Tri(3-pyridyl)phosphine as Amphiphilic Ligand in the Rhodium-catalysed Hydroformylation of 1-Hexene

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Z. Naturforsch. **2007**, *62b,* 339 – 345; received November 23, 2006

Dedicated to Prof. Helgard G. Raubenheimer on the occasion of his 65th birthday

The molecular structure of carbonylchloro*bis*(tri(3-pyridyl)phosphine)rhodium, **1**, has been determined by X-ray diffraction methods. The N-protonated trifluoromethanesulfonate (triflate) complex **3** was synthesised as a model compound for the extraction of a rhodium complex bearing amphiphilic ligands which can allow catalyst recycling in the hydroformylation of alkenes by using their distribution behavior in organic and aqueous solvents of different pH. The high water-solubility of the employed ligand renders the recycling method as only partly successful due to insufficient extraction from the water phase into the organic phase. In the hydroformylation of 1-hexene the production of *n*-heptanal is slightly disfavoured when using the ligand tri(3-pyridyl)phosphine as compared to triphenylphosphine which can be ascribed to a higher amount of ligand-deficient active rhodium complexes of the less basic pyridyl phosphine ligand under CO pressure.

Key words: Pyridylphosphine, Amphiphilic Ligand, Rhodium, Hydroformylation, X-Ray Structure

Introduction

Pyridylphosphines [1] as amphiphilic ligands [2] and their metal complexes exhibit a certain solubility in water depending on the pH value. This property can be utilised in catalyst-product separation in homogeneous catalysis and in catalyst recycling [2 – 10]. Some rhodium complexes with mixed phosphines containing the phenyl group and 2-pyridyl, 3-pyridyl or 4-pyridyl group(s) have been structurally characterised [11] and used as amphiphilic catalysts [9, 11 – 13]. The similar steric, but different electronic effects of these ligands as compared to triphenylphosphine lead to similar *n*/*i* isomer ratios (*n*-aldehyde/*i*-aldehyde) but faster reaction rates in the hydroformylation of l-octene [12, 13]. Rhodium complexes of 2-pyridylphosphines show intramolecular coordination of the nitrogen atom of the pyridyl ring in solution [14]. While the structure of a rhodium complex of tri(2-pyridyl)phosphine has been determined [14], the analogous complex with tri(3-pyridyl)phosphine has only been characterised by the frequency of its carbonyl stretching vibration, the chemical shift in the ^{31}P NMR spectrum and by CHN analysis [15].

Results and Discussion

The complex *trans*-[Rh(P(3-py)$_3$)$_2$(CO)Cl], **1**, was synthesised in our laboratories from the reaction of [Rh(CO)$_2$Cl]$_2$ and 4.2 equivalents of P(3-py)$_3$ in dichloromethane at r. t.. Yellow crystals were obtained *via* slow diffusion of pentane into the reaction solution after removal of a part of the solvent *in vacuo*. The reaction with P(4-py)$_3$, however, gave a yellow powder very insoluble in dimethyl sulfoxide (DMSO) or acetone, and we suspect the formation of oligomers by binding of the well-accessible nitrogen atoms to other rhodium centres. The chemical shift of the coordinated ligand in the ^{31}P NMR spectrum as well as the frequency of the CO stretching vibration are shown in Table 1 next to those values of the previous report where **1** was obtained in absolute ethanol from [Rh(CO)$_2$Cl]$_2$ and P(3-py)$_3$ [15]. The new cationic complexes *trans*-[Rh(P(3-pyH)$_3$)$_2$(CO)Cl][CF$_3$SO$_3$]$_6$, **3**, and *trans*-[Rh(P(4-pyH)$_3$)$_2$(CO)Cl][CF$_3$SO$_3$]$_6$, **4**, (Table 1) can be obtained *via* reaction of [Rh(CO)$_2$Cl]$_2$ with the protonated tri(3-pyridyl)-phosphine ligand as the tris(trifluoromethanesulfonate) salt [P(3-pyH)$_3$]$_3$[CF$_3$SO$_3$]$_3$ or its 4-pyridyl analogue

Table 1. Selected analytical data for *trans*-[Rh(PR_3)$_2$(CO)Cl] (R = 3-py, Ph) and *trans*-[Rh(PR'_3)$_2$(CO)Cl][CF_3SO_3]$_6$ (R' = 3-pyH, 4-pyH).

Compound	ν(CO), cm^{-1}	$\delta^{31}P\{^1H\}$, ppm	$^1J_{Rh-P}$, Hz	$\Delta\delta^{31}P\{^1H\}$, ppm	^{13}C δ(CO), ppm	Reference
[Rh(P(3-py)$_3$)$_2$(CO)Cl] (**1**)	1989[2]	16.7[4]	130.2	40.3	186.0	this work
[Rh(P(3-py)$_3$)$_2$(CO)Cl] (**1**)	1978	21.9	128.9	–	–	[15]
[Rh(PPh_3)$_2$(CO)Cl] (**2**)	1978[2]	29.6[4]	127.0	34.6	187.1	this work
"[Rh(P(4-py)$_3$)$_2$(CO)Cl]"	1994[2]	26.1[5]	–	36.8	–	this work
[Rh(P(3-pyH)$_3$)$_2$(CO)Cl][CF_3SO_3]$_6$ (**3**)	2014[3]	18.8[5]	127.3	2.4	–	this work
[Rh(P(4-pyH)$_3$)$_2$(CO)Cl][CF_3SO_3]$_6$ (**4**)	2015[3]	30.5[5]	144.1[6]	31.2	–	this work

[1] $\delta^{31}P\{^1H\}$(complex)– $\delta^{31}P\{^1H\}$(ligand); [2] CH_2Cl_2; [3] CH_3CN; [4] $CDCl_3$; [5] [D_6]DMSO; [6] [D_6]acetone.

Table 2. Calculated energy values for gas-phase protonation of phosphines.

Structure	ΔE_0, kcal mol^{-1}	Structure	ΔE_0, kcal mol^{-1}
PPh_3	−244.7	P(2-py)$_3$	−242.3
P(3-py)$_3$	−229.9	P(4-py)$_3$	−224.0

[P(4-pyH)$_3$]$_3$[CF_3SO_3]$_3$ in acetonitrile as yellow precipitates. Table 1 also includes the relevant reference compound *trans*-[Rh(PPh_3)$_2$(CO)Cl], **2**. The coordinative saturation of the nitrogen atoms of the protonated 4-pyridyl phosphine ligand was expected to prevent the previously noticed presumed oligomerisation when using the non-protonated ligand. Complex **3** can also be obtained *via* direct protonation of **1** with triflic acid in dichloromethane.

While *trans*-[Rh(P(2-py)$_3$)$_2$(CO)Cl], **5**, shows additional intramolecular coordination by the nitrogen atom of one pyridyl ring in solution [14], such behavior was not observed for complex **1**.

The increase in ν(CO) follows the sequence:

$$\mathbf{2} < \mathbf{1} < \text{"[Rh(P(4-py)}_3\text{)}_2\text{(CO)Cl]"} < \mathbf{3} < \mathbf{4},$$

and is in line with the decrease in the basicity or electron donor ability in the sequence:

$$PPh_3 > P(3\text{-py})_3 > P(4\text{-py})_3 > \\ > [P(3\text{-pyH})_3]^{3+} > [P(4\text{-pyH})_3]^{3+},$$

causing a more electropositive rhodium centre and the well-known effect of less electron donation to the π^* orbital of the CO moiety from the metal, resulting in a higher bond order of the CO fragment and consequently a higher ν(CO) stretching vibration [16].

The trend of ligand basicity was confirmed by molecular modeling calculations of the energy profile associated with the reaction:

$$\text{phosphine} + H^+ \longrightarrow \text{phosphine-}H^+$$

Protonation of the ligands decreases the basicity quite considerably (Table 2).

Table 3. Selected bond lengths (Å) and angles (deg) for **1** with estimated standard deviations in parentheses.

Rh(1)–C(1)	1.811(2)	Rh(1)–P(1)	2.3336(5)
Rh(1)–P(2)	2.3232(5)	Rh(1)–Cl(1)	2.3623(5)
C(1)–O(1)	1.138(2)		
O(1)–C(1)–Rh	176.1(2)	C(1)–Rh(1)–P(2)	92.44(7)
C(1)–Rh(1)–P(1)	89.93(7)	P(2)–Rh(1)–Cl(1)	85.712(19)
P(1)–Rh(1)–Cl(1)	92.455(18)	P(2)–Rh(1)–P(1)	172.898(17)
C(1)–Rh(1)–Cl(1)	175.03(8)		

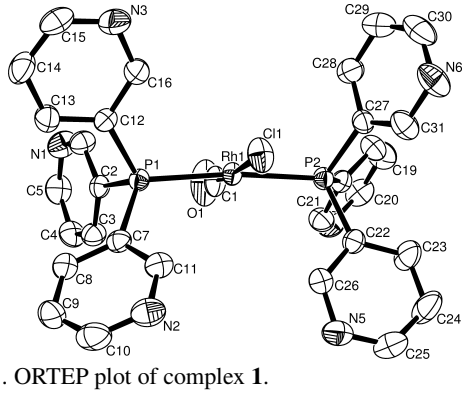

Fig. 1. ORTEP plot of complex **1**.

The crystal structure of **1** (Fig. 1) is similar to the structures of the PPh_3 [10 – 13], P(2-py)$_3$ [14], PPh_2(2-py) [14, 15] and PPh_2(3-py) [11] analogues with a near square planar coordination of the rhodium centre and the two phosphine ligands in *trans* position (see Table 3 for selected bond lengths and angles and Table 4 for crystal data and refinement details).

In the hydroformylation of 1-hexene with an *in situ* system consisting of acetylacetonatodicarbonylrhodium and either triphenylphosphine or tri(3-pyridyl)phosphine as ligand some differences are apparent concerning the ratio of formed *n*-aldehyde to *i*-aldehyde, turnover number and preformation *versus* non-preformation (Table 5). Under preformation conditions, a higher *n*/*i* ratio as well as higher turnover numbers are achieved using triphenylphosphine as ligand (compare runs 1, 2 and 3 with 4, 5 and 6). The re-

Table 4. Crystal data and refinement details for **1**.

Formula	$C_{31}H_{24}ClN_6OP_2Rh$
Formula weight	696.86
Temperature [K]	293(2)
Wavelength [Å]	0.71073
Crystal size [mm^3]	$0.40 \times 0.22 \times 0.20$
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions [Å], [deg]	a = 12.0017(13) b = 13.8843(15) c = 18.4256(19) β = 105.730(2)
Volume [Å^3]	2955.4(5)
Z	4
Density (calculated) [mg m^{-3}]	1.566
F(000) [e]	1408
Absorption coefficient [mm^{-1}]	0.813
Absorption correction	empirical
Max. and min. transmission	0.8542 / 0.7368
Theta range for data collection [°]	1.76 to 28.31
hkl ranges	$-15 \le h \le 10$, $-17 \le k \le 18$, $-23 \le l \le 24$
Reflections collected	20282
Completeness to θ = 28.31°	99.5 %
Independent reflections	7325 (R_{int} = 0.0233)
Data / parameters	7325 / 403
Goodness-of-fit on F^2	1.036
Final R indices [$I \ge 2\sigma(I)$]	$R1$ = 0.0255, $wR2$ = 0.0620
R indices (all data)*	$R1$ = 0.0372, $wR2$ = 0.0657
Largest diff. peak and hole [eÅ^{-3}]	0.316 / −0.313

* $w = 1/[\sigma^2(F_o^2) + (0.0342P)^2$ where $P = (F_o^2 + 2F_c^2)/3$

action is faster for triphenylphosphine as was observed by monitoring the pressure drop of the hydroformylation reaction. These differences are less obvious if catalyst preformation is not performed: the *n*/*i* ratio is slightly higher at lower L:Rh ratios (compare runs 7 and 8 with 10 and 11), but fairly equal at a L:Rh ratio of 10. Turnover numbers are in general slightly higher with triphenylphosphine as ligand. The trends are less consistent than in the case of catalyst preformation.

Considering equal steric bulk of the two different ligands, their electronic properties could be responsible for the different *n*/*i* ratios: For the more basic triphenylphosphine ligand the equilibrium of

$$[RhL_2(CO)H] + CO \rightleftarrows [RhL(CO)_2H] + L \quad (1)$$

would be shifted further to the left side than for the pyridylphosphine which in turn would result in a more preferred *n*-aldehyde formation due to the higher steric bulk near the rhodium centre. Simultaneously, a higher stabilising effect of the more basic ligand can be responsible for higher turnover numbers.

Table 5. Catalytic results of the hydroformylation of 1-hexene.

Run	Ligand	L:Rh	Time (min)	*n*/*i*	TON
1	PPh_3	10.0	30	3.4	300
2	PPh_3	10.0	30	5.6	300
3	PPh_3	10.0	30	4.4	310
4	$P(3\text{-py})_3$	10.0	30	3.3	190
5	$P(3\text{-py})_3$	10.0	30	3.1	260
6	$P(3\text{-py})_3$	10.0	30	3.5	250
7	PPh_3	2.0	180	2.6	420
8	PPh_3	3.0	120	2.5	420
9	PPh_3	10.0	120	2.9	400
10	$P(3\text{-py})_3$	2.0	120	1.9	460
11	$P(3\text{-py})_3$	3.5	120	2.3	340
12	$P(3\text{-py})_3$	10.0	120	3.2	380

Run 1 – 5 in 20 mL cyclohexane, run 6 – 12 in 20 mL toluene. Run 1 – 6: 1 h preformation at 80 °C, 20 bar CO/H_2. Run 7 – 12: no preformation. [$Rh(CO)_2$acac]: 9.4 mg, 1-hexene: 2.0 g, T = 80 °C, P = 20 bar CO/H_2.

To assess the extractability of the ligand either from an organic phase into a water phase at low pH or from water into an organic phase at higher pH, the distribution coefficient (D = c(in H_2O)/[c(in H_2O) + c(in organic phase)]) [13] was established in a cyclohexane-water mixture at different (final) pH values (Table 6 and Fig. 2). Less than 3 % of the $P(3\text{-py})_3$ ligand remains in the chosen organic phase in a single extraction with water of pH 2.5. However, a re-extraction of the ligand from water of pH $\sim$ 7 leaves about 45 % in the water phase. The ligand $P(3\text{-py})_3$ shows the expected trends when comparing it to the already investigated amphiphilic ligands $PPh(3\text{-py})_2$ and $PPh_2(3\text{-py})$ [13] by maintaining a higher water-solubility up to higher pH values. The distribution coefficient appears to be most favourable for $PPh_2(3\text{-py})$ of the ligand series $PPh_n(3\text{-py})_{3-n}$ (n = 0, 1, 2) with respect to the desired solubility switch from aqueous to organic solution depending on the pH value [13].

In two recycling experiments, extraction of the pyridylphosphine ligand and the rhodium complexes into a water phase and the re-extraction into toluene at different pH values of the water phase was attempted. In both cases the recycled catalyst showed activity and a constant selectivity within experimental error. According to ICP-AES analysis, 99.3 % ± 0.4 % of the employed rhodium in run 2 (Table 7) was extracted into the water phase, and 62.7 % ± 0.2 % recycled and used in run 2a. Although run 2a gave satisfactory results, the extraction procedure was not acceptable because of high rhodium losses due to an insufficient distribution coefficient in the different solvents, and due to visible decomposition producing a brown volumi-

pH	0.69	1.55	2.55	3.89	4.5	7.2
f	0.962	0.967	0.973	0.827	0.617	0.422
f′	0.959	0.965	0.970	0.815	0.625	0.494
f_{av}	0.960	0.966	0.972	0.821	0.621	0.458

Table 6. Distribution coefficient of P(3-py)$_3$ in water/cyclohexane at different pH values.

Table 7. Catalytic results of the recycle runs.

Run	Ligand	L:Rh	Time/min	*n*/*i*	Yield/%	TON	rel. Rh amount/%
1	P(3-py)$_3$	10.0	30	3.5	52	250	100
1a	P(3-py)$_3$	> 10.0	45	3.1	42	–	not determined
2	P(3-py)$_3$	10.0	30	3.1	51	260	100
2a	P(3-py)$_3$	> 10.0	30	2.9	53	680	63

All runs: Preformation and catalysis at 80 °C, 20 bar CO/H_2 in 20 mL toluene, hydroformylation of 2.0 g 1-hexene. Run 1 and 2: [$Rh(CO)_2$acac]: 9.4 mg. Run 1a: extracted at pH 1 into water (3 × 5 mL), re-extracted at pH 6 into toluene (3 × 6.7 mL). Run 2a: extracted at pH 1 into water (4 × 5 mL), re-extracted at pH 9 into toluene (4 × 5 mL).

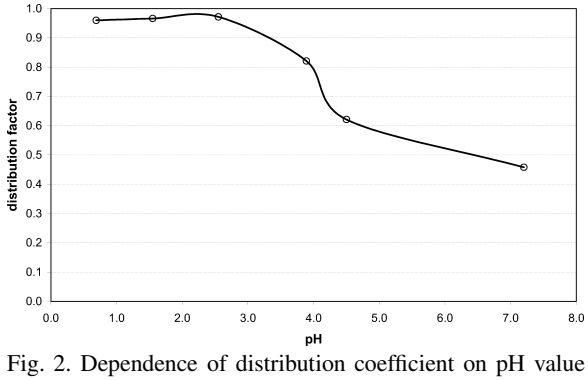

Fig. 2. Dependence of distribution coefficient on pH value for P(3-py)$_3$ in cyclohexane/water.

nous matter between the organic and water phase. The rhodium recovery of about 63 % is similar to that of van Leeuwen's group of 57 % using the ligand PPh(3-py)$_2$ who also reported an unsatisfactory retention of catalytic activity [13].

Conclusion

A protonated complex *trans*-[Rh(P(3-pyH)$_3$)$_2$(CO)Cl][CF_3SO_3]$_6$, **3**, can be formed either *via* the reaction of the triply protonated tri(3-pyridyl)phosphine ligand with [$Rh(CO)_2Cl]_2$ as the triflate salt or by direct protonation of *trans*-[Rh(P(3-py)$_3$)$_2$(CO)Cl], **1**, with triflic acid. Its formation together with the distribution behaviour of the amphiphilic ligand in mixtures of water and organic solvents at different pH values suggests the possibility of a recycling procedure of rhodium compounds. Such catalyst recycling was, however, found not feasible due to low catalyst recycle and visible catalyst decomposition. Thus, the ligand P(3-py)$_3$ does not show advantages over already investigated ligands in the series PPh$_n$(3-py)$_{3-n}$ (n = 0, 1, 2).

A comparison with PPh_3 of catalyst selectivity with respect to formation of *n*-aldehydes and *i*-aldehydes showed a slightly lower *n*/*i* ratio when using P(3-py)$_3$ under the chosen conditions. Since the cone angle and steric bulk of both ligands can be considered identical, the different basicity of the phosphines is considered responsible for this effect. It is presumed that both the lower electron density on the rhodium centre and a higher catalysis contribution of phosphine ligand-deficient active species as compared to PPh_3 contribute to this observation.

Experimental Section

Gas chromatography was performed on a Hewlett HP 3396A instrument fitted with a flame ionisation detector and with dimethylpolysiloxane as stationary phase, an oven temperature of 250 °C and a flow rate of 0.8 mm min^{-1} of helium. NMR spectroscopic analysis was carried out on a Bruker Advance DRX 400 instrument. Infrared spectra were recorded with a Bruker Vector 22 instrument. Rhodium concentrations were determined on an ICP-AES instrument Ciros by Spectro. For the determination of phosphine concentrations the UV-vis instrument Cary 100 by Varian was used. Solvents and 1-hexene were obtained from Aldrich and purified using standard laboratory procedures. Triflic acid, sodium carbonate, sodium acetate, magnesium sulphate, hydrochloric acid (PA), nitric acid (PA) and sulphuric acid (PA) were purchased from Aldrich and used without further treatment. *Bis*(dicarbonylchlororhodium) and acetylacetonatodi(carbonyl)-rhodium were obtained from Strem. Tri(3-pyridyl)phosphine [23], tri(4-pyridyl)phosphine [23] and carbonylchloro-*bis*(triphenylphosphine)rhodium [24] were synthesised according to published procedures. All manipulations were carried out under an inert atmosphere using Schlenk techniques.

*trans-[Rh(P(3-py)$_3$)$_2$(CO)Cl] (**1**)*

To 100 mg of $[Rh(CO)_2Cl]_2$ (0.257 mmol) in 4 mL of CH_2Cl_2 a solution of 280 mg P(3-py)$_3$ (1.055 mmol, 4.1 eq.) in 4 mL of CH_2Cl_2 was added at r. t. with stirring. After 2 h the volume of the solvent was reduced to about 2 mL *in vacuo*, the remaining solution layered with 3 mL of *n*-pentane, and the mixture stored at −20 °C. Yellow crystals (197 mg) were obtained after 2 d corresponding to a yield of 55 %. – IR (CH_2Cl_2): ν = 1989 cm^{-1} (CO). – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 8.83 (br, m, 1H), 8.73 (m, 6H), 8.08 (m, br, 6H), 7.41 (m, 6H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 186.0 (s, CO), 154.1 (s), 151.9 (s), 142.0 (s), 126.9 (m, C_{ipso}), 123.6 (s). – ^{31}P $\{^1H\}$ NMR (162.0 MHz, $CDCl_3$): δ = 16.7 (d, $^1J_{Rh-P}$ = 130.2 Hz). – $C_{31}H_{24}N_6ClOP_2Rh$ (696.9): calcd. C 53.43, H 3.47, N 12.06; found C 53.27, H 3.63, N 11.98.

*trans-[Rh(P(3-pyH)$_3$)$_2$(CO)Cl][CF$_3$SO$_3$]$_6$ (**3**)*

To 50 mg of $[Rh(CO)_2Cl]_2$ (0.129 mmol) in 3 mL of CH_2Cl_2 a solution of 377 mg $[P(3\text{-}pyH)_3][CF_3SO_3]_3$ (0.527 mmol, 4.1 eq.) in 3 mL of CH_3CN was added at r. t. with stirring. After 2 h, 342 mg of the precipitated complex was collected as a yellow powder in 83 % yield. – IR (CH_3CN): ν = 2014 cm^{-1} (CO). – ^{1}H NMR (400.1 MHz, [D$_6$]DMSO): δ = 13.4 (s, br, 6H, NH), 8.97 (m, br, 6H) and 8.86 (m, 6H), 8.29 (m, 6H), 7.75 (m, 6H), 2.06 (s, 1.5H, CH_3CN). – ^{31}P $\{^1H\}$ NMR (162.0 MHz, [D$_6$]DMSO): δ = 18.8 (d, $^1J_{Rh-P}$ = 127.3 Hz). – $C_{37}H_{30}N_6ClF_{18}O_{19}S_6P_2Rh$ (1597.3): calcd. C 27.82, H 1.89, N 5.26; found C 27.71, H 2.03, N 5.29.

[P(3-pyH)$_3$][CF$_3$SO$_3$]$_3$

To 150 mg of P(3-py)$_3$ (0.565 mmol) in 5 mL of CH_2Cl_2/CH_3CN 270 mg of CF_3SO_3H (1.8 mmol, 3.2 eq.) was added dropwise with stirring. The precipitate obtained after reducing the volume of the reaction mixture to almost dryness was washed with small amounts of cold CH_2Cl_2 and dried *in vacuo* resulting in 390 mg of a white powder corresponding to a yield of 96 %. – ^{1}H NMR (400.1 MHz, [D$_6$]DMSO): δ = 13.5 (s, br, 3H, NH), 9.13 (m, 3H), 9.06 (m, 3H), 8.59 (m, 3H), 7.98 (m, 3H). – ^{31}P$\{^1H\}$ NMR (162.0 MHz, [D$_6$]DMSO): δ = 16.4 (s). – $C_{18}H_{15}N_3F_9O_9S_3P$ (715.5): calcd. C 30.22, H 2.11, N 5.87; found C 29.49, H 2.37, N 5.80.

[P(4-pyH)$_3$][CF$_3$SO$_3$]$_3$

The procedure described above gave similar yields for the corresponding 4-pyridyl compound. – ^{1}H NMR (ppm, 400.1 MHz, [D$_6$]DMSO): δ = 12.6 (s, br, 3H, NH), 8.87 (m, 3H), 7.83 (m, 3H). – ^{31}P $\{^1H\}$ NMR (162.0 MHz, [D$_6$]DMSO): δ = −0.7 (s). – $C_{18}H_{15}N_3F_9O_9S_3P$ (715.5): calcd. C 30.22, H 2.11, N 5.87; found C 29.87, H 2.25, N 5.89.

*trans-[Rh(P(4-pyH)$_3$)$_2$(CO)Cl][CF$_3$SO$_3$]$_6$ (**4**)*

The procedure described above for **3** gave similar yields of **4**. – IR (CH_3CN): ν = 2015 cm^{-1} (CO). – ^{1}H NMR (400.1 MHz, [D$_6$]DMSO): δ = 14.47 (s, br, 6H, NH), 8.91 (d, $^3J_{HH}$ = 5.1 Hz, 12H), 7.94 (d, $^3J_{HH}$ = 5.1 Hz, 12H). – ^{31}P $\{^1H\}$ NMR (162.0 MHz, [D$_6$]acetone, 203K): δ = 34.7 (d, $^1J_{Rh-P}$ = 144.1 Hz). – $C_{37}H_{30}N_6ClF_{18}O_{19}S_6P_2Rh$ (1597.3): calcd. C 27.82, H 1.89, N 5.26; found C 27.35, H 2.05, N 5.11.

X-Ray structure determination

Intensity data were collected at ambient temperature on a Bruker SMART 1K CCD area detector diffractometer with graphite-monochromated MoK_α radiation. Data reduction was carried out using the program SAINT+ [25], and absorption corrections were made using the program SADABS [25].

The crystal structure of **1** was solved by Direct Methods using SHELXTL [26]. Non-hydrogen atoms were first refined isotropically, followed by anisotropic refinement by full-matrix least-squares calculations based on F^2 using SHELXL97 [27]. Hydrogen atoms were positioned geometrically and allowed to ride on their respective parent atoms for the final refinements, with isotropic thermal parameters, whilst allowing the C–H distance to refine. Diagrams and publication material were generated using WinGX [28] and PLATON [29].

CCDC 628116 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Catalysis

Catalytic hydroformylation runs were performed in a 50 mL stainless steel autoclave equipped with a dropping funnel in the case of preformation runs. About 13.4 mg $[Rh(CO)_2acac]$ (M = 258.0 g mol^{-1}, 51.9 μmol) and the desired amount of phosphine ligand were dissolved in 20 mL of toluene or cyclohexane and transferred to the autoclave after stirring for 5 min at r. t.. The catalyst was preformed at 80 °C and 20 bar CO/H_2 (1 : 1) followed by the addition of 2.0 g 1-hexene *via* the dropping funnel. If preformation was not carried out, 2.0 g 1-hexene was added to the catalyst solution before transfer of this solution to the autoclave and subsequent heating up to 80 °C under 20 bar CO/H_2 (1 : 1). In all cases the reactor was isolated from the gas supply and the pressure drop monitored over time. The reactor was cooled down in ice water after the desired reaction time and the solution was

submitted to a vacuum distillation to separate volatiles from the catalyst and excess ligand. This solution was transferred into a three-necked flask containing a suspension of a sufficient amount (about 0.5 g) of $LiAlH_4$ in 20 mL of ether to reduce the formed aldehydes to the alcohols overnight. After aqueous workup (pH $\sim$ 1) the alcohols as well as unreacted alkenes were extracted three times into ether. The combined organic phases were dried over $MgSO_4$ and analysed *via* gas chromatography using *n*-hexanol as a standard.

Recycling experiments were carried out with preformation (see above). After the catalysis the reaction mixture was transferred to a Schlenk tube under argon and extracted three times with 2×7 mL and 1×6 mL of distilled water of pH 1 (H_2SO_4). The remaining organic phase was dried and reduced with $LiAlH_4$ as described above. The aqueous phase (a part was kept for rhodium analysis) was neutralised using Na_2CO_3 and extracted with toluene (7 mL, 7 mL, 6 mL) at pH 6 for run 1 or at pH 9 after addition of NaAc for run 2. The determination of the rhodium amounts was carried out *via* ICP-AES after digesting all relevant rhodium residues with aqua regia.

The distribution coefficient of P(3-py)$_3$ in water-cyclohexane mixtures was determined at different final pH values (H_2SO_4 as acid, NaOH as base) according to the published formula [13]. Portions of 2 mL of the same amount of P(3-py)$_3$ in cyclohexane were shaken with 2 mL of water of a certain pH. After settling for about 15 min both phases were analysed *via* UV-vis at 259 nm (organic phase) or 261 nm (aqueous phase) to determine the phosphine concentration.

Computational details

All geometry optimisations were performed with the DMol^3 Density Functional Theory (DFT) code [30 – 32] as implemented in the MaterialsStudio^{TM} (Version 3.2) program suite released by Accelrys Inc. The revised PBE non-local generalised gradient approximation (GGA) exchange-correlation functional of Hammer, Hanson and Nørskov [33] (termed RPBE), was used throughout this study. DMol^3 utilises a basis set of numeric atomic functions, which are exact solutions to the Kohn-Sham equations for the atoms; in the present study an all electron polarised split valence basis set, termed double numeric polarised (DNP) has been used [34]. All geometry optimisations employed highly efficient delocalised internal coordinates [35]. The tolerance for convergence of the SCF density was set to 10^{-5} Ha while the tolerance for energy convergence was set to 2×10^{-6} Ha. Additional convergence criteria include the tolerance for converged gradient (4×10^{-4} Ha Å^{-1}) and the tolerance for converged atom displacement (5×10^{-4} Å).

Acknowledgement

The authors thank Jan-Albert van den Berg from Sasol Technology, R&D, Analytical Solutions for the molecular modeling calculations.

[1] G. R. Newkome, *Chem. Rev*. **1993**, *93*, 2067.
[2] P. C. J. Kamer, J. N. H. Reek, P. W. N. M. van Leeuwen in *Aqueous-Phase Organometallic Catalysis*, 2nd ed. (Eds.: B. Cornils, W. A. Herrmann), Wiley-VCH, Weinheim, **2004**, pp. 686.
[3] M. S. Goedheijt, P. C. J. Kamer, J. N. H. Reek, P. W. N. M. van Leeuwen in *Aqueous-Phase Organometallic Catalysis*, 2nd ed. (Eds.: B. Cornils, W. A. Herrmann), Wiley-VCH, Weinheim, **2004**, pp. 121.
[4] Q. Peng, Y. Yang, C. Wang, X. Liao, Y. Yuan, *Catalysis Lett*. **2003**, *88*, 219.
[5] A. Solsona, J. Suades, R. Mathieu, *J. Organomet. Chem*. **2003**, *669*, 172.
[6] S. Bischoff, M. Kant, *Catalysis Today* **2001**, *66*, 183.
[7] M. S. Goedheijt, B. E. Hanson, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, *J. Am. Chem. Soc*. **2000**, *122*, 1650.
[8] M. Karlsson, M. Johansson, C. Andersson, *J. Chem. Soc., Dalton Trans*. **1999**, 4187.
[9] K. Kurtev, D. Ribola, R. A. Jones, D. J. Cole-Hamilton, G. Wilkinson, *J. Chem. Soc., Dalton Trans*. **1980**, 55.
[10] A. Buhling, J. W. Elgersma, S. Nkrumah, P. C. J. Kamer, P. W. N. M. van Leeuwen, *J. Chem. Soc., Dalton. Trans*. **1996**, 2143.
[11] R. H. Laitinen, J. Soininen, P. Suomalainen, T. A. Pakkanen, M. Ahlgrén, J. Pursiainen, *Acta Chem. Scand*. **1999**, *53*, 335.
[12] A. Buhling, P. C. J. Kamer, P. W. N. M. van Leeuwen, *J. Mol. Catal. A* **1995**, *98*, 69.
[13] A. Buhling, P. C. J. Kamer, P. W. N. M. van Leeuwen, J. W. Elgersma, *J. Mol. Catal. A* **1997**, *116*, 297.
[14] K. Wajda, F. Pruchnik, T. Lis, *Inorg. Chim. Acta* **1980**, *40*, 207.
[15] K. Wajda-Hermanowicz, F. P. Pruchnik, *Transition Met. Chem*. **1988**, *13*, 101.
[16] J. D. Atwood, *Inorganic and Organometallic Reaction Mechanisms*, 2nd ed., Wiley-VCH, New York, **1997**, pp. 95.
[17] A. L. Rheingold, S. J. Geib, *Acta Cryst*. **1987**, *C43*, 784.
[18] P. A. Chaloner, C. Claver, P. B. Hitchcock, A. M. Masdeu, A. Ruiz, *Acta Cryst*. **1991**, *C47*, 1307.
[19] Y.-J. Chen, Y.-C. Wang, Y. Wang, *Acta Cryst*. **1991**, *C47*, 2441.

[20] K. R. Dunbar, S. C. Haefner, *Inorg. Chem.* **1992**, *31*, 3676.
[21] J. P. Farr, M. M. Olmstead, A. L. Balch, *J. Am. Chem. Soc.* **1980**, *102*, 6654.
[22] J. P. Farr, M. M. Olmstead, C. H. Hunt, A. L. Balch, *Inorg. Chem.* **1981**, *20*, 1182.
[23] R. J. Bowen, A. C. Garner, S. J. Berners-Price, I. D. Jenkins, R. E. Sue, *J. Organomet. Chem.* **1998**, *554*, 181.
[24] The same procedure as for the synthesis of compound **1** was applied.
[25] SAINT+ (version 6.02). Bruker AXS Inc., Madison, Wisconsin (USA) **1999**.
[26] G. M. Sheldrick, SHELXTL (version 5.1), Bruker AXS Inc., Madison, Wisconsin (USA) **1999**.
[27] G. M. Sheldrick, SHELXL97, Program for Crystal Structure Refinement, University of Göttingen, Göttingen (Germany) **1997**.
[28] L. J. Farrugia, *J. Appl. Cryst.*, **1999**, *32*, 837.
[29] A. L. Spek, P. LATON, A. Multipurpose Crystallographic Tool, Utrecht University, Utrecht (The Netherlands) **2002**. See also: A. L. Spek, *Acta Crystallogr.* **1990**, *A46*, C34.
[30] B. Delley, *J. Chem. Phys.* **1990**, *92*, 508.
[31] B. Delley, *J. Phys. Chem.* **1996**, *100*, 6107.
[32] B. Delley, *J. Chem. Phys.* **2000**, *113*, 7756.
[33] B. Hammer, L. B. Hansen, J. K. Nørskov, *Phys. Rev. B* **1999**, *59*, 7413.
[34] B. Delley, *Theoretical and Computational Chemistry* in *Modern Density Functional Theory: A. Tool for Chemistry*, Vol. 2 (Eds.: J. M. Seminario, P. Politzer), Elsevier, Amsterdam, **1995**.
[35] J. Andzelm, R. D. King-Smith, G. Fitzgerald, *Chem. Phys. Lett.* **2001**, *335*, 321.