Phosphabenzene–rhodium catalysts for the efficient hydroformylation of terminal and internal olefins

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COMMUNICATION

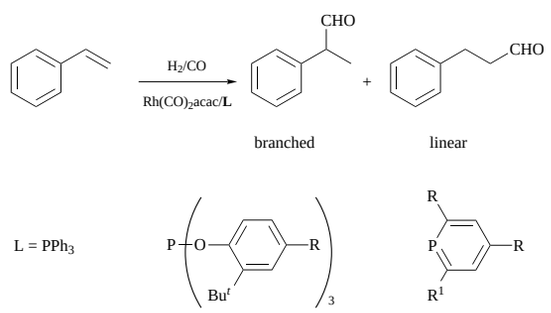
The use of rhodium-catalysts modified with bulky phosphabenzenes as π-acceptor ligands as highly efficient hydroformylation catalysts for terminal and internal olefins is reported, and a catalytically active phosphabenzene complex has been structurally characterized by X-ray crystallography.

Since its discovery in 1938 hydroformylation of olefins has evolved into one of the industrially most important homogeneously catalyzed processes.[1] In 1996 worldwide about 7 million tons of oxo products were produced, resulting in a tremendous economical interest to run this reaction with a maximum of activity and selectivity.[2] A problem still not satisfactorily solved is that of hydroformylation of internal olefins, which is of considerable interest in both industrial and synthetic organic contexts. The main difficulty stems from a low catalyst activity of the standard triphenylphosphine (**1**)–rhodium catalysts for the hydroformylation of internal olefins. Substitution of phosphines **1** by bulky phosphites **2** as modifying ligands for rhodium catalysts was an important advance in this field.[3] While the catalytic activity of such systems is extremely high, phosphites in general suffer from an inherent lability towards hydrolysis and a tendency to undergo degradation reactions. This makes the development of new catalysts for the efficient hydroformylation of internal olefins an important task.

We recently introduced new classes of strong π-acceptor-ligands for homogeneous catalysis that could have beneficial effects in hydroformylation chemistry.[4] We report here on the basis of those exploratory results on the development of rhodium catalysts modified with new bulky monophosphabenzenes **3** for the efficient hydroformylation of terminal and internal olefins, as well as on the preparation and X-ray crystal structure analysis of a defined monophosphabenzene–rhodium complex which is endowed with high catalytic activity.

The hydroformylation of styrene was chosen as a first test reaction, to compare the catalytic activity of phosphabenzene **3**† catalysts with that of phosphine **1** and phosphite **2** containing systems (Scheme 1, Table 1). For this particular reaction a combination of high activity and regioselectivity favoring the branched aldehyde is desirable with regard to the preparation of the anti-inflammatory 2-arylpropionic acids.[5] Employing extremely mild hydroformylation conditions (room temp., 20 bar $CO–H_2$, 1:1) the phosphabenzene catalysts showed the highest activity providing the desired 2-phenylpropanal in a regioselectivity of 20:1.

To study the catalytic activity of the monophosphabenzene rhodium catalyst for hydroformylation of internal olefins we turned to cyclohexene as a model substrate. Here the rhodium catalyst modified with the *o*,*o*′-diphenyl substituted monophosphabenzene **3a** showed 74 times higher activity than the standard PPh_3–rhodium catalyst for hydroformylation of cyclohexene (Table 2). Thus, this catalyst is as reactive as the most active hydroformylation catalysts known to date, the bulky monophosphite **2** modified rhodium systems. Interestingly the rhodium–phosphabenzene catalysts could be reused at least two more times to catalyze this reaction without loss in catalytic activity indicating their stability.



1 **2a** R = Me; **2b** R = Bu^t **3a** R,R^1 = Ph **3b** R = Ph, R^1 = Me

Scheme 1 *Reagents and conditions:* 0.357 mol% [$Rh(CO)_2acac$/5 **L**], $CO–H_2$ (1:1), 20 bar, 25 °C, toluene

Table 1 Results of regioselective hydroformylation of styrene

Entry[a]	Ligand	*t*/min	Conv. (%)[b]	TOF/h^{-1}[c]	b:l[b]
1	PPh_3	180	8	7.5	24:1
2	**2b**	180	17.6	16.4	20:1
3	**3a**	180	30.8	28.7	20:1

[a] Reactions were carried out at 25 °C in toluene ($[styrene]_0$ = 0.65 mol l^{-1}) in a 100 ml stainless-steel autoclave under an atmosphere of H_2 and CO (1:1) 20 bar initial total pressure, Rh:L:styrene = 1:5:280. [b] Conversions and branched to linear (b:l) ratios were determined by GC on a 0.25 mm × 30 m Supelcowax column with internal standard. For catalysts with ligands **2b** and **3b** quantitative conversion could be reached after 22 h; l:b ratio after complete conversion stays at 20:1. In all cases aldehyde selectivity was 100%. [c] Turn-over frequency (TOF) was calculated as (mol reacted substrate) × (mol catalyst)$^{-1}$ × (*t*/h)$^{-1}$.

In agreement with our initial concept[4] that catalyst activity in hydroformylation increases by coordination of a strong π-acceptor ligand to rhodium, it seemed reasonable to attribute this catalyst's activity to an η^1-coordination of the phosphabenzene nucleus to the rhodium(I) center. Since no structural data on that kind of coordination of a phosphabenzene to rhodium was available[6] we prepared a defined rhodium(I) phosphabenzene complex by reacting $Rh(1,5\text{-cod})_2BF_4$ (cod = cycloocta-1,5-diene) with 4 equiv. of the phosphabenzene **3b**. This afforded the phosphabenzene rhodium complex **4** as orange–red crystals in almost quantitative yield.‡ X-Ray

† The phosphabenzenes **3a**,**b** have been prepared from the corresponding pyrylium salts and $P(SiMe_3)_3$ according to Märkl *et al.*[8]

‡ Preparation and selected physical data of $Rh(\mathbf{36})_4BF_4$ (**4**): to a magnetically stirred solution of 23 mg (0.057 mmol) of $Rh(1,5\text{-cod})_2BF_4$ in 2 ml $CDCl_3$ were added at room temp. 60 mg (0.228 mmol) of phosphabenzene **3b**. The reaction mixture was heated to reflux for 15 min, cooled to room temp. and filtered over Celite with 20 ml of CH_2Cl_2. The solvent was removed *in vacuo* to give 67 mg (95%) of **4** as an orange solid. **4**: δ_P(161.978 MHz, C_6D_6) +170.4 (d, $^1J_{P,\,Rh}$ 154.4 Hz); *m*/*z* (FD) 1151 [$Rh(C_{18}H_{15}P)_4$], 262 ($C_{18}H_{15}P$).

Table 2 Results of hydroformylation of cyclohexene

Entry	Ligand	L/Rh	*t*/h	Conv. (%)[c]	TOF/h^{-1}[d]
1[a]	**1**	20	73	28.1	2.9
2[a]	**2b**	10	1	28.8	216
3[a]	**3a**	10	1	28.6	214
4[b]	**4**	4	1	18	127
5[b]	**3b**	4	1	12.2	92
6[b]	**3b**	10	1	7	53

[a] Reactions were carried out at 90 °C in toluene ([cyclohexene]$_0$ = 0.68 mol l^{-1}) in a 100 ml stainless-steel autoclave under an atmosphere of H_2 and CO (1:1) a 20 bar initial total pressure. Rh:cyclohexene = 1:750. [b] As described under ([a]) except [cyclohexene]$_0$ = 0.798 mol l^{-1} in toluene. [c] Conversions were determined by GC [see footnote ([b]) Table 1]. Quantitative conversion could be reached for all rhodium catalysts with ligands **2** and **3** at longer reaction times. In all cases aldehyde selectivity was 100%. [d] TOF is calculated as (mol reacted substrate) × (mol catalyst)$^{-1}$ × (*t*/h)$^{-1}$.

structure analysis revealed that four phosphabenzene nuclei are η^1-coordinated through the lone pair at phosphorus to the cationic rhodium(I) center in a square planar coordination geometry (see Fig. 1).§ The planes of the phosphabenzene nuclei are twisted between 48 and 51.1° from the plane defined by P(1)P(2)P(3)P(4). Interestingly the phosphabenzene nucleus of each ligand shows π-stacking with the *o*-phenyl substituent of one neighbouring phosphabenzene ligand and *vice versa*. This twofold attractive π-stacking interaction causes a narrowing of the P(1)–Rh–P(4) and P(2)–Rh–P(3) bond angles to 87° each between the interacting phosphabenzenes. Consequently, the remaining P–Rh–P angles between the non-interacting phosphabenzene nuclei are widened to 93°.

In a catalytically active rhodium hydroformylation catalyst no more than two P-donors may be coordinated to the rhodium center.[2] In the case of the bulky monophosphite ligands **2** only a single phosphite ligand is coordinated to rhodium within the catalytically active species.[7] Accordingly, a complex such as **4** has to lose at least two phosphabenzene ligands to generate the catalytically active species. To find out whether a coordination of four phosphabenzene ligands to rhodium(I) is reversible or rather a thermodynamic sink, we subjected complex **4** to hydroformylation conditions. Under the conditions indicated in Table 2 (entry 4) complex **4** showed a remarkable catalytic activity in the hydroformylation of cyclohexene. A catalyst prepared *in situ* from $Rh(CO)_2$acac (Hacac = acetylacetone) and the phosphabenzene **3b** performed with a comparable reactivity (entries 4 and 5). These results indicate two things: first, the coordination of at least two phosphabenzene nuclei to the rhodium(I) center of **4** is reversible although it remains unclear whether one or two phosphabenzene ligands stay coordinated within the catalytically active species. Second, η^1-coordinated phosphabenzene ligands to a rhodium(I) transition metal center can be regarded as the origin of the observed high catalyst activity.

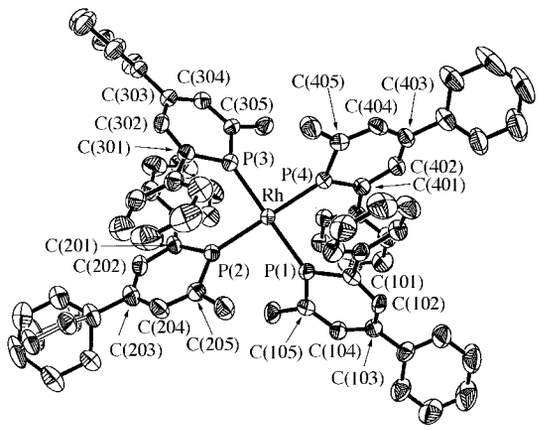


Fig. 1 Structure of the cation of **4** in the solid state; selected bond lengths (Å) and angles (°): Rh–P1 2.2918(11), Rh–P2 2.2661(11), Rh–P3 2.2628(11), Rh–P4 2.2721(11), P(3)–Rh–P(2) 86.85(4), P(2)–Rh–P(1) 93.55(4), P(3)–Rh–P(4) 92.99(4), P(4)–Rh–P(1) 86.60(4)

Acknowledgements

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§ Crystal data for **4**: crystals suitable for X-ray crystal structure analysis were obtained from a $CHCl_3$–C_6H_6 solution at room temperature. $[C_{72}H_{60}P_4Rh]^+[BF_4]^-\cdot CHCl_3\cdot 2C_6H_6$, M = 1514.38: monoclinic, space group $P2_1/c$, a = 18.666(3), b = 19.977(2), c = 21.253(3) Å, β = 107.96(1)°, U = 7539(2) Å^3, D_c = 1.334 g cm^{-3} for Z = 4, $F(000)$ = 3120, (Mo-Kα) = 0.472 mm^{-1}, λ = 0.710 73 Å, T = 213(2) K, crystal size 0.3 × 0.3 × 0.2 mm. A total of 13 684 reflections were collected (Enraf-Nonius CAD4) using scans in the range $4.6 < 2\theta < 50°$, 13 252 were unique (R_{int} = 0.0296). The structure was solved by direct methods. Full matrix least squares refinement was based on F^2, with all non-hydrogen atoms anisotropic and with hydrogens included in calculated positions with isotropic temperature factors 1.2 times that of the U_{eq} of the atom to which they were bonded.

The BF_4^- anion, one phenyl ring of the cation, and the solvent molecules ($CHCl_3$ and two molecules benzene in the asymmetric unit) were disordered. The 'calc squeeze' procedure[9] in the program PLATON[10] has been applied to the heavily disordered solvent molecules. The refinement converged at $R1$ = 0.0527 [for 8698 reflection with $I > 2\sigma(I)$] and $wR2$ = 0.1604 (all data) $\{w = [\sigma^2(F_o)^2 + (0.0940P)^2]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3\}$; final GOF = 1.034; largest peak and hole in the final difference fourier: 0.479/−0.450 e Å^{-3}.

Programs used were SHELXS-96,[11] SHELXL-96[12] and PLATON.[10] Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/138.