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Carbonylation (hydroformylation and hydrocarbalkoxylation) reactions in the presence of transition metal: *p-tert*-butyl-calix[4]arene-based phosphine and phosphinite systems

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Abstract

In this study, 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(2-diphenylphosphinoxy-ethoxy)calix[4]arene (**5**) and 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(2-diphenylphosphinoethoxy)-calix[4]arene (**6**), as well as their platinum and palladium complexes $(PtCl_2)_2$(**5**), $(PdCl_2)_2$(**5**) were synthesised and characterised. In addition to these transition metal-containing complexes the catalytic systems formed in situ, from catalytic precursors $PtCl_2(PhCN)_2$, $[Rh(nbd)Cl]_2$ and $PdCl_2(PhCN)_2$ and the corresponding calixarene ligand, were tested as catalysts in hydroformylation and hydrocarbalkoxylation, respectively. High chemoselectivity was obtained in hydroformylation in the presence of rhodium-containing catalysts both with the above calixarene-based phosphine and phosphinite ligands. The regioselectivity towards branched aldehyde shows a strong temperature dependence in case of phosphinite derivative. Although the platinum-containing systems show much lower catalytic activity, the regioselectivities are undoubtedly higher than those obtained with $PtCl_2$(diphosphine)–$SnCl_2$ systems.

1. Introduction

The importance of carbonylation reactions has given rise to many studies, aimed at extending the range of applicability and at elucidating the mechanism [1]. In particular, a large number of simple and functionalised olefins have been investigated with the aim of obtaining compounds of industrial interest [2,3]. Large efforts have been made for the synthesis of chiral building blocks and biologically important derivatives in asymmetric hydroformylation reaction as well [4].

Hundreds of ligands with different steric and electronic parameters, shapes and functionalities have already been tested in various homogeneous catalytic reactions [5], among them carbonylations. A number of mono- and bidentate phosphines have been used as ligands in transition metal complexes, which show hydroformylation and hydrocarbalkoxylation activity [6,7]. Of the various ligands used in catalytic hydroformylation, chiral diphosphines of C_2 symmetry proved to be excellent ligands in asymmetric hydroformylation [8–14]. Diphosphines with diphenylphosphino groups in stereochemically different environment have been also reported as efficient ligands [15]. However, recent studies with heterobidentate phosphine–phosphite ligands show the importance of different donor atoms in rhodium-catalysed reactions [16,17].

The hydroformylation of simple substrates is of high practical importance and the investigation of various ligands in mono- and biphasic reactions is still the frontier of homogeneous catalysis [3].

Although the 'lower rim' functionalization of calixarene derivatives has been studied in detail and the application of these host molecules for various purposes

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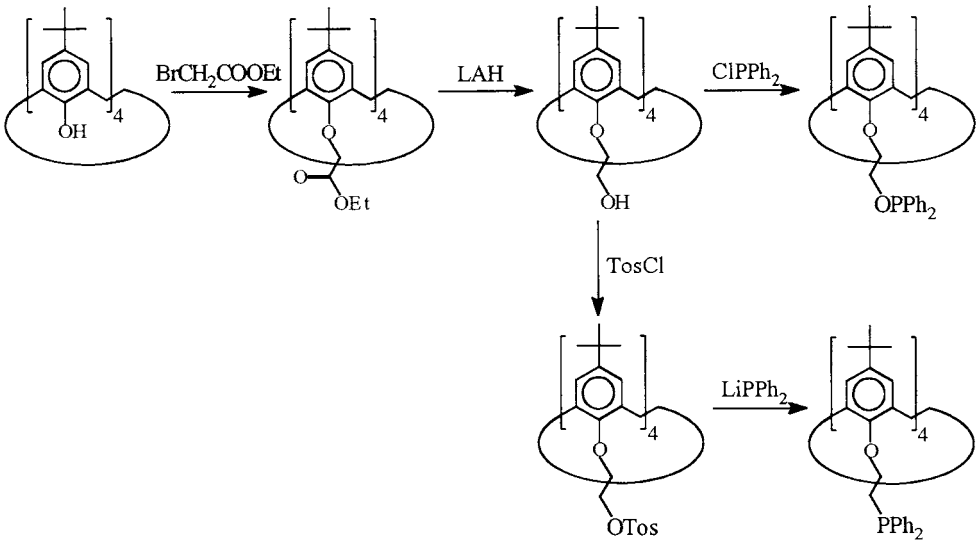


Scheme 1. Schematic pathway for **5** and **6**.

has been investigated [18], the number of applications as novel ligands in transition metal complexes is rather limited. A novel class of calixarene derivatives with phosphorus [19–23] and nitrogen donor atoms [24,25] was reported and their coordination to copper [19] and platinum [21,26,27] has been investigated. Calix[*n*]arene phosphine oxides have been used for the inter- and intra-group separations of lanthanides and actinides [22].

However, to the best of our knowledge, only one attempt has been made to employ these calixarene-based potential ligands in homogeneous catalytic reactions [28]. Their use as bidentate (and potentially multidentate) ligands, able to influence both steric and electronic properties of molecularly defined catalysts, was encouraged by the importance of obtaining new information on ligand structure–reactivity and ligand structure–stereochemical outcome relationships [29].

In the present paper the synthesis and characterization of calixarene phosphine and phosphinite ligands is described. Efforts to improve the chemo- and regioselectivities in carbonylation reactions led to the synthesis of platinum, palladium and rhodium complexes with these calixarene ligands, which were used as preformed or in situ catalysts in the hydroformylation and hydrocarbalkoxylation of styrene.

2. Results and discussion

2.1. Synthesis of p-^{t}Bu-calix[4]arenephosphinite (5) and phosphine (6)

The lower rim functionalised calixarene, 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(2-diphenylphosphinoethoxy)-calix[4]arene (**6**) was synthesised in an alternative route to that described earlier [22]. The appropriate ethyl carboxylate (**2**) [30] was reduced to the corresponding primary alcohol (**3**) by lithium aluminium hydride, followed by tosylation with toluene-*para*-sulfonyl chloride resulting in **4** [31], which was reacted with lithium diphenylphosphide (Scheme 1). In the ^{31}P-NMR spectrum of **6**, the phosphorus atoms appear as a singlet at -22.99 ppm.

The analogous phosphinite derivative, 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(2-diphenylphosphinoxy-ethoxy)-calix[4]arene (**5**), was obtained directly from the alcohol (**3**) by the reaction with chlorodiphenylphosphine in THF (Scheme 1). The ^{31}P-NMR spectrum of **5** shows a single peak at 113.78 ppm.

2.2. Investigation of the coordination of 5 and 6 to Pt, Pd and Rh

2.2.1. Complexes with 5

Both the preparation and the in situ reaction bring about the formation of $(PtCl_2)_2$(**5**) and the analogous $(PdCl_2)_2$(**5**) complexes where the two neighbouring phosphinite phosphorus donor coordinate to the metal in *cis* position (Scheme 2). The synthesis of both complexes was based on the facile benzonitrile substitution in the reaction of **5** with $PtCl_2(PhCN)_2$ and $PdCl_2(PhCN)_2$ precursors, respectively.

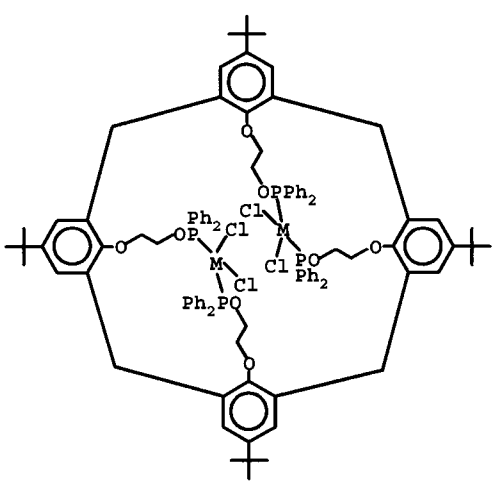
The ^{31}P-NMR spectra of the in situ reactions of **5** with $PtCl_2(PhCN)_2$, at molar ratio ligand (**5**)/$PtCl_2(PhCN)_2 = 1/2$, even at molar ratio 1/1, show only one signal at 85.8 ppm ($J(^{31}P, ^{195}Pt) = 4173$ Hz) upfield to the free ligand (113.78 ppm). The isolated platinum complex also gave the above signal exclusively. The structure proposed above is also proved by the two pairs of benzylic methylene doublets in ^{1}H-NMR (for

analytical data see Section 3). The formation of any oligomeric species can be ruled out by the presence of the above simple NMR pattern showing equivalent phosphorus donor atoms. Although the $(PtCl_2)_4$(**5**)$_2$ symmetric dimeric species (each of the four phosphorus donor atoms of the ligand is bound to different platinum *trans* to the chloro ligand) may possess the same simple ^{31}P-NMR spectrum, a single pair of doublets is expected as a consequence of the four equivalent benzylic methylene groups in ^{1}H-NMR.

The analogous reaction for palladium furnished a $(PdCl_2)_2$(**5**) dinuclear complex as major component, which shows a predominating signal at 112.7 ppm (at molar ratio ligand (**5**)/$PdCl_2(PhCN)_2 = 1/2$). The structure of the complex analogous to platinum shows a similar pattern for the benzylic methylene protons. The *cis* arrangement of both pairs of phosphorus atoms of **5** has also been shown by Raman spectroscopy. The bands with wavenumbers of 300.4 and 323.1 cm^{-1} have been assigned to ν(Pd–Cl) of the *cis*-$(PdCl_2)_2$(**5**) species as described for analogous platinum-containing systems [23].

In addition to the above *cis*-complex ca. 5% *trans*-Pd-P_2 moieties have also been observed in ^{31}P-NMR and Raman spectra (363.5 cm^{-1}). Since their amount increases upon standing, they could be considered as parts of oligomeric decomposition products. The presence of the suggested multinuclear species is in agreement with osmometric molecular weight determination. The molecular weight (2260 ± 50) higher than expected for *cis*-$(PdCl_2)_2$(**5**) (MW = 1916.5) can also be considered as an indication for the presence of oligomeric species.

The in situ reaction with $PdCl_2(PhCN)_2$ results in a species showing a signal at 110 ppm ($\Delta\nu_{1/2}$ = ca. 600 Hz). The line broadening can be explained both by the exchange between benzonitrile and phosphinite ligands, and the intramolecular exchange of the phosphinite donor moieties of **5**.



Scheme 2. Schematic representation of $(MCl_2)_2$(**5**) (M = Pt, Pd).

The in situ reaction of $[Rh(nbd)Cl]_2$ and **5** was also followed by ^{31}P-NMR at r.t. A broad signal at 122 ppm ($\Delta\nu_{1/2}$ = ca. 600 Hz) reflects fast exchange between coordinated and noncoordinated phosphorus donor atoms (molar ratio ligand (**5**)/$[Rh(nbd)Cl]_2 = 2/1$, P/Rh = 4/1). $RhClP_3$-type complex(es) and the free fourth phosphorus of the calixarene-based ligand are supposed to be involved in this exchange process. The variable temperature measurement up to 100°C in toluene-d_8 did not bring about substantial changes neither in the chemical shift nor the half-width of the above signal.

The stepwise addition of two further equivalents of the Rh precursor (P/Rh = 2/1 and P/Rh = l/l) results in three sets of doublets showing $^1J(^{31}P, ^{103}Rh) = 200$ Hz coupling only. These results reflect highly symmetric di- and tetranuclear complexes containing RhP_2 and Rh(nbd)P moieties, respectively.

2.2.2. Complexes with **6**

At a molar ratio ligand (**6**)/$PtCl_2(PhCN)_2 = 1/2$, two major components at -1.75 ppm, $J(^{31}P, ^{195}Pt) = 3558$ Hz and 10.02 ppm, $J(^{31}P, ^{195}Pt) = 3538$ Hz (their ratio is ca. 3/1) were observed. The lack of $J(^{31}P, ^{31}P)$ coupling is an indication for equivalent phosphorus donor atoms. The $J(^{31}P, ^{195}Pt)$ coupling constant of about 3500 Hz is an indication of their *cis*-arrangement.

The ^{31}P-NMR of the reaction of **6** with $PdCl_2(PhCN)_2$ (at a molar ratio ligand (**6**)/$PdCl_2(PhCN)_2 = 1/2$) shows an even more complicated reaction mixture: a sharp singlet at 16.61 ppm, four singlets of lower intensity between 10.04 and 11.17 ppm showing the presence of both mono and bidentate coordination resulting in a mixture of *cis* and *trans*-PdP_2-type complexes.

The in situ reaction of the tetraphosphine (**6**) with $[Rh(nbd)Cl]_2$ (ligand (**6**)/$[Rh(nbd)Cl]_2 = 2/1$, P/Rh = 4/1) resulted in a doublet at 15.67 ppm and a broad doublet at 15.05 ppm ($\Delta\nu_{1/2}$ = ca. 65 Hz), with the coupling constants being nearly the same ($J(^{31}P, ^{103}Rh) = 134$ Hz) reflecting a similar geometry.

Upon further addition of $[Rh(nbd)Cl]_2$ precursor (P/Rh = 2/1) the two doublets have been sharpened, their ratio is ca. 3/1, and in the same time a broad doublet at 20.58 ppm appeared ($J(^{31}P, ^{103}Rh)$ = ca. 170 Hz).

2.3. Homogeneous carbonylations using **5** and **6** as ligands in transition metal catalysed reactions

2.3.1. Platinum-catalysed hydroformylation reactions

Styrene (**7**) as model compound was reacted with CO/H_2 (1/1) at 50–105°C, under a pressure of 80 bar, in the presence of platinum-containing in situ catalysts prepared from $(PtCl_2)_2$(**5**) and tin(II)chloride, as well as $PtCl_2(PhCN)_2$, **6** and tin(II)chloride (Table 1).

Table 1
Hydroformylation of styrene in the presence of platinum–**5** and platinum–**6** systems[a]

Catalyst	R. temp. (°C)	R. time (h)	Conv[b] (%)	R_c^c (%)	R_{br}^d (%)
$(PtCl_2)_2$(**5**)	50	135	57	93.3	46.7
$(PtCl_2)_2$(**5**)	75	41	64	91.6	46.3
$(PtCl_2)_2$(**5**)	95	21	60	87.3	42.8
$(PtCl_2)_2$(**5**)+2PPh_3	95	21	37	86.9	40.6
$(PtCl_2)_2$(**5**)	105	17	54	87.7	39.8
$PtCl_2(PhCN)_2$+**6**	55	290	57	91.6	48.3
$PtCl_2(PhCN)_2$+**6**	75	100	60	87.5	48.2
$PtCl_2(PhCN)_2$+**6**	95	28	62	82.2	47.3
$PtCl_2(PhCN)_2$+**6**	105	28	85	80.1	46.3
$PtCl_2(PhCN)_2$+**6**+2PPh_3	105	28	71	80 5	43.6

[a] Reaction conditions: Pt/P/$SnCl_2$/styrene = 1/2/1/2000; 0.05 mol styrene; partial pressure of CO = partial pressure of H_2 = 40 bar, solvent: toluene.
[b] (Mol of **8**+mol of **9**+mol of **10**)/(initial mol of **7**)×100.
[c] (Mol of **8**+mol of **9**)/(mol of **8**+mol of **9**+mol of **10**)×100 (chemoselectivity towards aldehydes).
[d] Mol of **8**/(mol of **8**+mol of **9**)×100 (regioselectivity towards branched aldehyde).

$$\underset{\mathbf{7}}{PhCH{=}CH_2} \xrightarrow{CO/H_2} \underset{\mathbf{8}}{PhCH(CH_3)CHO} + \underset{\mathbf{9}}{Ph(CH_2)_2CHO} + \underset{\mathbf{10}}{PhC_2H_5} \quad (1)$$

The use of the two platinum catalysts described above in the hydroformylation reaction resulted in the formation of the two aldehyde regioisomers **8** and **9** which is accompanied by the hydrogenation product of the substrate (**10**) (Eq. (1)).

The catalytic activity of the systems containing calixarene-based ligands is much lower than that of the Pt(diphosphine)Cl_2 systems [6,7]. At low temperature the difference in the activity of systems containing **5** and **6** is much higher than at higher temperature.

The chemoselectivity of hydroformylation is similar to that of the widely used $PtCl(SnCl_3)$(PP) systems in case of **5** and lower when the phosphine (**6**) has been used as ligand. The regioselectivity towards branched aldehyde (**8**) is close to 50% at 50°C which is by ca. 10% higher than that obtained with $PtCl_2$(PP) catalysts, and shows some temperature dependence in case of **5,** falling from 46.7 to 39.8%. Surprisingly, an almost constant regioselectivity has been observed by the variation of the temperature in case of **6**.

The addition of PPh_3 to the above phosphinite- and phosphine-based catalytic systems resulted in a decrease of the catalytic activity and slightly lower chemo- and regioselectivities. This observation shows that the selectivities are still determined by the calixarene ligands bound to platinum. The formation of $PtCl_2(PPh_3)_2$ complex of low activity could be an explanation for this phenomenon.

2.3.2. Rhodium-catalysed hydroformylation reactions

Although the activities of the Rh–**5** and Rh–**6** systems are slightly lower than that of the usual rhodium–phosphine systems (especially in case of **6**), the aldehyde selectivities are similar to the best rhodium-catalysts (Table 2). At 55°C both rhodium-containing systems resulted in practically same regioselectivities. The regioselectivity towards branched aldehyde decreases strongly by the increasing temperature. This effect is more pronounced when the phosphinite derivative (**5**) was used. The addition of a monodentate phosphine (PPh_3) resulted in an increase in branched regioselectivity from 69.7 to 85.8%. The 86–87% branched selectivity at 105°C could be an indication for the presence of Rh–PPh_3 species, since much higher regioselectivities have been obtained with rhodium-catalysts with PPh_3 in the hydroformylation of styrene [32].

2.3.3. Palladium-catalysed hydroalkoxycarbonylation reactions

The two palladium containing catalysts, the preformed $(PdCl_2)_2$(**5**) and the in situ system formed from **6** and $PdCl_2(PhCN)_2$ (molar ratio = 1/2), have been tested in hydroalkoxycarbonylation of styrene at 130°C, with a CO pressure of 140 bar (Eq. (2)).

$$PhCH{=}CH_2 \xrightarrow{CO/ROH} \underset{\mathbf{11}}{PhCH(CH_3)COOR} + \underset{\mathbf{12}}{Ph(CH_2)_2COOR} \quad (2)$$

Extremely low conversion (< 3%) was obtained with **5** due to the cleavage of the C–O–P bond of the ligand by the alcohol (Table 3). Reasonable yields were obtained with **6** at 130°C. Neither the high branched regioselectivity characteristic for monodentate tertiary phosphines nor the linear selectivity characteristic for bidentate phosphines were observed under the reaction conditions used. Formation of branched and linear esters in a ratio of ca. 1:1 can be explained by the interplay of reaction mechanisms catalysed by palladium-complexes of monodentate and *cis*-chelate type coordination (see Section 2.2). The use of Pd–PPh_3 and Pd–diphosphine systems yields an almost exclusive for-

Table 2
Hydroformylation of styrene in the presence of rhodium–**5** and rhodium–**6** systems[a]

Catalyst	R. temp. (°C)	R. time (h)	Conv. (%)[b]	R_c^c	R_{br}^d
$[Rh(nbd)Cl]_2$+**5**	55	22	78	99.9	92.3
$[Rh(nbd)Cl]_2$+**5**	75	9	99	99.5	77.3
$[Rh(nbd)Cl]_2$+**5**	105	5	99	99.5	69.7
$[Rh(nbd)Cl]_2$+**5**+2PPh_3	105	5	15	98.2	85.8
$[Rh(nbd)Cl]_2$+**5**	130	4	100	98.0	52.1
$[Rh(nbd)Cl]_2$+**6**	55	32	96	99.8	92.6
$[Rh(nbd)Cl]_2$+**6**	75	12	98	99.7	87.0
$[Rh(nbd)Cl]_2$+**6**	105	7	94	99.6	76.5
$[Rh(nbd)Cl]_2$+**6**+2PPh_3	105	7	90	99.8	87.2
$[Rh(nbd)Cl]_2$+**6**	135	6	99	96.8	57.0

[a] Reaction conditions: Rh/P/styrene = 1/4/4000; 0.05 mol styrene; partial pressure of CO = partial pressure of H_2 = 40 bar, solvent: toluene.
[b] (Mol of **8**+mol of **9**+mol of **10**)/(initial mol of **7**) × 100.
[c] (Mol of **8**+mol of **9**)/(mol of **8**+mol of **9**+mol of **10**) × 100 (chemoselectivity towards aldehydes).
[d] Mol of **8**/(mol of **8**+mol of **9**) × 100 (regioselectivity towards branched aldehyde).

mation of branched and linear esters, respectively [33–35]. Even if multidentate coordination takes place, highly flexible chelates of various conformers are expected, which undergo a facile 'arm-off' dissociation of one of the PPh_2 moieties.

3. Experimental

3.1. Reagents

All reactions were performed under an argon atmosphere, and in the preparations of **5** and **6**, standard Schlenk techniques were used. Chlorodiphenylphosphine was a Fluka product, and distilled immediately prior to use. The catalytic precursors $PtCl_2(PhCN)_2$, $PdCl_2(PhCN)_2$ and $[Rh(nbd)Cl]_2$ were prepared as described previously [36,37]. Solvents were dried by conventional methods, and freshly distilled under argon before use.

Table 3
Hydroalkoxycarbonylation of styrene in the presence of palladiumñ**5** and palladium–**6** systems[a]

Catalyst	Alcohol	R. time (h)	Conv. (%)[b]	R_{br}^c
$(PdCl_2)_2$(**5**)	MeOH	48	—	—
$(PdCl_2)_2$(**5**)+2NaCl	MeOH	48	2	50.0
$(PdCl_2)_2$(**5**)	^{t}BuOH	48	3	75.0
$PdCl_2(PhCN)_2$+**6**	MeOH	48	39	62.3
$PdCl_2(PhCN)_2$+**6**	MeOH	140	68	54.5
$PdCl_2(PhCN)_2$+**6**	^{t}BuOH	48	42	48.6
$PdCl_2(PhCN)_2$+**6**	^{t}BuOH	140	70	47.2

[a] Reaction conditions: Pd/P/styrene/alcohol = 1/2/2000/4000; 0.05 mol styrene; pressure of CO = 140 bar, R. temp.: 130°C; solvent: toluene.
[b] (Mol of **11**+mol of **12**)/(initial mol of **7**) × 100.
[c] Mol of **11**/(mol of **11**+mol of **12**) × 100 (regioselectivity towards branched ester).

^{1}H-, ^{13}C-, and ^{31}P-NMR spectra were obtained on a Varian UNITY 300 spectrometer using $CDCl_3$ solvent. ^{1}H chemical shifts are reported relative to the residual nondeuterated solvent of chloroform at 7.24 ppm. The ^{13}C chemical shifts are given relative to $CDCl_3$ at 77.0 ppm. The ^{31}P-NMR data are referenced relative to external H_3PO_4. FAB MS spectra were recorded on a ZAB-2SEQ spectrometer. Elemental analysis were performed on a 1108 Carlo Erba instrument. The product distribution in catalytic experiment were determined with a Hewlett Packard 5830A gas chromatograph fitted with a capillary column coated with OV-1.

3.2. Synthesis of **5**

Compound **3** (420 mg, 0.51 mmol) was dissolved in dry THF (5 ml) under an inert atmosphere, and pyridine (412 μl, 5.1 mmol) was added. The solution was cooled to 0°C, and PPh_2Cl (3.87 mmol, 695 μl) was added dropwise. The reaction mixture was stirred for 1 h, and warmed to r.t. After filtration of the pyridinium–chloride, the solvent was evaporated. The residue was treated with toluene (6 ml) and addition of hexane (7 ml) yielded a white precipitate which was filtered off. The solvents were removed in vacuo to give a white solid. This compound requires careful handling since hydrolysis occurs readily.

^{1}H-NMR (300 MHz, $CDCl_3$, 20°C): 0.99 (s, 36H, $C(CH_3)_3$); 2.86 (d, J = 13 Hz, 4H, H_{eq} of $ArCH_2Ar$); 3.99 (brs, 8H, $ArOCH_2$); 4.10 (brs, 8H, CH_2OPPh_2); 4.25 (d, J = 13 Hz, 4H, H_{ax} of $ArCH_2Ar$); 6.63 (s, 8H, calixAr); 7.05–7.76 (m, 40H, PPh_2); ^{13}C-NMR (75 MHz, $CDCl_3$, 20°C): 31.40 ($C(CH_3)_3$ overlapped with $ArCH_2Ar$); 33.66 ($C(CH_3)_3$); 69.51 (d, $^3J_{PC}$ = 18 Hz; $ArOCH_2$); 75.33 (d, $^2J_{PC}$ = 8 Hz; CH_2OPPh_2); 124.56–151.33 (aromatic C); ^{31}P-NMR (121.4 MHz, $CDCl_3$, 20°C): 113.78 (s, $OPPh_2$); FAB MS: 1627 (oxidation does occur); Analysis calculated for $C_{100}H_{108}O_8P_4$

($M = 1561.85$): C, 76.90; H, 6.97; Found: C, 77.12; H, 6.68; yield: 76%.

3.3. Synthesis of **6**

A solution of **4** (720.3 mg, 0.5 mmol) in THF (5 ml) was added dropwise to a stirred solution of $LiPPh_2$ (4 mmol, prepared in situ from PPh_2Cl and Li) in THF (5 ml) at 0°C under an inert atmosphere. The reaction mixture was warmed to r.t., stirred for an additional 1 h, and deoxygenated water (10 ml) was added. The THF was removed under reduced pressure (40 mmHg) at 30–40°C, and chloroform (10 ml) was added. The organic phase was evaporated to give a white foam which was purified by column chromatography (Al_2O_3, toluene).

^{1}H-NMR (300 MHz, $CDCl_3$, 20°C): 1.03 (s, 36H, $C(CH_3)_3$); 2.68 (t, $J = 8.2$ Hz, 8H, CH_2PPh_2); 2.94 (d, $J = 12.8$ Hz, 4H, H_{eq} of $ArCH_2Ar$); 3.95 (brs, 8H, OCH_2); 4.21 (d, $J = 12.8$ Hz, 4H, H_{ax} of $ArCH_2Ar$); 6.69 (s, 8H, calixAr); 7.10–7.60 (m, 40H, PPh_2); ^{13}C-NMR (75 MHz, $CDCl_3$, 20°C): 28.45 (d, $^1J_{PC} = 13.2$ Hz; CH_2PPh_2); 31.42 ($C(CH_3)_3$ overlapped with $ArCH_2Ar$); 33.81 ($C(CH_3)_3$); 71.37 (d, $^2J_{PC} = 28.8$ Hz; OCH_2); 124.94152.47 (aromatic C); ^{31}P-NMR (121.4 MHz, $CDCl_3$, 20°C): -22.99 (s, PPh_2); FAB MS: 1562 (oxidation does occur); Analysis calculated for $C_{100}H_{108}O_4P_4$ ($M = 1497.85$): C, 80.19; H, 7.27; Found: C, 80.53; H, 7.75; yield: 62%.

3.4. Synthesis of $(PtCl_2)_2$(**5**)

A solution of **5** (234 mg, 0.15 mmol) in THF (5 ml) was slowly added to a solution of $PtCl_2(PhCN)_2$ (142 mg, 0.3 mmol) in THF (40 ml). After stirring 0.5 h, the solution was reduced to ca. 3 cm^3 and hexane (10 ml) was added affording an ivory precipitate which was filtered off.

Selected NMR data: ^{1}H-NMR (300 MHz, $CDCl_3$, 20°C): 2.75 (d, $J = 13$ Hz, 2H, H_{eq} of $ArCH_2Ar$); 3.04 (d, $J = 13$ Hz, 2H, H_{eq} of $ArCH_2Ar$); 3.75 (d, $J = 13$ Hz, 2H, H_{ax} of $ArCH_2Ar$); 4.69 (d, $J = 13$ Hz, 2H, H_{ax} of $ArCH_2Ar$); ^{13}C-NMR (75 MHz, $CDCl_3$, 20°C): 31.32 ($C(CH_3)_3$); 33.81 ($C(CH_3)_3$); 69.27 ($ArOCH_2$); 73.49 (CH_2OPPh_2); ^{31}P-NMR (121.4 MHz, $CDCl_3$, 20°C): 85.8 (s, PPh_2); FAB MS: 1986 $(M\text{-}3Cl)^+$; Analysis calculated for $C_{100}H_{108}O_8P_4Pt_2Cl_4$ ($M = 2093.82$): C, 57.36; H, 5.20; Cl, 6.77; Found: C, 57.08; H, 5.06; Cl, 7.15; m.p.: 250°C; yield: 85%.

3.5. Synthesis of $(PdCl_2)_2$(**5**)

A solution of **5** (234 mg, 0.15 mmol) in THF (5 ml) was slowly added to a suspension of $PdCl_2(PhCN)_2$ (115 mg, 0.3 mmol) in THF (40 ml). The reaction mixture turned yellow. After stirring 0.5 h, the solution was filtered and concentrated to ca. 3 cm^3. Addition of hexane (10 ml) afforded a yellow precipitate which was filtered off.

Selected NMR data: ^{1}H-NMR (300 MHz, $CDCl_3$, 20°C): 2.74 (d, $J = 13$ Hz, 2H, H_{eq} of $ArCH_2Ar$); 3.02 (d, $J = 13$ Hz, 2H, H_{eq} of $ArCH_2Ar$); 3.72 (d, $J = 13$ Hz, 2H, H_{ax} of $ArCH_2Ar$); 4.72 (d, $J = 13$ Hz, 2H, H_{ax} of $ArCH_2Ar$); ^{13}C-NMR (75 MHz, $CDCl_3$, 20°C): 31.30 ($C(CH_3)_3$); 33.75 ($C(CH_3)_3$); 69.20 ($ArOCH_2$); 73.50 (CH_2OPPh_2); ^{31}P-NMR (121.4 MHz, $CDCl_3$, 20°C): 112.7 (s, PPh_2); Analysis calculated for $C_{100}H_{108}O_8P_4Pd_2Cl_4$ ($M = 1916$ 50): C, 62.67; H, 5.68; Cl, 7.40; Found: C, 62.88; H, 5.90; Cl, 7.51; yield: 91%.

3.6. Hydroformylation experiments

In a typical experiment a solution of 26.2 mg (0.0125 mmol) of $(PtCl_2)_2$(**5**) and 4.7 mg (0.025 mmol) of $SnCl_2$ (or 5.8 mg (0.0125 mmol) $[Rh(nbd)Cl]_2$ and 39 mg (0.025 mmol) of **5**) in 15 ml toluene containing 5.5 ml (0.05 mol) of styrene was transferred under argon into a 150 ml stainless steel autoclave. The reaction vessel was pressurised to 80 bar total pressure ($CO/H_2 = 1/1$) and placed in an oil bath and the mixture stirred with a magnetic stirrer. The pressure was monitored throughout the reaction. After cooling and venting of the autoclave, the pale yellow solution was immediately analysed by GC.

3.7. Hydrocarbalkoxylation experiments

In a typical experiment 24 mg (0.0125 mmol) of $(PdCl_2)_2$(**5**) was placed under argon in a 150 ml stainless steel autoclave first, then 5.5 ml (0.05 mol) styrene, 10 ml toluene, 4 ml (0.1 mol) methanol and a drop of cc. hydrochloric acid were added. The reaction vessel was pressurised to 140 bar CO pressure and placed in an oil bath and the mixture stirred with a magnetic stirrer. The pressure was monitored throughout the reaction. After cooling and venting of the autoclave, the yellow solution was immediately analysed by GC.

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