CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200600180

Phosphabarrelenes as Ligands in Rhodium-Catalyzed Hydroformylation of Internal Alkenes Essentially Free of Alkene Isomerization

Evelyn Fuchs,[a] Manfred Keller,[a, b] and Bernhard Breit*[a]

Abstract: Despite significant research efforts in the past, one of the remaining problems to be solved in industrially important hydroformylation is the chemoselective low-pressure hydroformylation of internal alkenes. We report here on a new class of phosphabarrelene/rhodium catalysts **2** that display very high activity towards hydroformylation of internal alkenes with an unusually low tendency towards alkene isomerization. Preparation of new phosphabarrelene ligands, studies of their coordination properties, as well as results obtained in the rhodium-catalyzed hydroformylation of cyclic and acyclic internal alkenes are reported.

Keywords: chemoselectivity · homogeneous catalysis · hydroformylation · P ligands · rhodium

Introduction

Hydroformylation of alkenes is one of the industrially most important processes relying on homogeneous catalysis, and a synthetically attractive carbon–carbon bond-forming reaction meeting the criteria of atom economy.[1,2] Despite significant previous research efforts, a number of selectivity issues remain to be solved among which the challenge of chemoselective low-pressure hydroformylation of internal alkenes is an industrially and synthetically important one.[2] Major progress has been made by the group of van Leeuwen and co-workers who identified bulky monodentate phosphite/rhodium catalysts as highly active catalysts for hydroformylation of di- and trisubstituted alkenes.[3] More recently, phosphonite systems have been reported to show a similar behavior.[4] Unfortunately, the lability of phosphites and phosphonites towards hydrolysis and a tendency to undergo degradation reactions has limited their technical use. In order to circumvent catalyst stability problems we introduced phosphabenzenes as a new class of π-acceptor ligands with the idea of mimicking the electronic properties of phosphites. In fact, monodentate phosphabenzene–rhodium complexes **1** have been shown to be efficient catalysts for the low-pressure hydroformylation of terminal and internal alkenes.[5]

All of the above described catalysts designed for hydroformylation of internal alkenes simultaneously show a rather high activity towards alkene isomerization. This behavior may be desirable if an isomerizing hydroformylation is the goal.[4,6] In this respect, the conversion of C4 feedstock "Raffinate-2", that contains a mixture of internal and terminal butenes to yield linear C5 aldehydes and finally C10 alcohols by sequential isomerizing hydroformylation, aldol condensation, and hydrogenation is of particular industrial interest.[7]

However, if a position-selective hydroformylation of an internal alkene is the desired synthetic transformation, hydroformylation accompanied by alkene isomerization represents a significant synthetic problem. To the best of our knowledge, a catalyst that enables efficient hydroformylation of internal alkenes without catalyzing the alkene isomerization, is so far unknown.

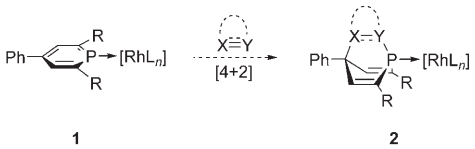
We report in full detail on a new class of phosphabarrelene/rhodium catalysts **2** that display very high activity towards hydroformylation of internal alkenes with an unusually low tendency towards alkene isomerization.[8] Preparation of phosphabarrelene ligands, studies of coordination properties, as well as results in the rhodium-catalyzed hydroformylation of cyclic and acyclic internal alkenes are reported.

[a] Dr. E. Fuchs, Dr. M. Keller, Prof. Dr. B. Breit
Chemisches Laboratorium, Institut für Organische Chemie und Biochemie
Albert-Ludwigs-Universität Freiburg
Albertstrasse 21, 79104 Freiburg i. Brsg. (Germany)
Fax: (+49) 761-203-8715
E-mail: bernhard.breit@organik.chemie.uni-freiburg.de

[b] Dr. M. Keller
X-ray crystal structure analyses of **5b** and **5c**.

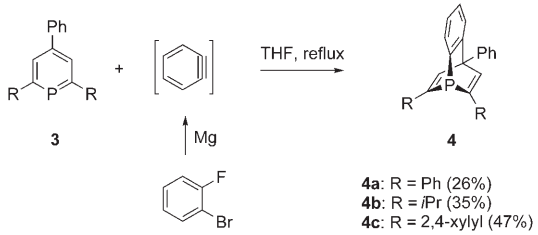
Results and Discussion

In previous studies on phosphabenzene–rhodium catalysts **1** we observed that hydroformylation activity is controlled significantly by the steric demand of the donor ligand.[5] This induced us to probe the effect of expanding a planar phosphabenzene skeleton into a "third dimension". Thus, the Diels–Alder addition of a reactive dienophile to the phosphabenzene nucleus would generate a phosphabarrelene cage (Scheme 1). A few systems of this structure are known from the work of G. Märkl,[9] but have never been explored as ligands in homogeneous catalysis.



Scheme 1. Generation of the phosphabarrelene cage.

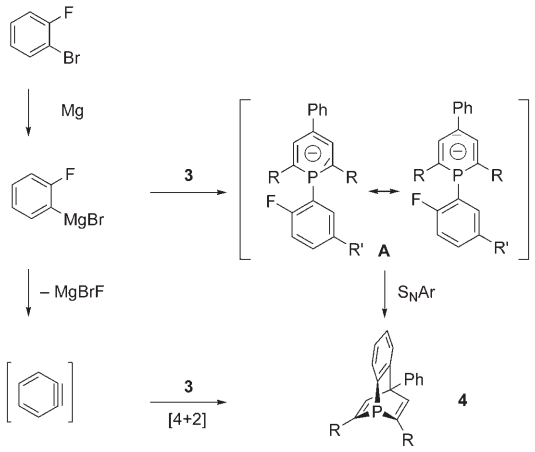
Addition of benzyne, generated in situ from *ortho*-fluorobromobenzene, to phosphabenzenes **3** furnished the phosphabarrelenes **4a–c** in moderate-to-fair yields as air-stable colorless crystalline compounds (Scheme 2).



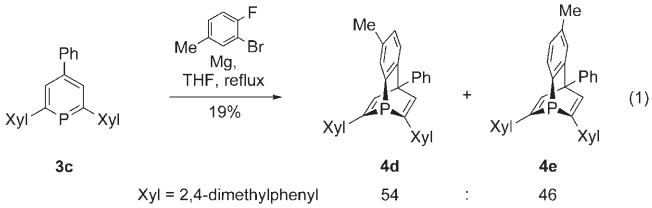
Scheme 2. Generation of the phosphabarrelene complexes **4a–c**.

Mechanistically, an alternative to the phosphabarrelene formation through a Diels–Alder reaction of a benzyne intermediate would be a stepwise reaction proceeding through a nucleophilic attack of the Grignard reagent (the benzyne precursor) at the phosphorus atom to give the phosphapentadienyl anion **A**. A subsequent nucleophilic aromatic displacement of the remaining fluoride substituent would provide the barrelene core. The stepwise process would be in accord with the known reaction of 2,4,6-triphenylphosphabenzene (**3a**) with organolithium and Grignard reagents to give pentadienyl anions of type **A** (Scheme 3), that have been either isolated as tetrabutylammonium salts, or trapped upon reaction with electrophiles.[10]

In order to distinguish between these two mechanisms, we chose 5-methyl-2-fluorobromobenzene as the starting material. If the reaction proceeds in a stepwise manner we should expect the exclusive formation of barrelene **4d**. If the reaction occurs through an aryne intermediate the formation of a mixture of the two regioisomeric phosphabarrelenes **4d** and **4e** should result.



Scheme 3. Mechanism of phosphabarrelene formation.



As a result, the reaction under identical conditions as before furnished a 54:46 mixture of phosphabarrelenes **4d** and **4e** indicating that the reaction has proceeded through a Diels–Alder addition of an aryne intermediate to the phosphabenzene nucleus.

X-ray crystal-structure analysis of phosphabarrelene **4a** (Figure 1, Table 1) revealed a strong pyramidalization at the phosphorus atom (phosphabarrelene **4a**: $\Sigma\measuredangle(CPC)=283°$ compared with PPh_3: $\Sigma\measuredangle(CPC)=308°$).[11] This should result in a more pronounced s character of the P lone pair of phosphabarrelene **4** that should render the phosphabarrelene a weaker σ-donor ligand and a better π-acceptor ligand if compared to a suitable phosphane.[12]

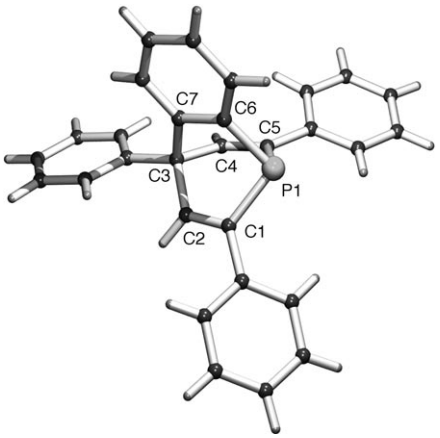
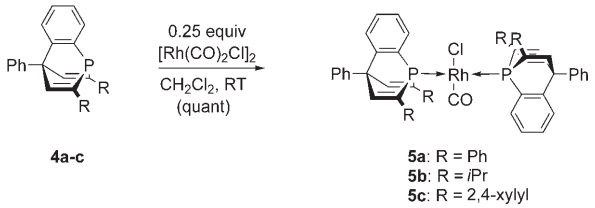


Figure 1. Structure of phosphabarrelene **4a** from X-ray diffraction analysis.

Table 1. Selected structural data for phosphabarrelene **4a**.

bond lengths [Å]			
P1–C1	1.8454(16)	C2–C3	1.527(2)
P1–C5	1.8601(16)	C3–C4	1.533(2)
P1–C6	1.8345(18)	C4–C5	1.333(2)
C1–C2	1.331(2)		
bond angles [°]			
C1-P1-C6	94.95(7)	C1-C2-C3	120.64(14)
C1-P1-C5	95.57(7)	C6-C7-C3	115.57(14)
C5-P1-C6	92.23(7)	C5-C4-C3	119.90(14)
P1-C1-C2	115.43(12)	C2-C3-C7	107.72(12)
P1-C6-C7	117.12(12)	C4-C3-C7	104.19(11)
P1-C5-C4	115.63(12)	C2-C3-C4	106.51(13)



Scheme 4. Preparation of rhodium/carbonyl complexes **5a–c**.

Table 2. Comparison of the IR stretching frequency of C–O for selected *trans*-[L_2RhCl(CO)] complexes.

Ligand	$\tilde{\nu}$ [cm^{-1}]	Ref.
PPh_3	1965	[14]
4b	1971	this work
4a	1993	this work
4c	1993	this work
phosphinine **3a**	1999	[5]
$P[O(2\text{-}t\text{Bu}C_6H_4)]_3$ (**6a**)	2013	[15]

In order to examine the coordination behavior of phosphabarrelenes the corresponding rhodium–carbonyl complexes **5a–c** were prepared (Scheme 4). According to the C–O stretching frequencies in the IR spectrum (see Table 2), a probe to evaluate the electronic properties of ligands,[13] the diisopropyl derivative **4b** was identified as the strongest donor while the aryl-substituted phosphabarrelenes **4a** and **4c** display donor properties that rank them in a range between phosphabenzenes and triarylphosphanes.

From rhodium complexes **5b** and **5c** an X-ray diffraction crystal structure could be obtained (Figure 2).[13] This allowed the estimation of the steric demand of the phosphabarrelene ligands according to Tolman's cone-angle concept to be about 161 (**4b**) and 181° (**4c**), respectively (Table 3).[16]

Catalyst performance was tested upon hydroformylation of internal cyclic olefins first because it allows the observation of the hydroformylation activity undisturbed by alkene isomerization (Table 4).

In both cases ($n=1,2$) the 2,4-xylyl-substituted phosphabarrelene–rhodium catalyst (Rh/**4c**) performed with the highest activity. Turnover frequencies up to 12000 h^{-1} were observed. In the case of cyclohexene, the result by using the Rh/**4c** catalyst is even six times faster than by using the Rh/phosphabenzene **3c** catalyst, and 1000 times faster than with the Rh/PPh_3 catalyst that

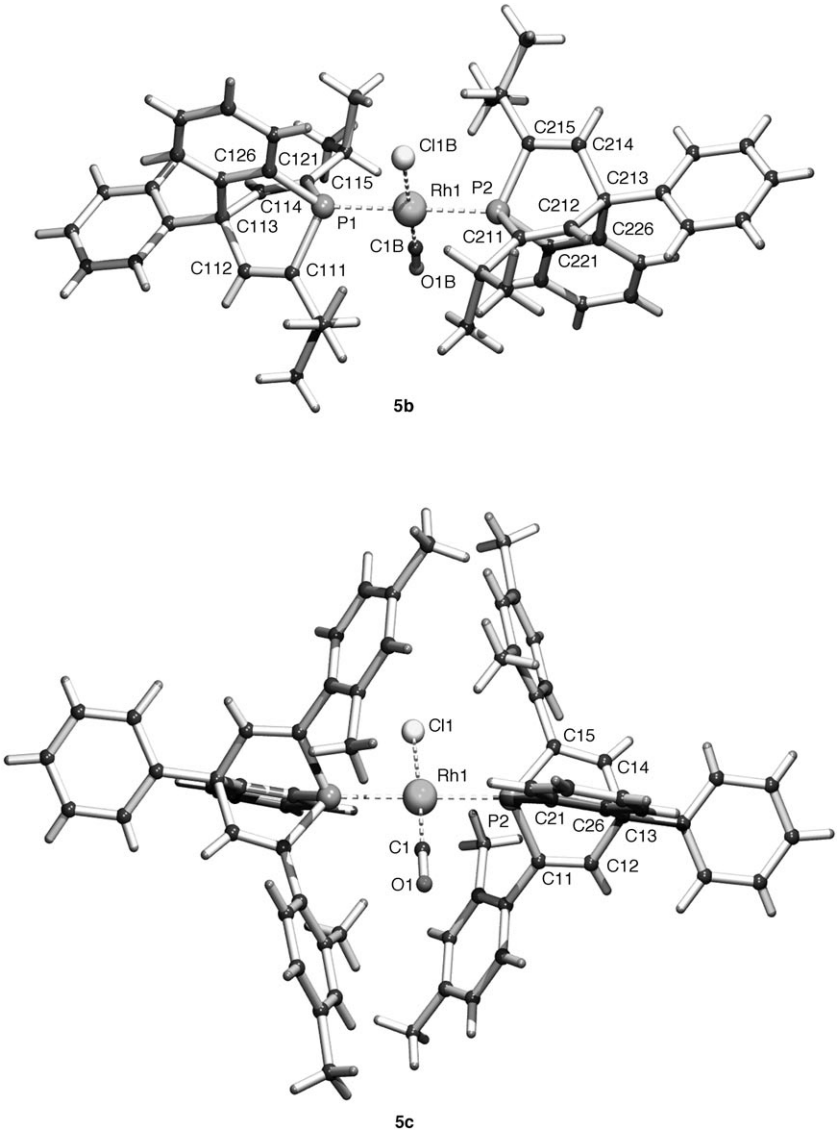


Figure 2. Structures of complexes **5b** and **5c** from X-ray diffraction analysis. a) Complex **5b**: Disordered Cl atoms and C–O groups are not displayed in the X-ray plot; b) complex **5c**: Inversion symmetrical Cl atoms and C–O groups are not displayed in the X-ray plot.

Table 3. Selected geometrical data for complexes **5b** and **5c**.

5b			
bond lengths [Å]			
Rh–P1	2.3226(7)	C113–C126	1.555(4)
Rh–P2	2.3190(7)	C121–C126	1.416(4)
Rh–Cl1B	2.407(4)	P2–C211	1.841(3)
Rh–C1B	1.808(18)	P2–C221	1.840(3)
C1B–O1B	1.08(3)	P2–C215	1.834(3)
P1–C111	1.832(3)	C211–C212	1.333(4)
P1–C121	1.838(3)	C212–C213	1.531(4)
P1–C115	1.846(3)	C213–C214	1.544(4)
C111–C112	1.327(4)	C214–C215	1.330(4)
C112–C113	1.535(4)	C213–C226	1.559(4)
C113–C114	1.535(4)	C221–C226	1.400(4)
C114–C115	1.327(4)		
bond angles [°]			
P1-Rh-P2	179.50(3)	C111-P1-C121	96.81(12)
P1-Rh-Cl1B	95.98(6)	C115-P1-C121	95.16(13)
P1-Rh-C1B	84.6(4)	Rh1-P2-C211	117.43(9)
P2-Rh-Cl1B	84.49(6)	Rh1-P2-C221	129.22(10)
P2-Rh-C1B	94.9(4)	Rh1-P2-C215	114.09(9)
Rh-P1-C111	114.34(10)	C211-P2-C215	98.91(13)
Rh-P1-C121	129.05(10)	C211-P2-C221	94.78(13)
Rh-P1-C115	117.14(9)	C215-P2-C221	96.67(12)
C111-P1-C115	98.61(13)		
5c			
bond lengths [Å]			
Rh–P2	2.3100(5)	C11–C12	1.323(3)
Rh–Cl1	2.366(2)	C12–C13	1.523(3)
Rh–C1	1.795(7)	C13–C14	1.530(3)
C1–O1	1.146(7)	C14–C15	1.334(3)
P2–C11	1.845(2)	C13–C26	1.563(3)
P2–C15	1.852(2)	C21–C26	1.403(3)
P2–C21	1.831(2)		
bond angles [°]			
P1-Rh-P2	180.00(3)	Rh-P2-C21	121.35(6)
P2-Rh-Cl1	85.41(5)	C11-P2-C15	96.94(9)
P2-Rh-C1	92.0(3)	C11-P2-C21	96.67(9)
Rh-P2-C11	113.69(7)	C15-P2-C21	94.76(10)
Rh-P2-C15	127.09(7)		

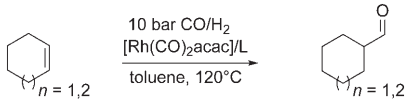
is one of the industrially employed hydroformylation catalysts.

To evaluate the tendency of the catalysts to undergo isomerization upon hydroformylation of internal alkenes, 2-octene was selected for study. Formation of nonanal (**7**) and/or 2-propylhexanal (**10**) would indicate alkene isomerization prior to hydroformylation (Scheme 5).

Thus, hydroformylation of 2-octene was performed at 70 °C with a syngas pressure of 10 bar by using rhodium catalysts prepared from phosphabarrelenes **4a–c** and the results were compared to those obtained from rhodium catalysts derived from triphenylphosphane, triarylphosphite P[O-(2,4-(tBu)$_2$C$_6$H$_3$)$_3$] (**6b**), and phosphabenzene **3c** (Table 5).

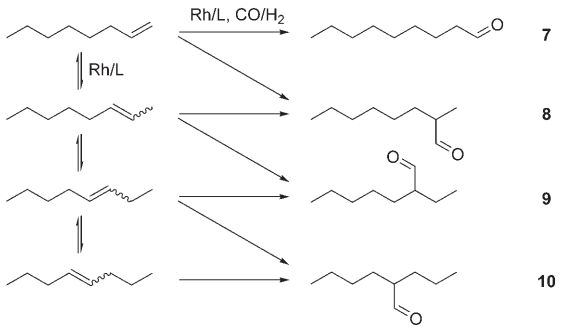
As expected, the standard industrial catalyst Rh/PPh$_3$ performed with low activity (see Table 5, entry 1). Employing catalysts designed for hydroformylation of internal alkenes, the Rh/phosphite (**6b**) and the Rh/phosphabenzene (**3c**) systems showed a remarkable activity with complete consumption of starting material. However, in both cases a significant amount of 2-propylhexanal (**10**) and *n*-nonanal (**7**) was formed, indicating severe alkene isomerization prior to hydroformylation (Table 5, entries 2,3). Conversely, the Rh/phosphabarrelene catalyst (**4c**) showed a high activity towards hydroformylation of the internal C=C double bond of 2-octene, but in this case hydroformylation occurred essentially free of alkene isomerization (Table 5, entry 4).

Table 4. Results of the hydroformylation of cyclohexene and cycloheptene with [Rh(CO)$_2$acac]L^{-1} at 120 °C, 10 bar (CO/H$_2$ 1:1) in toluene (c_0 = 3.56 M) after 10 min (cycloalkene/L/Rh 4160:20:1).



Entry[a]	L	Substrate	Conversion [%][b]	TOF[c] [h^{-1}]
1	PPh$_3$	n=1	0.04	11
2	**3c**	n=1	8	1906
3	**4a**	n=1	2.8	707
4	**4b**	n=1	3.5	875
5	**4c**	n=1	46	11429
6	PPh$_3$	n=2	5	1228
7	**3c**	n=2	4	918
8	**4c**	n=2	49	12231

[a] All catalysts have been preformed at 5 bar CO/H$_2$ (1:1) for 30 min at reaction temperature. The reaction was started by injection of the alkenic substrate. [b] Conversion was determined after 10 min reaction time in every case by GC analysis. [c] TOF = turnover frequency of aldehyde formation.



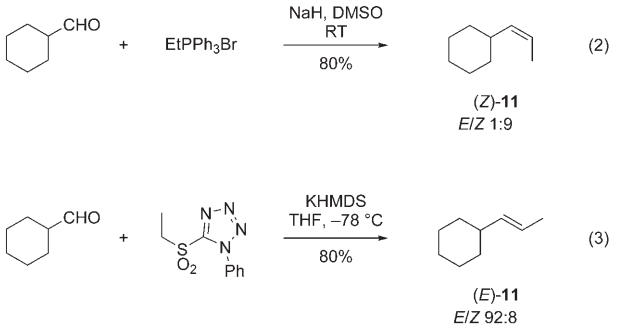
Scheme 5. Possible reaction routes to form compounds **7**–**10**, L = ligand.

Table 5. Results of the hydroformylation of 2-octene (*E*/*Z* 77:23) with [Rh(CO)$_2$acac]/L at 70 °C, 10 bar (CO/H$_2$ 1:1) in toluene (c_0 = 7.68 M) after 4 h (2-octene/L/Rh 7187:20:1).

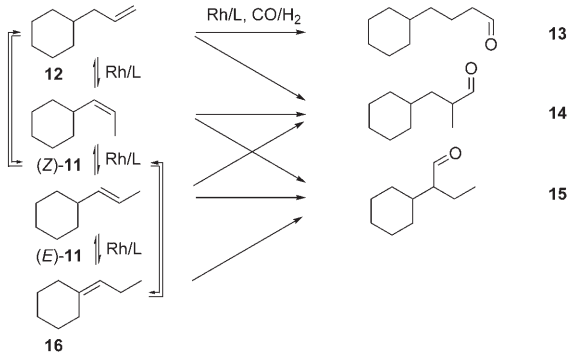
Entry[a]	L	2-Octene [mol %][b]	3/4-Octene [mol %][b]	**7** [mol %][b]	**8** [mol %][b]	**9** [mol %][b]	**10** [mol %][b]
1	PPh$_3$	73.7	1.2	0.0	16.9	8.2	0.0
2	**6b**	0.0	0.2	2.9	51.1	33.5	12.2
3	**3c**	0.5	3.9	6.4	54.1	22.4	12.7
4	**4c**	4.5	2.0	0.0	57.6	35.7	0.2

[a] See footnote [a] Table 4. [b] Reaction mixture composition was analyzed by GC.

To probe the influence of double-bond geometry as well as the influence of α-branching adjacent to the alkene function, we became interested in hydroformylation of (*E*)- and (*Z*)-1-cyclohexylpropene (**11**). The corresponding alkene isomers were prepared by using standard olefination techniques. Thus, Wittig olefination of cyclohexane carbaldehyde under salt-free conditions provided alkene (*Z*)-**11**. Conversely, employing the Kocienski variant of the Julia–Lythgoe olefination[17] furnished the corresponding *E* isomer of internal alkene **11**.



The expected hydroformylation products from either (*Z*)- or (*E*)-**11** alkenes are aldehydes **14** and **15**. If, however, an alkene isomerization occurs prior to hydroformylation, the formation of the linear aldehyde **13** should be observed (Scheme 6).



Scheme 6. Possible reaction pathways and products upon hydroformylation of alkenes **11**.

Thus, hydroformylations of (*Z*)- and (*E*)-**11** alkenes were performed at 70 °C with a syngas pressure of 10 bar and by using the rhodium catalyst prepared from phosphabarrelene **4c** and the results were compared to those obtained from the rhodium catalyst derived from triarylphosphite P[O-(2,4-(tBu)$_2$C$_6$H$_3$)$_3$] (**6b**) (Table 6).

For the phosphabarrelene catalyst starting from alkene (*Z*)-**11** after 8 h of reaction time an almost 90% chemoselective conversion towards aldehydes was observed (Table 6, entry 1). The branched aldehyde **14** was formed with a selectivity of 17.2:3.3:1 (compounds **14**/**15**/**13**). Only small amounts of linear aldehyde **13** were formed indicative of this catalyst's ability to catalyze hydroformylation without alkene isomerization. A hydroformylation that was essentially free of alkene isomerization occurred with the same catalyst and alkene (*E*)-**11** (entry 3). However, the conversion obtained for this substrate was considerably lower, possibly due to the generally observed lower reactivity of *E* alkenes towards hydroformylation.[2]

Table 6. Results of the hydroformylation of (*Z*)- and (*E*)-1-cyclohexylpropene (**11**) with [Rh(CO)$_2$acac]/L at 70 °C, 10 bar (CO/H$_2$ 1:1) in toluene.

Entry[a]	Substrate	L	Conversion [%][b]	**13**[c] [%]	**14**[c] [%]	**15**[c] [%]
1[d]	(*Z*)-**11**[e]	**4c**	88	4.1	70.4	13.5
2[f]	(*Z*)-**11**[e]	**6b**	89	11.0	65.8	12.2
3[d]	(*E*)-**11**[g]	**4c**	18	0	15.5	2.5
4[h]	(*E*)-**11**[g]	**6b**	86	12.6	62.9	10.5

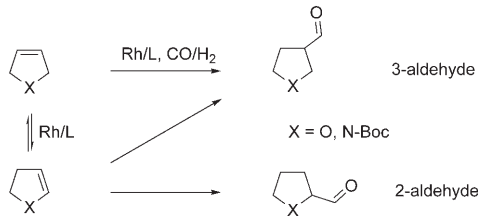
[a] All catalysts have been preformed at 5 bar CO/H$_2$ (1:1) for 30 min at the reaction temperature. The reaction was started by injection of the alkenic substrate. [b] Conversion was determined after 8 h of reaction time by NMR spectroscopy; [c] Aldehyde distribution determined by GC analysis. [d] Rh/L/substrate = 1:20:7318, c_0(substrate) = 2.68 M. [e] (*Z*)-**11** (*E*/*Z* = 1:9). [f] Rh/L/substrate = 1:20:6955, c_0(substrate) = 2.55 M. [g] (*E*)-**11** (*E*/*Z* = 11.7:1). [h] Rh/L/substrate = 1:20:7235, c_0(substrate) = 2.30 M.

Conversely, the bulky phosphite/rhodium catalyst showed similar activity towards both (*Z*)- and (*E*)-**11** alkenes (entries 2, 4). However, in both cases significant amounts of linear aldehydes **13** were found, indicative of the tendency of this catalyst for alkene isomerization. The fact that almost similar rates for both alkene isomers were found suggests a fast *E*/*Z* alkene isomerization equilibrium prior to hydroformylation. The significantly different hydroformylation rates for *Z* and *E* alkenes **11** for the phosphabarrelene catalyst are a further proof for the ability of this catalyst to catalyze the hydroformylation without alkene isomerization.

The ratio of branched aldehydes **14** and **15** seems to be largely independent of catalyst structure and varies only marginally between 5.2:1 and 6.2:1 in favor of aldehyde **14** (Table 6). Thus, it reflects a tendency to minimize steric repulsion between catalyst and substrate (α-branching) in the course of the transition state for hydrometalation. This is also in agreement with the lower regioselectivity observed in the course of the 2-octene hydroformylation (compare Table 5).

To see whether this unusual but synthetically useful behavior of the Rh/phosphabarrelene **4c** catalyst to catalyze hydroformylation without alkene isomerization is more general, we looked also at heterocyclic alkenes that are known to isomerize easily.[18] Thus, hydroformylation of heteroatom-substituted cyclopentenes such as 2,5-dihydrofuran and N-Boc-pyrroline was examined and the results were compared with those obtained by using the Rh/phosphite (**6b**) catalyst (Scheme 7, Table 7).

Both catalysts showed a remarkable activity upon hydroformylation of 2,5-dihydrofuran (Table 7, entries 1,2). However, whereas the phosphite system produced 27% of the 2-aldehyde as a result of severe alkene isomerization, in the



Scheme 7. Possible reaction pathways upon hydroformylation of 2,5-dihydrofuran and N-Boc-pyrroline.

Table 7. Results of the hydroformylation of 2,5-dihydrofuran and N-Boc-pyrroline.

Entry[a]	Substrate X =	L	3-Aldehyde[b] [%]	2-Aldehyde[b] [%]
1	O	**6b**	67	27
2	O	**4c**	79	6
3	N-Boc	**6b**	82	18
4	N-Boc	**4c**	72	–

[a] Conditions: With $[Rh(CO)_2acac]$/L at 50 °C, 10 bar (CO/H_2 1:1) in toluene ($c_0 = 1.537$ M) after 4 h (substrate/L/Rh 2011:20:1). [b] Determined by ^1H NMR spectroscopy, aldehyde selectivity was 100 % in all cases.

case of the xylylbarrelene **4c**, tendency towards isomerization was very low. Even better results were obtained in the case of the N-Boc-pyrroline. Here, the Rh/phosphite (**6b**) catalyst furnished almost 20 % of the 2-aldehyde arising from prior alkene isomerization. Conversely, the Rh/xylylbarrelene (**4c**) operated isomerization free to give the 3-aldehyde only (Table 7, entries 3, 4).

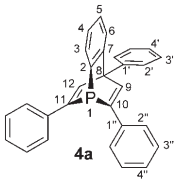
Conclusion

Phosphabarrelene/rhodium complexes have been prepared and identified as extremely active hydroformylation catalysts. Most notably, and in contrast to known catalysts designed for hydroformylation of internal alkenes, the phosphabarrelene catalysts enable a selective hydroformylation of an internal C=C double bond essentially free of alkene isomerization.

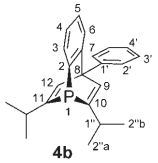
Experimental Section

General methods: Reactions were performed in flame-dried glassware under argon gas. The solvents were dried by standard procedures, distilled, and stored under argon. All temperatures quoted are not corrected. NMR spectra were obtained on a Varian Mercury spectrometer (300 MHz, 121.5 MHz, and 75.5 MHz for ^1H, ^{31}P, and ^{13}C, respectively), a Bruker AMX 400 (400 and 100.6 MHz for ^1H and ^{13}C, respectively) and a Bruker DRX 500 (500 and 125 MHz for ^1H and ^{13}C, respectively), and were referenced internally according to residual proton solvent signals (^{31}P NMR: 85 % H_3PO_4 as external standard); s, singlet; br, broad signal; d, doublet; t, triplet; q, quartet; quint, quintet; hept, heptet; oct, octet; m, multiplet; m_c, symmetrical multiplet; p, pseudo. IR spectroscopy was performed on a FTIR Spectrum 1000 (Perkin–Elmer)). Mass spectrometry: High-resolution mass spectra were obtained on a Finnigan MAT 8200 instrument. CI, ESI, and APCI experiments were performed on TSQ 7000 and LCQ Advantage instruments (both Finnigan MAT), respectively. Melting points were determined by using a melting point apparatus by Dr. Tottoli (Büchi). Elemental analyses were conducted with an Elementar Vario EL (Elementar Analysensysteme GmbH). Flash chromatography was performed by using silica gel Si 60, E. Merck AG, Darmstadt, 40–63 μm. Analytical gas chromatography was performed on a CP3800 instrument (Varian), column: CP-Sil5CB LOW BLEED/MS, 30 m × 0.32 mm ID (CHROMPACK). Hydroformylation reactions were performed in a 100 mL stainless-steel autoclave equipped with a sampling device and a gas-transfer stirrer (Premex, Switzerland). The stirrer engine was a "Eurodigi-visk" (Ika). A thermostat type CC301 (Huber) filled with synthetic oil served as the heating device. In all hydroformylation experiments the autoclave was connected to a gas reservoir that kept the CO/H_2 gas pressure constant throughout the reaction. Gases: Carbon monoxide 3.7, hydrogen 4.3 (1:1, Messer–Griesheim). The following compounds were prepared according to literature procedures: 2,3,6-Triphenylphosphinine (**3a**),[5a] 2,6-diisopropyl-4-phenylphosphinine (**3b**),[5a] 2,6-bis-(2,4-dimethylphenyl)-4-phenylphosphinine (**3c**),[5a] N-Boc-pyrroline.[19]

8,10,11-Triphenyl-1-phosphatricyclo[6.2.2.0^{2,7}]dodeca-2(7),3,5,9,11-pentaene (4a): *ortho*-Fluorobromobenzene (1.26 g, 24.66 mmol) was added at such a rate that the mixture was kept under slight reflux to a magnetically stirred suspension of magnesium turnings (0.60 g, 24.66 mmol) and 2,4,6-triphenylphosphabenzene (**3a**) (4.00 g (12.33 mmol) in THF (30 mL). After the exothermic reaction had ceased, the mixture was heated for a further 3 h under reflux. After cooling to RT, water was added (7 mL) and the solvent was removed in vacuo. The residue was suspended in toluene (100 mL) and was washed with water (3 × 120 mL). The combined aqueous phases were extracted with additional toluene (2 × 50 mL) and the combined organic phases were dried (Na_2SO_4) and the solvent evaporated in vacuo. The residue was dissolved in dichloromethane (150 mL), was sucked onto a plug of silica gel (100 g), and the "loaded silica" was stored for three days under air (during this treatment the reddish color, which was caused by an unidentified minor component of the crude reaction mixture, faded). Subsequently, the adsorbate was filtered through additional silica gel (150 g) with another portion of dichloromethane (600 mL). The solvent was removed in vacuo, the residue was suspended in Et_2O (50 mL), was filtered, and was dried in vacuo to give phosphabarrelene **4a** (1.290 g, 26 %) as a colorless solid. M.p. 198 °C (lit: 207–208 °C);[9] ^1H NMR (499.873 MHz, $CDCl_3$): $\delta = 6.60$ (d, $^3J_{H,H} = 6.8$ Hz, 1H; H-6), 7.02–7.05 (m, 2H; H-4, H-5), 7.28 (t, $^3J_{H,H} = 7.3$ Hz, 2H; H-4″), 7.36–7.38 (m, 4H; H-3″), 7.53 (t, $^3J_{H,H} = 7.0$ Hz, 1H; H-4′), 7.64–7.67 (m, 2H; H-3′), 7.72 (d, $^3J_{H,H} = 7.0$ Hz, 4H; H-2″), 7.84–7.85 (m, 3H; H-3, H-2′), 8.11 ppm (d, $^3J_{H,P} = 5.8$ Hz, 2H; H-9, H-12); ^{13}C NMR (125.692 MHz, $CDCl_3$): $\delta = 63.8$ (C-8), 124.1 (d, $^3J_{C,P} = 13.0$ Hz, C-4), 124.3 (d, $^3J_{C,P} = 0.9$ Hz, C-6), 125.9 (d, $^3J_{C,P} = 13.0$ Hz, 4C; C-2″), 127.2 (d, $^4J_{C,P} = 1.5$ Hz, C-5), 127.6 (C-4′), 127.6 (d, $^5J_{C,P} = 1.5$ Hz, 2C; C-4″), 128.5 (d, $^4J_{C,P} = 0.6$ Hz, 4C; C-3″), 128.9 (2C; C-2′), 129.1 (2C; C-3′), 131.7 (d, $^2J_{C,P} = 39.1$ Hz, C-3), 138.7 (d, $^2J_{C,P} = 24.8$ Hz, 2C; C-1″), 141.1 (d, $^1J_{C,P} = 11.5$ Hz, C-2), 141.2 (C-1′), 147.3 (d, $^2J_{C,P} = 4.9$ Hz, 2C; C-9, C-12), 152.5 (d, $^1J_{C,P} = 16.0$ Hz, 2C; C-10, C-11), 155.2 ppm (d, $^2J_{C,P} = 3.3$ Hz, C-7). Assignment of ^1H and ^{13}C resonances was based on APT, DQF-COSY (short-range H,H-COSY) and edHSQC (short-range H,C-COSY) experiments; ^{31}P NMR (121.474 MHz, $CDCl_3$): $\delta = -69.0$ ppm (s); HRMS (EI): m/z: calcd for $C_{29}H_{21}P$: 400.1381; found: 400.1379. From a saturated solution of compound **4a** in petroleum ether (boiling point 40–60 °C)/ethyl acetate (99:1) we obtained single crystals suitable for X-ray crystal-structure analysis.[11]

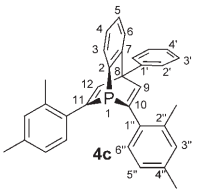


10,11-Diisopropyl-8-phenyl-1-phosphatricyclo[6.2.2.0^{2,7}]dodeca-2(7),3,5,9,11-pentaene (4b): A few drops of *ortho*-fluorobromobenzene (total amount: 17.47 g, 99.83 mmol) was added to a suspension of magnesium turnings (2.54 g, 104.53 mmol) and 2,6-diisopropyl-4-phenylphosphabenzene (**3b**) in THF (110 mL). After the exothermic reaction had started the remaining *ortho*-fluorobromobenzene was added slowly and the mixture was heated under reflux for a further 4 h. After cooling to RT, water (7 mL) was added, the solvent was removed in vacuo, and the residue suspended



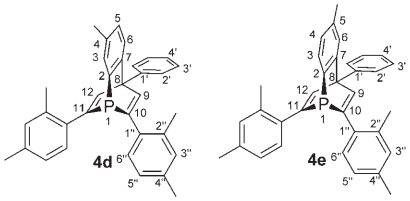
in toluene (300 mL). The suspension was washed with water (5×100 mL) and the aqueous phases were extracted with more toluene (5×100 mL). The combined organic phases were dried (Na_2SO_4) and the solvent was removed in vacuo. The residue was dissolved in petroleum ether (600 mL, 5% triethylamine) and was filtered through a plug of silica (7 cm in diameter and 7 cm in height) with additional petroleum ether (600 mL, 5% triethylamine). The solvent was removed in vacuo and the remaining red residue was dissolved in methanol (150 mL) and heated at reflux for 2 h. A precipitate formed that was collected by filtration, was washed with a little methanol, and was dried in vacuum to give phosphabarrelene **4b** (5.48 g, 35%) as a colorless solid. M.p. 110–112 °C; ^{1}H NMR (500.003 MHz, $CDCl_3$): δ = 1.17 (d, $^3J_{H,H}$ = 6.8 Hz, 12H; H-2″), 2.73 (sept, 2H; H-1″), 6.49–6.50 (m, 1H; H-6), 6.94–6.99 (m, 2H; H-4, H-5), 7.40 (d, $^3J_{H,P}$ = 7.3 Hz, 2H; H-9, H-12), 7.45–7.58 (m, 1H; H-4′), 7.56–7.60 (m, 2H; H-3′), 7.69–7.71 (m, 1H; H-3), 7.73–7.74 ppm (m, 2H; H-2′); ^{13}C NMR (125.725 MHz, $CDCl_3$): δ = 21.9 (d, $^3J_{C,P}$ = 8.2 Hz, 2C; C-2″a), 22.1 (d, $^3J_{C,P}$ = 8.8 Hz, 2C; C-2″b), 34.3 (d, $^2J_{C,P}$ = 27.3 Hz, 2C; C-1″), 61.9 (C-8), 123.4 (d, $^3J_{C,P}$ = 0.9 Hz, C-6), 123.4 (d, $^3J_{C,P}$ = 12.7 Hz, C-4), 126.4 (d, $^4J_{C,P}$ = 1.5 Hz, C-5), 127.1 (C-4′), 128.7 (2C; C-3′), 128.9 (2C; C-2′), 130.8 (d, $^2J_{C,P}$ = 37.8 Hz, C-3), 142.0 (C-1′), 142.6 (d, $^1J_{C,P}$ = 11.5 Hz, C-2), 143.7 (d, $^2J_{C,P}$ = 5.5 Hz, 2C; C-9, C-12), 156.9 (d, $^2J_{C,P}$ = 4.2 Hz, C-7), 160.5 ppm (d, $^1J_{C,P}$ = 17.3 Hz, 2C; C-10, C-11). Assignment of ^{1}H and ^{13}C resonances was based on APT, DQF-COSY (short-range H,H COSY) and edHSQC (short-range H,C COSY) experiments; ^{31}P NMR (121.469 MHz, $CDCl_3$): δ = −72.6 ppm (s); elemental analysis calcd (%) for $C_{23}H_{25}P$ (332.4): C 83.10, H 7.57; found: C 83.24, H 7.82.

10,11-Bis-(2,4-dimethylphenyl)-8-phenyl-1-phosphatricyclo[6.2.2.0^{2,7}]dodeca-2(7),3,5,9,11-pentaene (4c): *ortho*-Fluorobromobenzene (0.5 mL of a total amount of 6.20 mL, 9.93 g, 56.73 mmol) was added to a suspension of magnesium turnings (1.37 g, 56.73 mmol) and bis-2,6-(2,4-dimethylphenyl)-4-phenylphosphabenzene (**3c**) in THF (70 mL). After the start of the reaction (exothermicity) the remaining *ortho*-fluorobromobenzene was added slowly to keep the mixture under smooth reflux. Subsequently, the mixture was heated for a further 3 h under reflux. After cooling to RT, the mixture was quenched with water (5 mL) and the solvent was removed in vacuo.



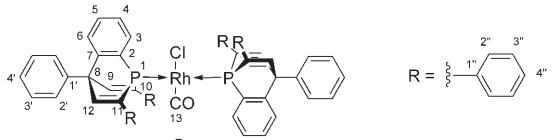
The residue was extracted with diethyl ether (200 mL) and dichloromethane (200 mL). The combined organic phases were washed with water (3×150 mL), and the aqueous phases were reextracted with diethyl ether (3×120 mL). The combined organic phases were dried (Na_2SO_4) and the solvent was removed in vacuo. The residue was suspended in petroleum ether (5% triethylamine) and was filtered through silica (plug diameter 7 cm, height 6 cm) followed by washing the silica gel with more petroleum ether (600 mL, 5% triethylamine). The solvent was removed in vacuo and the oily residue was taken up in methanol (400 mL) and heated under reflux for 2 h. The precipitate formed was collected by filtration and was washed with a small portion of methanol to give phosphabarrelene **4c** (5.64 g, 47%) as a colorless powder. M.p. 168–169 °C; ^{1}H NMR (499.870 MHz, $CDCl_3$): δ = 2.23 (s, 6H; CH_3), 2.33 (s, 6H; CH_3), 6.59 (d, $^3J_{H,H}$ = 7.1 Hz, 1H; H-6), 6.96–7.02 (m, 6H; H-3″, H-5″, H-6″), 7.04–7.10 (m, 2H; H-4, H-5), 7.49 (t, $^3J_{H,H}$ = 7.4 Hz, 1H; H-4′), 7.58–7.61 (m, 2H; H-3′), 7.75 (d, $^3J_{H,H}$ = 7.4 Hz, 2H; H-2′), 7.76 (d, $^2J_{H,P}$ = 6.3 Hz, 2H; H-9, H-12), 7.82–7.86 ppm (m, 1H; H-3); ^{13}C NMR (125.692 MHz, $CDCl_3$): δ = 21.0 (2C; C-4″-CH_3), 21.1 (d, $^4J_{C,P}$ = 7.9 Hz, 2C; C-2″-CH_3), 63.5 (C-8), 123.9 (d, $^3J_{C,P}$ = 12.4 Hz, C-4), 124.0 (d, $^3J_{C,P}$ = 0.6 Hz, C-6), 126.4 (2C; C-5″ or C-6″), 126.8 (d, $^4J_{C,P}$ = 1.5 Hz, C-5), 127.4 (C-4′), 128.1 (d, $J_{C,P}$ = 6.1 Hz, 2C; C-5″ or C-6″), 128.9 (2C; C-2′), 129.0 (2C; C-3′), 131.0 (2C; C-3″), 131.3 (d, $^2J_{C,P}$ = 36.9 Hz, C-3), 135.2 (d, $J_{C,P}$ = 1.8 Hz, 2C; C-2″ or C-4″), 136.9 (d, $J_{C,P}$ = 1.5 Hz, 2C; C-2″ or C-4″), 137.4 (d, $^2J_{C,P}$ = 22.1 Hz, 2C; C-1″), 141.3 (C-1′), 142.1 (d, $^1J_{C,P}$ = 15.1 Hz, C-2), 149.6 (d, $^2J_{C,P}$ = 3.6 Hz, 2C; C-9, C-12), 154.7 (d, $^1J_{C,P}$ = 21.2 Hz, 2C; C-10, C-11), 155.3 ppm (d, $^2J_{C,P}$ = 3.3 Hz, C-7). Assignment of ^{1}H and ^{13}C resonances was based on APT, DQF-COSY (short-range H,H COSY), and edHSQC (short-range H,C COSY) experiments; ^{31}P NMR (121.474 MHz, $CDCl_3$): δ = −57.1 ppm (s); HRMS (EI): *m/z*: calcd for $C_{33}H_{29}P$: 456.2007; found: 456.2004.

10,11-Bis-(2,4-dimethylphenyl)-4-methyl-8-phenyl-1-phosphatricyclo[6.2.2.0^{2,7}]dodeca-2(7),3,5,9,11-pentaene (4d) and 10,11-bis-(2,4-dimethylphenyl)-5-methyl-8-phenyl-1-phosphatricyclo[6.2.2.0^{2,7}]dodeca-2(7),3,5,9,11-pentaene (4e): 3-Bromo-4-fluorotoluene (0.5 mL of a total amount of 2.20 mL, 3.30 g, 17.46 mmol) was added to a suspension of magnesium turnings (0.508 g, 20.91 mmol) and bis-2,6-(2,4-dimethylphenyl)-4-phenylphosphabenzene (**3c**) in THF (35 mL). After the reaction started (exothermicity) the remaining 3-bromo-4-fluorotoluene was added slowly, to keep the mixture at smooth reflux. Subsequently, the mixture was heated for a further 3 h under reflux. After cooling to RT, the mixture was quenched with water (5 mL). The solvent was removed in vacuo and the residue was extracted with diethyl ether (200 mL) and dichloromethane (150 mL). The combined organic phases were washed with water (3× 150 mL), and the aqueous phases were reextracted with diethyl ether (3× 120 mL). The combined organic phases were dried (Na_2SO_4) and the solvent was removed in vacuo. The residue was suspended in petroleum ether (150 mL, 5% triethylamine) and was filtered through silica gel (3 cm diameter, 5 cm height). The silica gel was washed with additional petroleum ether (50 mL, 5% triethylamine) and the solvent was evaporated in vacuo. The red residue was dissolved in methanol (250 mL) and heated under reflux for 2 h. The precipitate formed was collected by filtration, was washed with a little methanol, and was dried in vacuo to give the phosphabarrelene isomer mixture **4d** and **4e** (0.120 g, 3%). Concentration of the mother liquor and cooling to 4 °C afforded a further product mixture **4d** and **4e** (0.770 g, 16%) as a colorless solid (total yield: 19%, ratio **4d**/**4e** 54:46 determined by NMR spectroscopy). M.p. 125–126 °C; ^{1}H NMR (400.136 MHz, $CDCl_3$): δ = 2.18 (s, 3H; CH_3), 2.20 (s, 6H; CH_3), 2.21 (s, 6H; CH_3), 2.31 (s, 12H; CH_3), 2.32 (s, 3H; CH_3), 6.38 (s, 1H; H-6, **4e**), 6.44 (d, $^3J_{H,H}$ = 7.7 Hz, 1H; H-6, **4d**), 6.81 (d, $^3J_{H,H}$ = 7.7 Hz, 1H; H-5, **4d**), 6.87 (d, $^3J_{H,H}$ = 6.8 Hz, 1H; H-4, **4e**), 6.93–6.99 (m, 12H; H-3″, H-5″, H-6″, **4d** and **4e**), 7.45–7.50 (m, 2H; H-4′, **4d** and **4e**), 7.55–7.60 (m, 4H; H-3′, **4d** and **4e**), 7.64 (d, J = 9.0 Hz, 1H), 7.69 (d, J = 8.6 Hz, 1H), 7.71–7.75 ppm (m, 8H); ^{13}C NMR (125.725 MHz, $CDCl_3$): δ = 20.6 (CH_3), 21.0 (4C; C-4″-CH_3, **4d** and **4e**), 21.1 (d, $^4J_{C,P}$ = 2.9 Hz, 2C; C2″-CH_3), 21.2 (d, $^4J_{C,P}$ = 2.9 Hz, 2C; C2″-CH_3), 21.5 (CH_3), 63.2 (d, $^3J_{C,P}$ = 2.9 Hz, C-8), 63.5 (d, $^3J_{C,P}$ = 2.9 Hz, C-8), 123.8 (C-6), 124.4 (d, $^3J_{C,P}$ = 13.1 Hz, C-4, **4e**), 125.3 (C-6), 126.4 (4C; C-5″ or C-6″), 127.2 (C-5, **4d**), 127.3 (C-4′), 127.4 (C-4′), 128.09 (d, $J_{C,P}$ = 7.3 Hz, 2C; C-5″ or C-6″), 128.13 (d, $J_{C,P}$ = 5.8 Hz, 2C; C-5″ or C-6″), 128.90 (4C; C-2′ or C-3′), 128.94 (4C; C-2′ or C-3′), 131.0 (4C; C-3″), 131.4, 132.3 (d, $^2J_{C,P}$ = 36.3 Hz, C-3), 133.4 (d, $J_{C,P}$ = 13.1 Hz), 135.2 (4C; C-2″*), 136.8, 136.9 (4C; C-4″*), 137.5 (d, $^2J_{C,P}$ = 21.8 Hz, 2C; C-1″), 137.6 (d, $^2J_{C,P}$ = 23.6 Hz, 2C; C-1″), 138.7 (d, $J_{C,P}$ = 14.5 Hz), 141.4 (C-1′), 141.6 (C-1′), 142.2 (d, $^1J_{C,P}$ = 14.5 Hz, C-2), 149.6 (d, $^2J_{C,P}$ = 4.4 Hz, 2C; C-9, C-12), 149.9 (d, $^2J_{C,P}$ = 2.9 Hz, 2C; C-9, C-12), 152.6 (d, $^2J_{C,P}$ = 2.9 Hz, C-7), 154.6 (d, $^1J_{C,P}$ = 20.4 Hz, 2C; C-10, C-11), 155.0 (d, $^1J_{C,P}$ = 21.8 Hz, 2C; C-10, C-11), 155.6 ppm (d, $^2J_{C,P}$ = 4.4 Hz, C-7). *Assignment interchangeable; ^{31}P NMR (121.474 MHz, $CDCl_3$): δ = −56.5 (s), −57.8 ppm (s); elemental analysis calcd (%) for $C_{34}H_{31}P$ (470.3): C 86.82, H 6.59; found: C 86.41, H 6.64.



General procedure for the preparation of rhodium complexes 5a–c: The corresponding phosphabarrelene **4a–c** (221.2 μmol) was added to a solution of rhodium dicarbonyl chloride dimer (21.5 mg, 55.3 μmol) in dichloromethane (4 mL). Gas evolution was observed. After stirring for 30 min at room temperature the solvent was removed in vacuo to give the corresponding rhodium complex **5a–c** in quantitative yield.

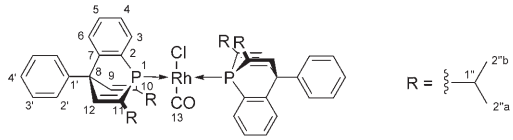
Chloro-bis-(8,10,11-triphenyl-1-phosphatricyclo[6.2.2.0^{2,7}]dodeca-2(7),3,5,9,11-pentaene)carbonyl rhodium(I) (5a): ^{1}H NMR (250.130 MHz, $CDCl_3$): δ = 6.45–6.48 (m, 2H; H-6), 6.92–6.98 (m, 2H; H-5*), 7.01–7.08 (m, 2H; H-4*), 7.18–7.26 (m, 12H; H-4″, H-3″), 7.33–7.40 (m, 2H; H-4′), 7.45–7.50 (m, 4H; H-3′), 7.56–7.68 (m, 12H; H-2′, H-2″), 7.83 (pt, J =



5a

9.6 Hz, 4H; H-9, H-12), 8.69–8.77 ppm (m, 2H; H-3). *Signal assignment interchangeable; ^{13}C NMR (75.459 MHz, $CDCl_3$): δ = 61.7 (d, $J_{C,P}$ = 6.0 Hz, 2C; C-8), 124.3 (2C; C-4*), 124.4 (2C; C-6*), 127.5 (2C), 127.6 (2C), 127.9 (2 signals, C-12), 128.0 (C-8), 128.7 (4C; C-2′), 129.2 (4C; C-3′), 134.7 (d, $J_{C,P}$ = 9.5 Hz, 2C; C-3), 137.0 (pt, $J_{C,P}$ = 19.0 Hz, 4C; C-1″), 138.6 (pt, $J_{C,P}$ = 7.3 Hz, 2C; C-2), 140.1 (2C; C-1′), 150.2 (dt, $J_{C,P}$ = 14.4 Hz, $J_{C,P}$ = 1.4 Hz, 4C; C-10, C-11), 150.6 (4C; C-9, C-12), 152.5 (2C; C-7), 182.7 ppm (C-13). *Signal assignment interchangeable; ^{31}P NMR (121.474 MHz, $CDCl_3$): δ = −10.6 ppm (d, $^1J_{P,Rh}$ = 144.8 Hz); IR: $\tilde{\nu}$ = 1993 cm^{-1} (C–O).

Chloro-bis-(10,11-diisopropyl-8-phenyl-1-phosphatricyclo[6.2.2.0^{2,7}]dodeca-2(7),3,5,9,11-pentaene)carbonyl rhodium(I) (5b): ^{1}H NMR (499.870 MHz, $CDCl_3$): δ = 1.22 (d, $^3J_{H,H}$ = 6.6 Hz, 12H; H-2″a), 1.24 (d, $^3J_{H,H}$ = 6.8 Hz, 12H; H-2″b), 3.55–3.68 (m, 4H; H-1″), 6.48 (dd, $^3J_{H,H}$ =



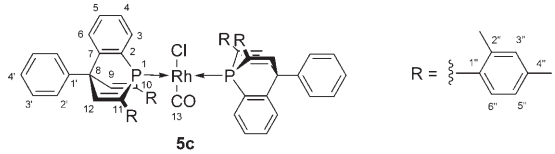
5b

7.7 Hz, J = 0.7 Hz, 2H; H-6), 6.98 (pt, $^3J_{H,H}$ = 7.4 Hz, 2H; H-5*), 7.06 (dpt, $^3J_{H,H}$ = 7.3 Hz, J = 1.1 Hz, 2H; H-4*), 7.45–7.55 (m, 6H; H-9, H-12, H-4′), 7.59 (m, 4H; H-3′), 7.72 (d, $^3J_{H,H}$ = 7.4 Hz, 4H; H-2′), 8.35 ppm (m, 2H; H-3). *Signal assignment interchangeable; ^{13}C NMR (125.692 MHz, $CDCl_3$): δ = 22.2 (pt, $J_{C,P}$ = 3.3 Hz, 4C; C-2″a), 22.8 (pt, $J_{C,P}$ = 3.0 Hz, 4C; C-2″b), 31.9 (pt, $J_{C,P}$ = 7.7 Hz, 4C; C-1″), 59.9 (pt, $J_{C,P}$ = 8.0 Hz, 2C; C-8), 123.7 (2C; C-6), 123.9 (pt, $J_{C,P}$ = 6.4 Hz, 2C; C-4), 127.1 (2C; C-5), 127.6 (2C; C-4′), 128.8 (4C; C-3′), 129.0 (4C; C-2′), 131.8 (pt, $J_{C,P}$ = 9.1 Hz, 2C; C-3), 138.1 (ptd, $J_{C,P}$ = 19.2, 1.6 Hz, 2C; C-2), 141.3 (2C; C-1′), 144.2 (4C; C-9, C-12), 154.3 (2C; C-7), 156.1 (pt, $J_{C,P}$ = 13.6 Hz, 4C; C-10, C-11), 188.5 ppm (d, $J_{C,P}$ = 71.8 Hz, 1C; C-13); ^{31}P NMR (121.468 MHz, $CDCl_3$): δ = −6.9 ppm (d, $^1J_{P,Rh}$ = 135.0 Hz); IR: $\tilde{\nu}$ = 1971 cm^{-1} (C–O). Single crystals suitable for X-ray diffraction were grown from a saturated solution of compound **5b** in dichloromethane.

X-ray crystal-structure analysis of compound 5b:[11] The reflections were collected with a Nonius–Kappa CCD diffractometer ($Mo_{K\alpha}$ radiation, graphite monochromator). The structure was solved by direct methods (SHELXS-97[20]). The structural parameters of the non-hydrogen atoms were refined anisotropically according to a full-matrix least-squares technique (F^2). The hydrogen atoms were calculated at idealized positions and refined in a riding model. Refinement was carried out with SHELXL-97.[21]

$C_{47}H_{50}ClOP_2Rh$; M_r = 831.17; crystal size: 0.2 × 0.2 × 0.2 mm^3; monoclinic; P_{21}; a = 8.5160(2), b = 18.4015(5), c = 13.0365(3) Å; V = 2038.90(9) Å^3; ρ_{calcd} = 1.354 mg mm^{-3}; $2\theta_{max}$ = 55°; T = 100(2) K; 13691 reflections collected, 8706 reflections unique, 8097 reflections observed [$I > 2\sigma(I)$], transition$_{min}$ = 0.960, transition$_{max}$ = 1.032, variables = 498, R indices (all data): R_1 = 0.0334, wR_2 = 0.0762, $(\Delta\rho)_{max}$ = 0.834 e Å^{-3}, $(\Delta\rho)_{min}$ = −0.453 e Å^{-3}.

Chloro-bis-(10,11-bis(2,4-dimethylphenyl)-8-phenyl-1-phosphatricyclo-[6.2.2.0^{2,7}]dodeca-2(7),3,5,9,11-pentaene)carbonyl rhodium(I) (5c): ^{1}H NMR (499.870 MHz, $CDCl_3$): δ = 2.06 (s, 6H; CH_3), 2.16 (s, 6H; CH_3), 2.32 (s, 12H; CH_3), 6.43–6.44 (m, 2H; H-6), 6.89–6.96 (m, 12H; H-3″, H-5‴, H-6‴), 6.99–7.00 (m, 4H; H-4, H-5), 7.41–7.45 (m, 2H; H-4′),



5c

7.50–7.53 (m, 4H; H-3′), 7.61–7.72 ppm (m, 10H; H-2′, H-9, H-12, H-3); ^{13}C NMR (100.620 MHz, $CDCl_3$): δ = 21.2 (4C; CH_3), 21.5 (4C; CH_3), 61.2 (pt, $J_{C,P}$ = 5.8 Hz, 2C; C-8), 123.6 (2C; C-6), 123.8 (pt, $J_{C,P}$ = 5.8 Hz, 2C; C-4), 126.0 (4C; C-5″*), 126.9 (2C; C-5), 127.6 (2C; C-4′), 128.7 (4C; C-2′), 129.0 (4C; C-3′), 129.4 (4C; C-6″*), 130.5 (4C; C-3″), 134.6 (pt, $J_{C,P}$ = 8.7 Hz, 2C; C-3), 136.0 (pt, $J_{C,P}$ = 6.6 Hz, 2C; C-2), 136.1 (4C; C-4″**), 136.9 (4C; C-2″**), 137.6 (pt, $J_{C,P}$ = 18.9 Hz, 4C; C-1″), 140.5 (2C; C-1′), 150.7 (pt, $J_{C,P}$ = 12.4 Hz, 4C; C-10, C-11), 151.0 (4C; C-9, C-12), 152.5 (2C; C-7), 182.6 ppm (dt, $^1J_{C,Rh}$ = 69.8 Hz, $^2J_{C,P}$ = 16.0 Hz, 1C; C-13). For * and ** signal assignment interchangeable; ^{31}P NMR (121.474 MHz, $CDCl_3$): δ = −3.0 ppm (d, $^1J_{P,Rh}$ = 143.7 Hz); IR: $\tilde{\nu}$ = 1993 cm^{-1} (C–O). Single crystals suitable for X-ray diffraction were grown from a saturated solution of compound **5c** in dichloromethane.

X-ray crystal-structure analysis of compound 5c:[11] The reflections were collected with a Nonius–Kappa CCD diffractometer ($Mo_{K\alpha}$ radiation, graphite monochromator). The structure was solved by direct methods (SHELXS-97[20]). The structural parameters of the non-hydrogen atoms were refined anisotropically according to a full-matrix least-squares technique (F^2). The hydrogen atoms at C4x and C5x were calculated at idealized positions and refined in a riding model. The other hydrogen atoms were found by using difference-Fourier analysis and refined isotropically. Refinement was carried out with SHELXL-97.[21]

$C_{67}H_{58}ClOP_2Rh$; M_r = 1079.43; crystal size: 0.2 × 0.2 × 0.2 mm^3; triclinic, P; a = 10.6716(4), b = 10.8642(3), c = 12.1352(4) Å; V = 1333.09(8) Å^3; ρ_{calcd} = 1.345 mg mm^{-3}; $2\theta_{max}$ = 54.86°; T = 150(2) K; 16379 reflections collected, 6054 reflections unique, 5227 reflections observed [$I > 2\sigma(I)$], transition$_{min}$ = 0.971, transition$_{max}$ = 1.025, variables = 384, R indices (all data): R_1 = 0.0448, wR_2 = 0.1151, $(\Delta\rho)_{max}$ = 0.858 e Å^{-3}, $(\Delta\rho)_{min}$ = −0.661 e Å^{-3}.

Preparation of alkenes for hydroformylation

5-Ethylsulfanyl-1-phenyl-1*H*-tetrazole: 1-Phenyl-1*H*-tetrazol-5-thiol (0.51 g, 11.0 mmol) was added in portions at 0 °C to a solution of triphenylphosphine (3.03 g, 11.6 mmol) and ethanol (0.51 g, 11.0 mmol) in THF (45 mL). After stirring for 2 min, diisopropyl azodicarboxylate (DIAD, 2.27 g, 11.2 mmol) was added dropwise. After a further 5 min at 0 °C the mixture was allowed to warm to RT. The solvent was removed in vacuo and the residue was purified by column chromatography with cyclohexane/ethyl acetate 10:1 to give the title compound (2.12 g, 93%) as a colorless oil. R_f = 0.13 (cyclohexane/ethyl acetate 10:1); ^{1}H NMR (400.130 MHz, $CDCl_3$): δ = 1.41 (t, $^3J_{H,H}$ = 7.3 Hz, 3H; CH_3), 3.32 (q, $^3J_{H,H}$ = 7.3 Hz, 2H; CH_2), 7.44–7.51 ppm (m, 5H; Ph); ^{13}C NMR (100.620 MHz, $CDCl_3$): δ = 14.4 (CH_3), 27.6 (CH_2), 123.6 (Ar-C), 129.6 (2C; Ar-C), 129.9 (2C; Ar-C), 133.5 (quat Ar-C), 154.1 ppm (N=C). The spectroscopic data correspond to those reported previously.[22]

5-Ethanesulfonyl-1-phenyl-1*H*-tetrazole: A solution of ammonium heptamolybdate (0.60 g, 0.49 mmol) in aq hydrogen peroxide (35 mass%, 4.71 g, 48.49 mmol) was added at RT to a solution of 5-ethylsulfanyl-1-phenyl-1*H*-tetrazole (1.00 g, 4.85 mmol) in ethanol (25 mL). After stirring the mixture overnight diethyl ether (80 mL) and water (50 mL) were added. The aqueous phase was extracted with diethyl ether (3 × 80 mL). The combined organic layers were washed with water (3 × 80 mL), brine (2 × 80 mL), and dried ($MgSO_4$). The solvent was removed in vacuo and the remaining crude product was purified by column chromatography

with cyclohexane/ethyl acetate (10:1) to give the sulfone (1.11 g, 96%) as a viscous colorless oil, that crystallized upon standing at RT. $R_f = 0.19$ (cyclohexane/ethyl acetate 10:1); ^{1}H NMR (400.130 MHz, $CDCl_3$): $\delta = 1.51$ (t, $^3J_{H,H} = 7.5$ Hz, 3H; CH_3), 3.73 (q, $^3J_{H,H} = 7.5$ Hz, 2H; CH_2), 7.56–7.61 (m, 3H; Ph), 7.66–7.68 ppm (m, 2H; Ph); ^{13}C NMR (100.620 MHz, $CDCl_3$): $\delta = 6.9$ (CH_3), 50.8 (CH_2), 125.0 (Ar-C), 129.7 (Ar-C), 131.4 (2C; Ar-C), 133.0 (quat Ar-C), 153.1 ppm (N=C). The spectroscopic data correspond to those reported previously.[23]

(*E*)-1-Cyclohexyl-1-propene [(*E*)-11]: A solution of potassium hexamethyldisilazide (7.85 g, 39.37 mmol) in THF (40 mL) was added at −78°C over 90 min (syringe pump) to a solution of 5-ethanesulfonyl-1-phenyl-1*H*-tetrazole (8.27 g, 34.63 mmol) and cyclohexane carbaldehyde (3.01 g, 26.75 mmol) and the mixture was kept for a further 30 min at this temperature. Water was added (6 mL) and the mixture was allowed to warm to RT. Additional water (60 mL) and diethyl ether (100 mL) were added. The ethereal phase was washed with water (2×30 mL). The aqueous phase was extracted with diethyl ether (2×30 mL) and the combined organic phases were dried ($MgSO_4$). The solvent was removed by distillation (Vigreux). The residue was dissolved in pentane (50 mL) and washed again with water (4×40 mL) in order to remove the last traces of THF. The aqueous phases were reextracted with pentane (4×40 mL) and the combined pentane phases were dried ($MgSO_4$), concentrated (850 mbar, rotavap), and the residue was purified by fractional distillation (Vigreux) to furnish the alkene (*E*)-**11** (1.80 g, 54%) as a colorless oil (*E*/*Z* 92:8, determined by GC). B.p. 153°C; ^{1}H NMR (400.130 MHz, $CDCl_3$): $\delta = 0.97$–1.29 (m, 6H; CH_2), 1.61 (d, $^3J_{H,H} = 3.9$ Hz, 3H), 1.63–1.71 (m, 4H; CH_2), 1.83–1.90 (m, 1H; C*H*), 5.34–5.37 ppm (m, 2H); ^{13}C NMR (100.620 MHz, $CDCl_3$): $\delta = 18.0$ (C-3), 26.1 (2C; CH_2), 26.3 (CH_2), 33.2 (2C; CH_2), 40.7 (*C*H), 122.0, 137.7 ppm. The spectroscopic data correspond to those reported previously.[24]

(*Z*)-1-Cyclohexyl-1-propene [(*Z*)-11]:[25] A mixture of sodium hydride (60% in paraffins, 4.36 g, 109.0 mmol) in DMSO (50 mL) was heated for 45 min to 80°C, until gas evolution ceased. After cooling to RT a suspension of ethyltriphenylphosphonium bromide (37.1 g, 99.9 mmol) in DMSO (100 mL) was added and the resulting orange suspension was stirred for 15 min. Subsequently, a solution of cyclohexane carbaldehyde (10.19 g, 90.8 mmol) in DMSO (20 mL) was added dropwise and the mixture was stirred for 2 h at RT. Water (100 mL) was added and the mixture was extracted with pentane (5×100 mL). The pentane phases were washed successively with water (100 mL), brine (100 mL), and were dried (Na_2SO_4). After filtration through silica the residue was concentrated (850 mbar, rotavap). Fractional distillation furnished the alkene (*Z*)-**11** (9.00 g, 72.4 mmol) as a colorless oil (*E*/*Z* 10:90, determined by GC). B.p. 150°C; ^{1}H NMR (400.130 MHz, $CDCl_3$): $\delta = 0.99$–1.34 (m, 6H; CH_2), 1.62 (dd, $^3J_{H,H} = 6.7$ Hz, $^4J_{H,H} = 1.5$ Hz, 3H; CH_3), 1.65–1.74 (m, 4H; CH_2), 2.22–2.32 (m, 1H; CH), 5.18–5.24 (m, 1H), 5.28–5.38 ppm (m, 1H); ^{13}C NMR (100.620 MHz, $CDCl_3$): $\delta = 12.8$ (C-3), 26.0 (2C; CH_2), 26.2 (CH_2), 33.1 (2C; CH_2), 35.9 (CH), 121.8, 136.9 ppm. The spectroscopic data correspond to those reported previously.[24]

General procedure for hydroformylation experiments: In an argon atmosphere the corresponding ligand and [$Rh(CO)_2$acac] were dissolved in toluene and stirred for 20 min at RT. The resulting solution was transferred into the autoclave (stainless steel, 100 mL) that was subsequently flushed three times with a CO/H_2 1:1 mixture (5 bar). A pressure of 5 bar CO/H_2 1:1 gas mixture was finally adjusted, and the autoclave was heated within 30 min to the reaction temperature while the solution was stirred (1000 min^{-1}). The olefin was added to the mixture through a pressure chamber, and then the syngas pressure was adjusted to the reaction pressure indicated. Reaction samples were taken through a sample valve and analyzed by GC and/or NMR spectroscopy.

Representative example of hydroformylation of cyclohexene with the Rh/4c catalyst: Following the general procedure described above from [$Rh(CO)_2$acac] (3.1 mg, 12.0 μmol), compound **4c** (109.8 mg, 0.24 mmol), cyclohexene (4.11 g, 50.04 mmol) in toluene (12 mL) was obtained after 4 h at 120°C and 10 bar (CO/H_2 1:1) a quantitative conversion to cyclohexane carbaldehyde (GC analysis: CP-Sil5CB LOW BLEED/MS, CHROMPACK). After cooling the autoclave to RT it was depressurized and the crude product was purified by Kugelrohr distillation (B.p. 161°C, ambient pressure) to give cyclohexane carbaldehyde (4.95 g, 97%). Spectroscopic and analytical data were identical to those obtained from a commercial sample of cyclohexane carbaldehyde purchased from Aldrich.

Acknowledgements

This work was supported by the Fonds der Chemischen Industrie, the Alfried Krupp Award for young university teachers of the Krupp foundation (to B.B.), as well as BASF AG. We thank Drs. T. Mackewitz, R. Paciello, and M. Volland (all BASF AG) for valuable discussions and Dr. T. Oeser (Universität Heidelberg) for the X-ray crystal-structure analysis of compound **4a**.

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Received: February 9, 2006
Published online: July 3, 2006

