$); 122.93 (s, 4 C, *p*-$\underline{C}$); 128.13 (s, 8 C, m-$\underline{C}$); 134.50 (s, 8 C, *o*-$\underline{C}$); 147.77 (s, 4 C, *ipso*-$\underline{C}$); ^{31}P NMR (81.0 MHz, $CDCl_3$): $\delta = 124.9$ (s); FAB MS, *m/z* (%): 791 (10) $[M + Li]^+$, 701 (4) $[M + Li - PO_2C_2H_4]^+$; Anal. Calcd. for $C_{36}H_{36}O_{12}P_4$ (784.57): C, 55.11; H, 4.62. Found: C, 55.90; H 4.92.

p-tert-Butyl-dimethoxy-bis(1,3,5-trimethyl-1,3,5-triaza-2$\sigma^3\lambda^3$-phosphorin-4,6-dionyloxy)-calix[4]arene **5** *(cone conformation)*

A hexane solution of *n*-BuLi (1 ml, 1.6 M, 1.6 mmol) was added slowly to a solution of *p-tert*-butyl-bis-dimethoxycalix[4]arene (0.54 g, 0.8 mmol) in 5 mL of THF at room temperature. The immediate formation of a yellowish solution was observed. After stirring for 2 hours at room temperature, 2-chloro-1,3,5-trimethyl-1,3,5-triaza-2$\sigma^3\lambda^3$-phosphorin-4,6-dione (0.34 g, 1.61 mmol) was added slowly to the yellow suspension, using a cannula, and the reaction mixture was stirred for 15 hours at room temperature. A ^{31}P NMR spectrum showed the formation of **5** ($\delta = 94.6$). Removal of the precipitate by filtration led to a yellow solution, which, after evaporation, gave a yellowish solid. The yellow solid was dissolved in 10 mL of toluene, and LiCl was removed by filtration through Celite. The filtrate and the toluene washings were combined before evaporation to dryness. The resulting colorless solid **5** was dried *i.v.* for 15 hours at 40°C (0.43 g, 55 %), m.p. 301°C; ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 0.70$ (s, 18 H, C($C\underline{H}_3$)$_3$); 1.26 (s, 18 H, C($C\underline{H}_3$)$_3$); 2.73 (s, 6 H, $C\underline{H}_3NC(:O)$); 3.11 (d, 4 H, ^2J(HH) = 12.6 Hz, Ar-$C\underline{H}^1H^2$-Ar); 3.21 (d, 12 H, ^3J(HP) = 12.2 Hz, $C\underline{H}_3NP$); 3.75 (s, 6 H, O-$C\underline{H}_3$); 3.92 (d, 4 H, ^2J(HH) = 12.4 Hz, Ar-$CH^1\underline{H}^2$-Ar); 6.35 (s, 4 H, Ar-$\underline{H}$); 7.07–7.20 (m, 4 H, Ar-$\underline{H}$); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 30.06$ (s, 2 C, $\underline{C}H_3NC(:O)$); 30.83 (s, 12 C, C($\underline{C}H_3$)$_3$); 31.63 (s, 12 C, C($\underline{C}H_3$)$_3$); the ^{13}C NMR-signals of the bridging methylene C-atoms were overlapping with the very intense signals of the methyl carbon atoms of the *tert*-butyl groups; 33.62 (s, 4 C, $\underline{C}(CH_3)_3$); 34.21 (s, 4 C, $\underline{C}(CH_3)_3$); 34.74 (d, 4 C, ^2J(CP) = 39.1 Hz, $\underline{C}H_3NP$); 59.85 (s, 2 C, O-$\underline{C}H_3$); 124.62–145.48 (m, 24 H, $\underline{C}_{arom.}$); 153.32 (d, 4 C, ^2J(CP) = 7.5 Hz, $\underline{C}(:O)NP$); ^{31}P NMR (81.0 MHz, $CDCl_3$): $\delta = 94.6$ (s); FAB MS, *m/z* (%): 1029 (100) $[M + Li]^+$, 848 (35) $[M-(C_5H_9N_3O_2P)]^+$, 676 (14) $[C_{46}H_{60}O_4]^+$, 174 (86) $[C_5H_9N_3O_2P]$. Anal. Calcd. for $C_{56}H_{76}N_6O_8P_2$ (1023.20): C, 65.73; H, 7.50; N, 8.21. Found: C, 65.23; H, 7.46; N, 6.82.

2-(2,6-Dimethylphenoxy)-1,3,5-trimethyl-1,3,5-triaza-2$\sigma^3\lambda^3$-phosphorin-4,6-dione **6**

To 2,6-dimethylphenol (4.0 g, 32.7 mmol) dissolved in 80 mL of THF, *n*-BuLi (20.44 ml, 1.6 M in hexane, 32.7 mmol) was slowly added at room temperature. The resulting yellow mixture was stirred for 2 hours. Subsequently, 2-chloro-1,3,5-trimethyl-1,3,5-triaza-2$\sigma^3\lambda^3$-phosphorin-4,6-dione (6.86 g, 32.7 mmol) was added slowly to the yellow suspension, using a cannula. Stirring at room temperature was continued for 15 hours to complete the reaction. Examination of the brownish mixture by ^{31}P NMR spectroscopy indicated the formation of **6**. The brownish mixture was separated from the precipitate by filtration, and the solvent was evaporated *i.v.* at room temperature. The resulting oily liquid was dissolved in 30 mL of CH_2Cl_2 and filtered again to remove the LiCl completely. Subsequently, the solvent and the CH_2Cl_2 washings were evaporated *i.v.* Distillation of the oily residue at 137°C (0.1 mm Hg) provided 3.10 g (32%) of **6** as a colorless viscous liquid. ^{1}H NMR (200.1 MHz, $CDCl_3$): $\delta = 1.99$ (s, 6 H, Ar-$C\underline{H}_3$); 2.73 (s, 3 H, $C\underline{H}_3NC(:O)$); 3.17 (d, 6 H, ^3J(HP) = 12.6 Hz, $C\underline{H}_3NP$); 6.80–6.91 (AB_2 System, 3 H, Ar-$\underline{H}$); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 16.91$ (s, 2 C, Ar-$\underline{C}H_3$); 30.14 (s,1 C, $\underline{C}H_3NC(:O)$); 33.77 (d, 2C ^2J(CP) = 36.2 Hz, $\underline{C}H_3NP$); 124.73 (s, 1 C, Ar-*p*-$\underline{C}$); 129.59 (s, 2 C, Ar-*m*-$\underline{C}$); 129.90 (s, 2 C, Ar-*o*-$\underline{C}$); 149.03 (s, 1 C, Ar-*ipso*-$\underline{C}$); 153.18 (d, 2 C, ^2J(CP) = 7.5 Hz, $\underline{C}(:O)NP$); ^{31}P NMR (81.0 MHz, $CDCl_3$): $\delta = 101.7$ (s); EI-MS, *m/z* (%): 295 (18) $[M]^+$; Anal. Calcd. for $C_{13}H_{18}N_3O_3P$ (295.28): C, 52.88; H, 6.14; N, 14.23. Found: C, 52.72; H, 7.05; N, 13.62.

2-(2,6-Dimethylphenoxy)-1,3-dioxa-2$\sigma^3\lambda^3$-phospholane **7**

To 2,6-dimethylphenol (5.0 g, 40.9 mmol) dissolved in 50 mL of THF, *n*-BuLi (25.56 ml, 1.6 M in hexane, 40.9 mmol) was slowly added at room temperature. After stirring for 2 hours, 2-chloro-1,3,2-dioxaphospholane (5.17 g, 40.9 mmol) was added slowly, using a cannula. The reaction mixture was stirred for a further 15 hours. Examination by ^{31}P NMR spectroscopy indicated the formation of **7**. The suspension was separated from the precipitate by filtration. The solvent was evaporated, and the oily liquid residue was dissolved in 40 mL of CH_2Cl_2. LiCl was removed by filtration through Celite. Subsequently the solvent and the CH_2Cl_2 washings were evaporated *i.v.* Distillation of the oily residue at 91°C (0.3 mm Hg) provided 5.65 g (65%) of **7** as a colorless viscous liquid. ^{1}H NMR (200.1 MHz, $CDCl_3$): $\delta = 2.41$ (s, 6 H, Ar-$C\underline{H}_3$); 4.09–4.29 (m, 4 H, O-P-O-$C\underline{H}_2$); 7.00–7.12 (AB_2 System, 3 H, Ar-$\underline{H}$); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 17.37$ (s, 2 C, Ar-$\underline{C}H_3$); 64.01 (s, 2 C, O-P-O-$C\underline{H}_2$); 123.88 (s, 1 C, *p*-$\underline{C}$); 128.52 (s, 2 C, *m*-$\underline{C}$); 130.14 (s, 2 C, *o*-$\underline{C}$); 148.93 (s, 1 C, *ipso*-$\underline{C}$); ^{31}P NMR (81.0 MHz, $CDCl_3$): $\delta = 131.6$ (s); EI-MS, *m/z* (%): 212 (34) $[M]^+$, 197 (4) $[M-CH3]^+$,

121 (100) $[M-OPO_2(CH_2)_2]^+$, 91 (100) $[OPO_2(CH_2)_2]$; Anal. Calcd. for $C_{10}H_{13}O_3P$ (212.19): C, 56.61; H, 6.18. Found: C, 56.77; H, 6.38.

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REFERENCES

[1] For reviews see: (a) Neda, I.; Kaukorat, T.; Schmutzler, R. Main Group Chemistry News 1998, 6 (2/3)4; (b) Wieser, C.; Dieleman, C. B.; Matt, D. Coord Chem Rev 1997, 165, 93.
[2] (a) Wieser, C.; Matt, D.; Fischer, J.; Harriman, A. J Chem Soc Dalton Trans 1997, 2391; (b) Loeber, C.; Wieser, C.; Matt, D.; De Cian, A.; Fischer, J.; Toupet, L. Bull Soc Chim Fr 1995, 132, 166.
[3] (a) Wieser-Jeunesse, C.; Matt, D.; De Cian, A. Angew Chem 1998, 110, 3027; (b) Angew Chem Int Ed Engl 1998, 37, 2861.
[4] Dieleman, C. B.; Marsol, C.; Matt, D.; Kyritsakas, N.; Harriman, A.; Kintzinger, J.-P. J Chem Soc Dalton Trans 1999, 4139.
[5] See, for example, Faidherbe, P.; Wieser, C.; Matt, D.; Harriman, A.; De Cian, A.; Fischer, J. Eur J Inorg Chem 1998, 451.
[6] See, for example, Matt, D.; Loeber, C.; Vicens, J.; Asfari, Z. J Chem Soc 1993, 604.
[7] See, for example, (a) Dieleman, C. B.; Matt, D.; Neda, I.; Schmutzler, R.; Harriman, A.; Yaftian, R. Chem Commun 1999, 1911; (b) Vollbrecht, A.; Neda, I.; Thönnessen, H.; Jones, P. G.; Harris, R. K.; Crowe, L. A.; Schmutzler, R. Chem Ber/Recueil 1997, 130, 1715.
[8] See, for example, Dieleman, C. B.; Loeber, C.; Matt, D.; De Cian, A.; Fischer, J. J Chem Soc Dalton Trans 1995, 3097.
[9] Neda, I.; Vollbrecht, A.; Grunenberg, J.; Schmutzler, R. Heteroatom Chem 1998, 9, 553.
[10] Dieleman, C. B.; Matt, D.; Neda, I.; Schmutzler, R.; Thönnessen, H.; Jones, P. G.; Harriman, A. J Chem Dalton Trans 1998, 2215.
[11] (a) Frohning, C. D.; Kohlpaintner, C. W. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B.; Herrmann, W. A., Eds.; VCH: Weinheim, 1996; Vol. 1, p 29; (b) Botteghi, C.; Marchetti, M.; Paganelli, S. In *Transition Metals for Organic Synthesis*; Beller, M.; Bolm, C. Wiley-VCH: Weinheim, 1998; Vol. 1, p 25.
[12] van Leeuwen, P. W. N. M.; Kamer, P. C. J.; Reek, J. N. H.; Dierkes, P. Chem Rev 2000, 100, 2741.
[13] (a) Unruh, J. D.; Christenson, J. R. J Mol Catal 1982, 14, 19; (b) Moser, W. R.; Papile, C. J.; Brennon, D. A.; Duwell, R. A. J Mol Catal 1987, 41, 271.
[14] Selent, D.; Wiese, K.-D.; Röttger, D.; Börner, A. Angew Chem 2000, 112, 1694; Angew Chem Int Ed Engl 2000, 39, 1639.
[15] Paciello, R.; Siggel, L.; Röper, M. Angew Chem 1999, 111, 2045; Angew Chem Int Ed Engl, 1999, 38, 1920.
[16] Csok, Z.; Szalontai, G.; Czira, G.; Kollar, L. J Organomet Chem 1998, 570, 23.
[17] Cobley, C. J.; Ellis, D. D.; Orpen, A. G.; Pringle, P. G. J Chem Soc, Dalton Trans 2000, 1109.
[18] Shimizu, S.; Shirakawa, S.; Sasaki, Y.; Hirai, C. Angew Chem 2000, 112, 1313; Angew Chem Int Ed Engl, 2000, 39, 1256.
[19] Neda, I.; Plinta, H.-J.; Sonnenburg, R.; Fischer, A.; Jones, P. G.; Schmutzler, R. Chem Ber 1995, 128, 267.
[20] van der Slot, S. C.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Fraanje, J.; Goubitz, K.; Lutz, M.; Spek, A. L. Organometallics 2000, 19, 2504.
[21] (a) Bader, A.; Lindner, E. Coord Chem Rev 1991, 108, 27; (b) Börner, A. Eur J Inorg Chem 2001, 327.
[22] (a) Gutsche, C. D.; Muthukrishnan, R. J Org Chem, 1978, 43, 4905; (b) Gutsche, C. D.; Iqbal, M. Org Synth 1990, 68, 234.
[23] Gutsche, C. D.; Lin, L.-G. Tetrahedron 1986, 42, 1633.
[24] Dijkstra, P. J.; Brunink, J. A. J.; Bugge, K.-E.; Reinhoudt, D. N.; Harkema, S.; Ungaro, R.; Ugozzoli, F.; Ghidini, E. J Am Chem Soc 1989, 111, 7567.
[25] Meyer, T. G.; Jones, P. G.; Schmutzler, R. Z Naturforsch 1992, 47b, 517.
[26] Sheldrick, G. M. Acta Crystallogr 1990, A46, 467.
[27] Sheldrick, G. M. SHELXL-97: A Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.