DALTON

Novel amphiphilic diphosphines: synthesis, rhodium complexes, use in hydroformylation and rhodium recycling †

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For the rhodium-catalysed hydroformylation of higher alkenes the novel amphiphilic diphosphines 2,2′-bis[phenyl(3-pyridyl)phosphinomethyl]-1,1′-biphenyl (L^1), 2,2′-bis(diphenylphosphinomethyl)-3,3′-bipyridine (L^2), 2,2′-bis[phenyl(3-pyridyl)phosphinomethyl]-3,3′-bipyridine (L^3) and 2,2′-bis{[4-(diethylaminomethyl)-phenyl]phenylphosphinomethyl}-1,1′-biphenyl (L^4) have been synthesised. With oct-1-ene (80 °C, 20 bar $CO–H_2$, toluene), high normal : branded ratios (up to 51 : 1) were found with 6–8% of isomerised octenes. The diphosphines L^1–L^3 gave rhodium catalysts up to twice as active as those derived from 2,2′-bis(diphenyl-phosphinomethyl)-1,1′-biphenyl (bisbi). The rate of hydroformylation using L^1–L^4 was first order and approximately first order respectively in the rhodium and oct-1-ene concentration; the order in CO pressure was negative and that in H_2 pressure slightly negative. For L^1 the influence of the L : Rh ratio, temperature and substrate were investigated. Phosphorus-31 and ^1H NMR studies showed that the diphosphines (L–L) form $[RhH(CO)(PPh_3)(L–L)]$ and $[RhH(CO)_2(L–L)]$ complexes, analogously to bisbi. The formation of P–N chelates was not observed. The pH-dependent distribution characteristics of the free diphosphines have been determined; L^3 and L^4 were quantitatively extracted from an Et_2O solution into a H_2SO_4 solution of pH 2. When L^4 was used, rhodium and the excess of L^4 were extracted into an acidic aqueous phase at pH 5, allowing separation of the aldehydes, and re-extracted into fresh toluene after neutralisation of the aqueous phase by $NaHCO_3$. Inductively coupled plasma atomic emission spectroscopy established a rhodium recovery up to 92%. Pressurising the recovered rhodium and excess of phosphine to 20 bar $CO–H_2$ at 80 °C resulted in regeneration of the original catalytically active species. A retention of catalytic activity of 72% was achieved. Diphosphines L^1–L^3 proved inappropriate for rhodium-recycling experiments. Extraction into an acidic aqueous phase was effective, but neutralisation of the acidic phase resulted in the formation of rhodium species which cannot be extracted from the aqueous layer.

Homogeneous catalysts are extensively used in several chemical processes, mainly because of their high activity and selectivity.[1–5] However, separation of the catalyst from the reactants can be troublesome. This separation is an economical and environmental necessity and various pathways have been reported to achieve it,[6–14] biphasic catalysis using water now being the prevailing theme.[15–18] The number of water-soluble ligands reported has steadily increased over the last years.[19–32]

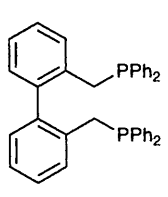
So far, the only two commercial successes of transition-metal catalysis in aqueous media were achieved in the hydroformylation process. Palladium complexes of monosulfonated PPh_3 are used by the Kuraray company in the synthesis of nonane-1,9-diol.[33] The Ruhrchemie/Rhône Poulenc process[34] was introduced in 1984 and uses rhodium complexes of trisulfonated PPh_3. Propene is converted with high selectivity into *n*-butanal which no longer has to be separated by expensive and energy-consuming distillation from the catalyst. As a consequence, thermal decomposition of the expensive rhodium catalyst is minimal. This process is limited to low-molecular-weight alkenes which are moderately soluble in water, although the use of surface-active agents has been proposed to overcome this limitation.[35] There is also a demand for a rhodium-based hydroformylation process for higher alkenes. Conventional processes still use the less active and selective cobalt carbonyl catalysts.[4,5] Owing to the low catalyst price, metal loss due to decomposition is commercially acceptable.

Horváth and Rábai[8] introduced a novel concept for the separation of catalyst and product: a biphasic system consisting of a fluorocarbon-rich phase, containing rhodium complexed to the fluorinated ligand $P[CH_2CH_2(CF_2)_5CF_3]_3$, and a common organic solvent. This system seems promising for the hydroformylation of higher alkenes since their solubility in it is high, in contrast to that of the product aldehydes.

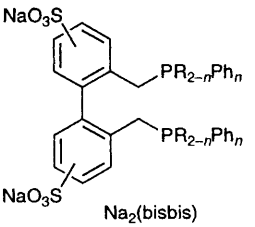
In our ongoing work on the rhodium-catalysed hydroformylation of higher alkenes[36,37] we have adopted an approach that differs from biphasic catalysis. The rhodium catalysts which are used are modified with amphiphilic phosphines. Thus, the hydroformylation can be conducted in a homogeneous (organic) phase. Unlike the biphasic system, this system allows high alkene concentrations which result in high reaction rates, since the hydroformylation reaction is first order in alkene concentration. After (partial) conversion of the alkene the catalyst is extracted into an acidic aqueous phase, thus allowing separation of the organic products, and re-extracted into a fresh organic phase after neutralisation of the aqueous phase. There are few other reports concerning a recycling system of this kind.[38–42] We investigated this system using modified triphenylphosphines, and demonstrated that rhodium was almost completely recycled.[36,43] The recovered rhodium and excess of ligand exhibited a high retention of activity.

The linear-to-branched aldehyde selectivity that can be achieved in the rhodium-catalysed hydroformylation using

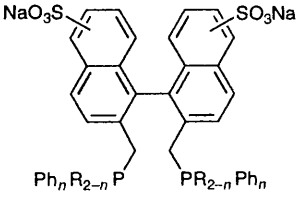
† *Non-SI unit employed:* bar = 10^5 Pa, cal = 4.184 J.



bisbi



Na_2(bisbis)



Na_2(binas)

R = *m*-$C_6H_4SO_3Na$

PPh_3 is modest. Chelating diphosphines[44–46] have been reported which show significantly improved regioselectivity in the hydroformylation, for example 2,2′-bis(diphenylphosphinomethyl)-1,1′-biphenyl (bisbi).[47–50] This diphosphine preferentially occupies two equatorial sites in the rhodium hydride intermediate during hydroformylation owing to its relatively large natural bite angle. This geometry leads to a higher proportion of *n*-aldehyde formation than geometries with apical–equatorial chelates.[49]

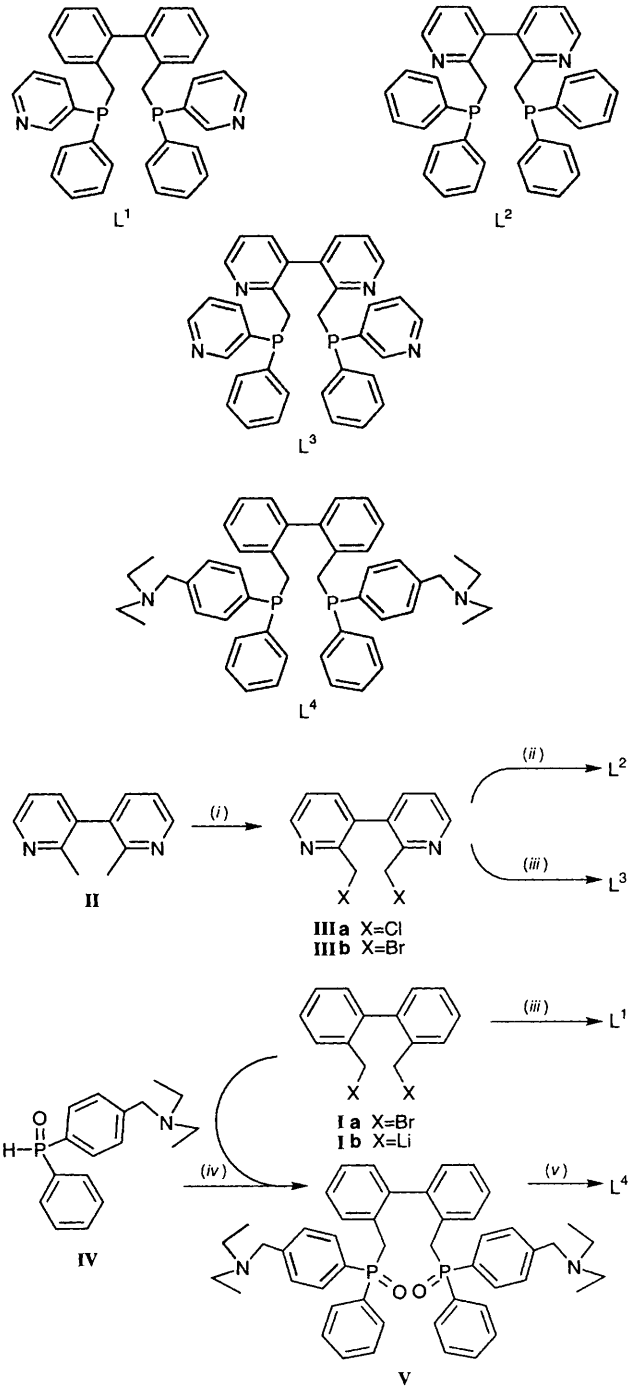
Herrmann *et al.*[51–53] prepared water-soluble, sulfonated bisbi, Na_2(bisbi), and used it in the biphasic rhodium-catalysed hydroformylation of propene. With a twelve times smaller P:Rh ratio, the activity obtained was three times higher than with trisulfonated PPh_3.[34] The normal:branched (n:b) ratio increased from 94:6 to nearly 97:3. Hydroformylation of hex-1-ene, however, gave low reaction rates. The reaction rate increased on raising the temperature to 155 °C which, however, resulted in a decrease of the n:b ratio to 94:6. Recently, the same group reported the new sulfonated compound Na_2(binas).[19] In the hydroformylation of propene the catalyst derived from this compound is almost twice as active as that formed from Na_2(bisbis), with an even higher n:b ratio of 98:2.

For the rhodium-catalysed hydroformylation of higher alkenes we synthesised novel amphiphilic diphosphines, based on bisbi, which can be used in the rhodium recycling system. Here, we report on the co-ordination chemistry of the novel compounds and their performance in the hydroformylation of hex-1-ene, oct-1-ene and dodec-1-ene. The distribution characteristics of the free compounds have been determined as a function of the pH. Also, the efficiency of the rhodium recycling system using this series of diphosphines has been established in terms of rhodium recovery, as measured by inductively coupled plasma atomic emission spectrometry (ICP-AES), and retention of activity.

Results and Discussion

Synthesis

Compound L^1 was synthesised by the reaction of Li[PPh(C_5H_4N-3)] with dibromide **Ia** (see Scheme 1). The lithium phosphide was prepared by lithiation of PH(Ph)(C_5H_4N-3)[54] with *n*-butyllithium. This route gave a cleaner reaction than the reaction of **Ia** with Na[PPh(C_5H_4N-3)], generated *in situ* by the sodium reduction of PCl(Ph)(C_5H_4N-3).[55] Also, the alternative route *via* reaction of the latter with the dilithio compound **Ib**, obtained by direct dilithiation[48] of 2,2′-dimethyl-1,1′-biphenyl, resulted in the formation of side products and accordingly low yields.



Scheme 1 Syntheses of compounds L^1–L^4. (*i*) *N*-Chlorosuccinimide (NCS); (*ii*) Li[PPh_2]; (*iii*) Li[PPh(C_5H_4N-3)]; (*iv*) NaH; (*v*) $SiHCl_3$

Compounds L^2 and L^3 were obtained by the reaction of respectively Li[PPh_2] and Li[PPh(C_5H_4N-3)] with the dichloride **IIIa**. Synthesis of the analogous dibromide **IIIb** from the reaction of *N*-bromosuccinimide with the bipyridine **II** failed. Many complex brominated products were formed of which only less than 5% are mono-, di- and tri-brominated bipyridines. Newkome *et al.*[56,57] observed the same for the dibromination of 6,6′-dimethyl-2,2′-bipyridine, and successfully used *N*-chlorosuccinimide. When applied to **II**, NCS slowly generated the desired *sym*-dichloride **IIIa**. Unchanged starting material, mono-, tri- and tetra-chloride were also isolated. In an attempt to prepare compounds with a 4,4′-bipyridine backbone, 3,3′-dimethyl-4,4′-bipyridine was treated with NCS. Apart from dark brown polymer-like substances, only traces of chlorinated products were obtained.

Compound L^4 was synthesised *via* a different route, starting from the phosphine oxide **IV**.[43] Deprotonated **IV** was added to dibromide **Ia**, giving the dioxide **V**. After laborious purification, this dioxide was converted by reduction with $SiHCl_3$ into the pure, diastereomeric mixture of L^4.

Stereochemistry of L^1–L^4

Compounds L^1, L^3 and L^4 possess chiral phosphorus atoms and, hence, are obtained as diastereomeric mixtures. It was not expected that individual isomers would show different behaviour in the hydroformylation reaction and recycling experiments. Isolation of the pure diastereomers is possible[58] but was not pursued. Consequently, the ^{31}P NMR spectra for these compounds were complex while L^2 only showed one resonance of the pure compound in the spectrum. The spectra of L^1 and L^3 revealed similar patterns, consisting of two doublets both flanked by a singlet (in a ratio of 1 : 1 : 1 : 1). This means that rotation about the single bonds connecting the two backbone aryl groups must be slow on the NMR time-scale at room temperature, thus giving rise to atropisomerism. The two doublets can be assigned to one diastereoisomeric pair, *SSR* and *RRS*, which is identical to the pair *RSS* and *SRR* due to a C_2 axis within the molecule. The non-equivalent phosphorus nuclei in these isomers exhibit through-space coupling.[59] The fact that these diastereomers are observed indeed implies that rotation about the biphenyl bond, which constitutes the chiral axis, must be slow on the NMR time-scale, since rapid rotation would render the phosphorus atoms enantiotopic. This also applies to the rotation in the two other diastereoisomeric pairs, *RRR*/*SSS* and *RSR*/*SRS*. Two singlets were observed while fast rotation would result in a single ^{31}P resonance. The phosphorus atoms within both diastereoisomers are equivalent, homotopic due to the above-mentioned C_2 axis, and do not exhibit coupling to one another. The rotational barrier in the biphenyl moiety on the NMR time-scale was still observed at higher temperatures. The ^{31}P NMR spectrum of L^1, measured at 90 °C in $[^2H_8]$toluene, revealed no interconversion between the diastereoisomers.

The ^{31}P NMR spectrum of compound L^4 exhibited four peaks within a very narrow range of chemical shifts. In contrast with the 3-pyridyl and phenyl ring in L^1 and L^3, the two aryl groups on the phosphorus atoms in L^4 are stereoelectronically very similar.

The through-space coupling constants ($^7J_{PP}$) observed for the non-equivalent phosphorus atoms in the diastereomeric pair *RRS*/*SSR* in compounds L^1, L^3 and L^4 are 1–2 Hz. These are relatively small when compared to the values of 10–30 Hz reported by Pastor *et al.*[59,60] for the structurally related oxazaphospholidines. The large substituents at phosphorus in these compounds induce a stronger interaction of the phosphorus lone pairs. The larger steric hindrance between the substituents at phosphorus in Pastor's compounds is also reflected in the formation of the four diastereomeric pairs in a non-statistical ratio.

Rhodium complexes

In order to investigate the co-ordination behaviour of the novel compounds, solution structures of rhodium complexes were studied with NMR and IR spectroscopy. The desired co-ordination mode is bis(equatorial) P–P chelation since this is the geometry that was shown to induce high linearity in the hydroformylation reaction. These functionalised compounds, however, can potentially form P–N chelating complexes. To avoid P–N chelation, *m*-pyridyl rings and *para*-substituted amino groups were used. However, apart from intramolecular P–N chelation of rhodium,[61] also bimetallic rhodium complexes with pyridylphosphines are known.[55,62]

To establish the co-ordination behaviour of the diphosphines (L–L), $[RhH(CO)(PPh_3)(L–L)]$ complexes were synthesised *in situ* by exchange of PPh_3 in $[RhH(CO)(PPh_3)_3]$ and compared to $[RhH(CO)(PPh_3)(bisbi)]$ as a reference complex.[49] The NMR spectra of the complex obtained from the exchange of L^2 with $[RhH(CO)(PPh_3)_3]$ are consistent with the formation of $[RhH(CO)(PPh_3)L^2]$. The ^{31}P-$\{^1H\}$ spectrum at −35 °C consists of an ABMX pattern due to complexed PPh_3 and the two phosphorus atoms of L^2 (Fig. 1 and Table 1). The phosphorus atoms in L^2, which are equivalent in free L^2 due to C_2 symmetry, are inequivalent in the rhodium complex. The hydride signal at −35 °C is a double triplet. The rhodium–hydride coupling constant was estimated to be less than 2 Hz from the linewidth of the hydride resonance. The infrared spectrum of the complex shows combination bands of ν_{RhH} and ν_{CO} at 2006s and 1929m cm^{-1}. All these data are in exact agreement with those for the analogous bisbi complex, in which an apical hydride is *cis* co-ordinated to both the diphosphine and PPh_3 in the equatorial plane.

Attempts to displace the remaining PPh_3 by bubbling of CO through the solution of the complex led to the formation of only a very small amount of $[RhH(CO)_2L^2]$. A considerable amount of red precipitate was observed, which indicates that the latter complex, assumed to be the catalytically active species, is not stable under 1 bar CO pressure. Reaction of $[Rh(acac)(CO)_2]$ (acac = acetylacetonate) and 1 equivalent of L^2 at 80 °C under 20 bar of $CO–H_2$ (syngas) in a high-pressure NMR tube did result in the formation of this complex. The ^{31}P-$\{^1H\}$ NMR spectrum at −35 °C under 20 bar syngas exhibited a doublet at δ 36.8 (J_{RhP} = 145.8 Hz). The equivalence of the phosphorus atoms in L^2 can be accounted for by Berry pseudo-rotations[49] or other rotational processes.[63,64] The rhodium hydride signal at δ −10.39 is a broad singlet.

The exchange reaction of compounds L^1, L^3 and L^4 with $[RhH(CO)(PPh_3)_3]$ resulted in more complicated NMR spectra, due to the existence of many diastereomers. In the case of L^1 the ^{31}P-$\{^1H\}$ NMR spectrum at −35 °C in $[^2H_8]$toluene revealed a cluster of about 80 peaks in the region δ 31–43. Compound L^1 can form four diastereomeric rhodium complexes, each of which can theoretically give 18 (3 × dt) to 24 (3 × ddd) peaks in a first-order spectrum. In C_6D_6 or CD_2Cl_2 approximately the same number of peaks is found in the same region but separated in the regions δ 42.5–39 assigned to PPh_3 and δ 38–31 assigned to L^1. At room temperature the spectrum consists of a huge multiplet. The hydride in the ^1H NMR spectrum appeared as a distorted quintet at δ −10.32. Infrared bands were observed at 2017s and 1933m cm^{-1}. The complex $[RhH(CO)_2L^1]$ was prepared from $[Rh(acac)(CO)_2]$ as described above for L^2. The ^{31}P-$\{^1H\}$ NMR spectrum at

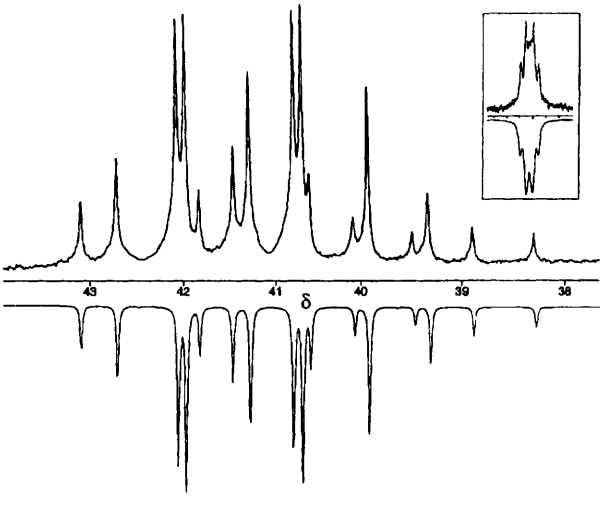


Fig. 1 Experimental (upper) and simulated (lower) ^{31}P-$\{^1H\}$ NMR spectra of $[RhH(CO)(PPh_3)L^2]$. The insert shows the corresponding ^1H NMR spectra in the hydride region

Table 1 Simulation data for the ^{31}P and ^{1}H* NMR spectra of [RhH(CO)(PPh$_3$)L^2]

				J(P–P)/Hz	
	P	δ	J(Rh–P)/Hz	1	2
^{31}P	1	41.77	142		
	2	41.65	160	110	
	3	39.99	155	111	115

* δ −10.46, J(H–PPh$_3$) 17.0, J(H–PP) 6.0 Hz.

−35 °C revealed several diastereomeric complexes, in which the phosphorus atoms in L^1 are equivalent, having J_{RhP} values of 147–149 Hz. The rhodium hydride signal at δ −10.45 appeared as a multiplet.

The ^{31}P-{^1H} NMR spectra obtained upon exchange with [RhH(CO)(PPh$_3$)$_3$] showed approximately 50 peaks for compounds L^3 (δ 36–45) and L^4 (PPh$_3$, δ 43–39.5; L^4, δ 38–33). The ^1H NMR spectra showed hydrides at respectively δ −10.19 and −10.51, both multiplets. Infrared bands were observed at 2009s and 1930m cm^{-1} for L^3 and at 2014s and 1930m cm^{-1} for L^4.

These complexation experiments conclusively showed that the novel diphosphines quantitatively form P–P-chelated complexes in the presence of 1 equivalent of rhodium precursor. The formation of P–N chelates was not observed under these conditions.

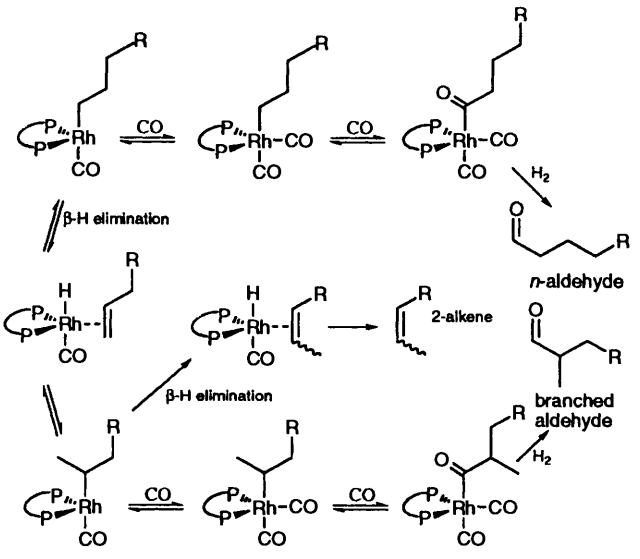
Catalysis

The new diphosphines have been tested in the rhodium-catalysed hydroformylation of hex-1-ene, oct-1-ene and dodec-1-ene, which served as representatives of higher alkenes. The catalytically active species [RhH(CO)$_2$L] was formed *in situ* from [Rh(acac)(CO)$_2$] and a ten-fold excess of the diphosphine. Under the chosen standard conditions it was established that this species was formed within 1 h since this gave the highest initial activity. Unmodified bisbi was used under the same conditions for comparison. From Table 2 it can be seen that the novel phosphines form active and highly selective catalysts.

The reaction rates for the catalysts derived from pyridyl-modified compounds L^1–L^3 are higher than those of bisbi and L^4, consistent with our earlier observations made for pyridyl-modified triphenylphosphines.[36] This effect was ascribed to the electron-withdrawing capacity of the pyridyl ring, causing the CO molecules to be less strongly bonded to the rhodium centre and thus facilitating alkene co-ordination. It is remarkable that L^2 induces an even higher activity than L^1, since the electronic influence of the bipyridine backbone *via* the methylene bridge upon the phosphorus atoms is considerably less than that of a pyridyl ring (for steric factors, see below). The high rate observed for L^3 is a result of the presence of both rate-enhancing functionalities.

The selectivities of all diphosphine-modified catalysts towards the formation of linear aldehyde are around 90%. There are, however, small differences in the distribution between the branched nonanal and internal octenes. Compound L^1 gives rise to a higher n:b ratio than does bisbi, but a concomitantly higher proportion of isomerised octenes is obtained. Owing to the more electrophilic rhodium, the unsaturated rhodium alkyl species reacts less readily with CO which results in an increased tendency towards β-H elimination (Scheme 2). Since the branched alkyl species is relatively more prone to undergo β-H elimination than the linear alkyl species the relative amount of branched aldehyde formed decreases and the n:b ratio increases.

In contrast, compound L^2 gives rise to a significantly higher



Scheme 2 Hydroformylation and isomerisation routes

percentage of branched aldehyde, while the amount of isomerisation is similar to that with bisbi and L^1. Apparently, the bipyridine backbone induces a geometry in which the rhodium centre is less sterically crowded, resulting in both a rate enhancement and a decreased preference for the linear alkyl species. Molecular mechanics calculations[65] established that the natural bite angle of L^2 (β_n = 119.3°) is comparable with that of bisbi[46] (β_n = 122.6°). The flexibility range, defined as the accessible range of bite angles within 3 kcal mol^{-1} excess strain energy from the calculated natural bite angle, also mimics that of bisbi. Presumably, the nitrogen atoms in L^2 only cause a slightly different orientation of the phenyl groups at phosphorus. The behaviour of L^3 appears to be in between that of L^1 and L^2, resulting in both a relatively small proportion of linear aldehyde and large proportion of oct-2- and -3-enes.

The amino groups in compound L^4 have a modest effect on the catalytic properties. The reaction rate is somewhat lower when compared with that of the bisbi catalyst. The n:b ratio is lower which is compensated by a lower percentage of isomerised octenes.

Using compound L^1 the hydroformylation characteristics of this group of compounds were further investigated. The temperature dependence of the hydroformylation of oct-1-ene has been examined (Table 3). At lower temperatures the time for the formation of the active rhodium complex was prolonged. At 60 °C the reaction still proceeded whereas at 40 °C no significant conversion was achieved. The selectivity of the reaction is improved; especially the amount of isomerisation drops while the n:b ratio rises. At 120 °C the turnover frequency increased dramatically at the expense of the selectivity towards the linear aldehyde. Also the isomerisation activity increased substantially.

Variation of the ligand-to-rhodium ratio showed that at relatively low rhodium concentrations a L:Rh ratio of 10:1 is required (Table 4). At lower ratios (entry 2) formation of [RhH(CO)$_2$L] is incomplete and sterically less-demanding rhodium carbonyl complexes are present. Typically, the resulting hydroformylation reaction is fast but extensive amounts of oct-2- and -3-enes are formed. When oct-1-ene has been completely converted the internal octenes are hydroformylated giving primarily 2-methyloctanal. Hence, the measured amount of oct-2-ene falls as does the n:b ratio. At a higher rhodium concentration a L:Rh ratio of 1.1:1 is adequate for the formation of a selective catalyst.

From entries 1 and 3–5 it can be concluded that the hydroformylation using compound L^1 is approximately first order in rhodium concentration; at 8.2–11.7% conversion the

Table 2 Hydroformylation of oct-1-ene under standard conditions

Phosphine	t/h	Extent of conversion (%)[a]	Selectivity (%)				
			Isomers[b]	*n*-Aldehyde	Branched aldehyde	n:b	Turnover frequency[c]
bisbi	1	6.7	7.4	90.3	2.3	38	308
	4.5	27.3	7.6	90.2	2.2	41	280
	21	82.8	7.6	90.2	2.2	41	182
L^1	1	9.4	7.8	90.4	1.8	50	435
	4.5	38.0	8.0	90.2	1.8	51	388
	20	91.4	7.9	90.3	1.8	51	210
L^2	1	10.8	6.8	89.3	3.9	23	504
	4.5	39.3	6.2	89.9	3.9	23	410
	21	91.5	7.2	89.0	3.8	24	204
L^3	1	15.9	8.3	88.8	2.9	28	732
	4.5	50.1	8.4	88.7	2.9	30	510
	21	93.6	7.8	89.2	3.0	30	206
L^4	1	5.5	6.4	90.6	3.0	28	261
	4.5	22.9	6.3	90.7	3.0	30	240
	21	76.9	6.5	90.6	2.9	32	172

Conditions: 20 bar H_2–CO (1 : 1), 80 °C, toluene (20 cm^3), [L] = 17 × 10^{-4} mol dm^{-3}, [Rh] = 1.7 × 10^{-4} mol dm^{-3}, [oct-1-ene] = 0.84 mol dm^{-3}. [a] Percentage of oct-1-ene converted. [b] Percentage of oct-2-, -3- and -4-enes formed. [c] Turnover frequency in mol aldehydes per mol Rh per hour, averaged over the time given.

Table 3 Temperature variation in the hydroformylation of oct-1-ene with phosphine L^1

T/°C	t/h	Extent of conversion (%)[a]	Selectivity (%)				
			Isomers	*n*-Aldehyde	Branched aldehyde	n:b	Turnover frequency
40	19	6.3	~1.5	96.7	1.8	53	17
60	3.7	5.0	4.9	93.3	1.8	52	65
	57	42.9	4.6	93.6	1.8	52	36
80	1	9.4	7.8	90.4	1.8	50	435
	4.5	38.0	8.0	90.2	1.8	51	388
	20	91.4	7.9	90.3	1.8	51	210
120	0.1	33.5	15.4	82.7	1.9	41	14 200
	0.25	64.6	16.2	81.9	1.9	44	10 810
	1	93.9	15.8	82.2	1.9	44	3 950

Conditions (except temperature) as in Table 2.

average turnover frequency is 495 ± 60. It was further shown* that the hydroformylation is approximately first order with respect to the oct-1-ene concentration. This was confirmed by the high rates found for the hydroformylation in neat oct-1-ene (entry 6). The selectivity towards oct-2-enes is low and the selectivity towards linear aldehyde high. The hydroformylation reaction is exothermic, and the reaction temperature initially increased to 95 °C.

Hex-1-ene and dodec-1-ene were also used as substrates in the hydroformylation (Table 5). As observed by others,[66] increasing the length of the aliphatic chain from C_6 to C_{12} causes a small but significant decrease in rate.

Variation of the partial pressure of CO revealed that the hydroformylation has a negative order in CO pressure (Table 6, entries 1–4). Variation of the partial pressure of hydrogen revealed a zeroth or a slightly negative reaction order with respect to the hydrogen pressure (entries 5 and 6). It can be seen that at a low CO pressure of 5 bar the increase of the n : b ratio is accompanied by a significant increase in isomerisation. The decreased CO pressure leads to an increased tendency towards β-H elimination and, as discussed above, an elevated n : b ratio. Thus, at higher partial CO pressures the rate of isomerisation decreases and more branched aldehyde is formed. This does, however, not fully account for the increase in the formation of branched aldehyde. The formation of an excess of branched aldehyde is tentatively ascribed to the occurrence of rhodium carbonyl species which give a lower linearity but are less susceptible for β-H elimination due to the high CO pressure. In addition, these species give relatively higher rates which explains the small decrease in rate on going from P_{CO} = 30 to 50 bar.

The observed dependencies of the rates on oct-1-ene concentration and the CO and hydrogen pressures suggest that complexation of oct-1-ene, or less likely one of the migration steps that follows, is rate determining.[67] The hydrogenolysis of the rhodium acyl species is definitely not rate determining, although this is suggested in many textbooks.[1,5] Hydroformylation under an increased syngas pressure of 60 bar (entry 7) gives results that are clearly dominated by the influence of CO and closely resemble those in entry 3. The pressure-variation experiments were also done for compounds L^2–L^4 and gave identical results. The kinetic behaviour of this group of diphosphines closely resembles that of structurally related bulky diphosphites.[67]

Distribution characteristics of the free phosphines

We determined the pH-dependent distribution characteristics of the free amphiphilic compounds (see Experimental section for details) by adding an aqueous H_2SO_4 solution of different pH values to an organic solution of the phosphine. The phosphine concentrations in both layers (c_{H_2O} and c_{org}) were measured by UV absorption and expressed, at each specific final pH value, as a distribution coefficient D; equation (1). For

* A plot of ln (turnover frequency) *vs.* reaction time for experiment 2 in Table 1 gave a straight line, indicating a first-order dependence on oct-1-ene concentration.

Table 4 Variation of L : Rh ratio in the hydroformylation of oct-1-ene with phosphine L^1

Entry	L : Rh	10^4 [Rh]/ mol dm^{-3}	Substrate : Rh	t/h	Extent of conversion (%)	Selectivity (%)				
						Isomers	n-Aldehyde	Branched aldehyde	n : b	Turnover frequency[c]
1	10	1.7	5 000	1	9.4	7.8	90.4	1.8	50	435
				4.5	38.0	8.0	90.2	1.8	51	388
				20	91.4	7.9	90.3	1.8	51	210
2	2.2	1.7	5 000	1	36.5	40.4	48.9	10.7	4.6	1086
				4.5	92.2[a]	29.1	49.0	21.9	2.2	728
3	1.1	14.0	600	0.1	8.7	11.0	86.8	2.2	38	476
				0.5	40.0	12.5	84.7	2.8	30	422
				1.5	78.7	10.3	85.7	4.0	22	283
4	5	6.7	1 250	0.17	8.2	8.3	89.8	1.9	49	560
				1	40.3	8.4	89.7	1.9	49	461
				4.5	90.4	8.6	89.3	1.9	47	229
5	10	3.4	2 500	0.5	11.7	5.1	92.7	2.1	45	555
				1	22.6	6.3	91.8	1.9	48	530
				4.5	67.9	8.7	89.5	1.8	52	344
6	10	1.7	33 500[b]	0.1	1.8	6.9	91.1	2.0	45	5550[c]
				0.5	5.1	6.8	91.2	2.0	44	3283
				3	27.7	7.2	91.3	1.5	62	2870

Conditions: 20 bar H_2–CO (1 : 1), 80 °C, toluene (20 cm^3), [oct-1-ene] = 0.84 mol dm^{-3}. [a] Extensive formation of aldehydes derived from internal octenes. [b] This reaction was performed in neat oct-1-ene (5.7 mol dm^{-3}). [c] Initial reaction temperature increased to 95 °C.

Table 5 Hydroformylation of other alkenes with phosphine L^1

Alkene	t/h	Extent of conversion (%)	Selectivity (%)				
			Isomers	n-Aldehyde	Branched aldehyde	n : b	Turnover frequency
Hex-1-ene	1	9.7	7.9	90.3	1.8	49	452
	4.5	38.6	7.6	90.5	1.9	49	399
	20	94.2	7.9	90.3	1.8	49	218
Oct-1-ene	1	9.4	7.8	90.4	1.8	50	435
	4.5	38.0	8.0	90.2	1.8	51	388
	20	91.4	7.9	90.3	1.8	51	210
Dodec-1-ene	1	9.3	8.2	90.1	1.7	55	431
	4.5	37.2	8.4	89.1	1.7	54	379
	20	87.2	8.4	89.9	1.7	54	201

Conditions as in Table 2 except [alkene] = 0.84 mol dm^{-3}.

$$D = \frac{c_{H_2O}}{c_{H_2O} + c_{org}} \times 100\% \quad (1)$$

functionalised triphenylphosphines the extraction behaviour of the free phosphine was shown to be similar to that of the corresponding rhodium complexes.[37] Hence, plots of *D vs.* pH can be used to determine the required extraction conditions in the recycling system. Moreover, they indicate whether the phosphines themselves can be recycled. Recovery of the relatively expensive diphosphine is also important.

In Fig. 2 the *D vs.* pH plots are depicted for compounds L^1 and L^2. At pH > 5.5 the phosphines are largely located in the Et_2O layer, and only at pH < 1 both are extracted into the aqueous phase. Compound L^1 was extracted at a slightly higher pH than was L^2. The basicity of the pyridyl ring in L^1 is somewhat lower than that of the bipyridine system, due to the electron-withdrawing phosphorus atom. However, the protonated nitrogen atoms in the bipyridine backbone may be sterically less accessible for solvation by water due to the neighbouring diphenylphosphino moiety. Compound L^3, in which the bipyridine backbone and pyridyl rings are combined, was more readily extracted (Fig. 3). It was largely present in the organic phase at neutral pH, but was quantitatively extracted at the relatively mild pH of 2. This curve closely resembles that of phenylbis(3-pyridyl)phosphine.[37] The ratio of pyridyl rings and hydrophobic phenyl rings is identical in both compounds. A similar distribution behaviour was found for L^4. This

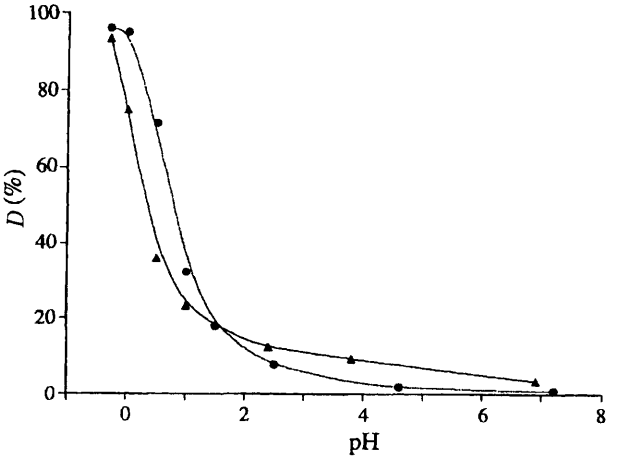


Fig. 2 Extraction curves for compound L^1 (●) and L^2 (▲)

compound contains only two benzylic diethylamino groups which are more basic. In the extraction region the curve is less steep than that of L^3; it was extracted more readily into the aqueous phase, but extraction was complete at a pH < 2. Extraction experiments with L^4 gave rise to the formation of emulsions, but phase separation was complete after about 1 h.

Table 6 Variations in P_{CO} and P_{H_2} in the hydroformylation of oct-1-ene with phosphine L^1

Entry	P_{H_2}/bar	P_{CO}/bar	t/h	Extent of conversion (%)	Selectivity (%)				
					Isomers	*n*-Aldehyde	Branched aldehyde	n:b	Turnover frequency
1	10	5	1	17.8	12.7	85.9	1.4	61	778
			4.5	57.4	12.7	86.0	1.3	65	556
			21	94.8	12.4	86.3	1.3	65	
2	10	10	1	9.4	7.8	90.4	1.8	50	435
			4.5	38.0	8.0	90.2	1.8	51	388
			20	91.4	7.9	90.3	1.8	51	210
3	10	30	1	3.9	5.5	90.0	4.5	20	184
			4.5	14.8	5.4	90.2	4.4	21	156
			20	55.9	5.5	90.1	4.4	21	129
4	10	50	2	6.2	4.8	88.9	6.3	14	148
			4.5	11.4	5.0	88.7	6.3	14	136
			20	49.8	4.7	90.0	6.3	15	118
5	5	10	1	10.6	7.7	90.3	2.0	45	489
			4.5	37.7	7.8	90.3	1.9	48	387
			21	89.8	7.8	90.4	1.8	49	197
6	30	10	1	8.9	9.9	87.7	2.4	38	399
			4.5	36.2	10.0	87.6	2.4	36	362
			21	85.6	10.0	87.6	2.4	36	189
7	30	30	2	7.4	7.7	88.4	3.9	23	170
			4.5	16.3	7.8	88.2	4.0	21	167
			21	61.9	7.9	88.2	3.9	23	136

Conditions as in Table 2 except pressure.

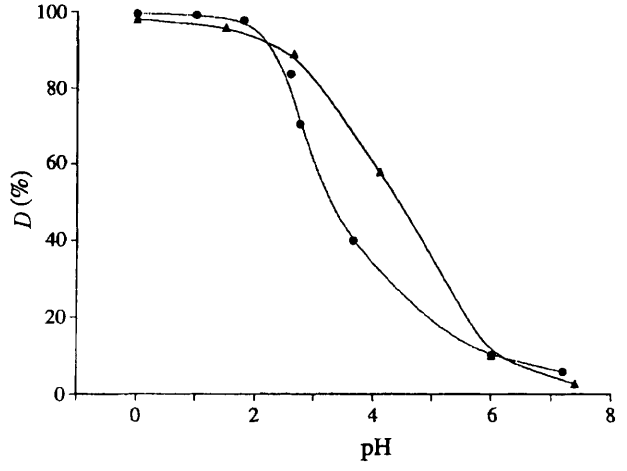


Fig. 3 Extraction curves for compounds L^3 (●) and L^4 (▲)

Rhodium-recycling experiments

The group of novel amphiphilic phosphines was used in rhodium-recycling experiments in which the extraction and re-extraction principle, as outlined in the introduction, was applied. The rhodium contents of the aqueous and organic phases were analysed by ICP-AES. Furthermore, the recovered rhodium was subjected to a second hydroformylation run. The observed catalytic activity was compared to that of the original activity in the first run.

Optimum conditions for the recycling procedure were established in experiments with the modified PPh_3 ligands.[36,37] These conditions, described in detail in the Experimental section, were used in the experiments with L^1–L^4. In a typical recovery experiment, a mixture of $[Rh(acac)(CO)_2]$ (0.012 mmol), phosphine (0.12 mmol) and toluene (15 cm^3) was pressurised to 20 bar syngas at 80 °C in an autoclave for 1 h. Oct-1-ene was added and a small sample was taken after 30 min. The entire content was siphoned into a separatory funnel containing demineralised water, and titrated with an aqueous H_2SO_4 solution until the typical yellow colour of rhodium was partly transferred to the aqueous layer. At this point extraction is not complete, but successive extractions, again by titration, effect quantitative extraction of rhodium into the aqueous phase. The combined aqueous layers were neutralised with a saturated aqueous $NaHCO_3$ solution to pH 6–7, and successively extracted with fresh toluene. The combined toluene layers were again pressurised to 20 bar syngas at 80 °C in the autoclave for 1 h, oct-1-ene was added and three successive samples were taken at the same extent of conversion as that of the first run, as judged from the pressure drop.

In addition, recycling experiments have been done in which the rhodium and phosphine were quantitatively extracted into the aqueous phase by a *single* extraction. The required pH was estimated from the extraction curves for the free phosphines. These experiments were only done for L^3 and L^4, since quantitative single extraction of L^1 and L^2 requires pH < −0.5.

The results of the recycling experiments are shown in Table 7. For each experiment the conditions, under which the acidic extraction was done, are given. The hydroformylation reaction is first order in oct-1-ene concentration and so is the turnover frequency. The turnover value of the first run is taken as the number of moles of aldehyde formed per mol rhodium averaged over the first 30 min. Since the turnover frequency of the second run was determined after a similar conversion of oct-1-ene, the quotient of both values is a measure of the recovery of catalytically active rhodium and is referred to as the retention of activity.

Compound L^1. When the catalytic mixture was titrated with a H_2SO_4 solution of pH 0 the aqueous layer turned yellow at pH 1. This is in agreement with the results in Fig. 2. Four successive extractions at pH 1 resulted in an almost colourless toluene layer. A persistent yellowish emulsion remained which most likely gives rise to the rhodium loss of 252 μg (Table 7, entry 1). Upon neutralisation of the combined aqueous layers to pH 7, in the presence of toluene, the aqueous layer remained yellow and an emulsion/precipitate was formed. Rhodium analysis by AES confirmed that most of the rhodium remained in the aqueous

Table 7 Results of the recycling experiments; rhodium measurements by ICP-AES and retention of activity

Entry	Phosphine	Acidic extraction	Rhodium content (μg)			Rhodium (%)		Retention of activity[c] (%)
			First organic layer	Aqueous layer	New organic layer	Recovery[a]	Balance[b]	
1	L^1	Titration: 5 × extraction at pH 1	252[d]	719	219	18	96	14.1
2	L^2	Titration: 5 × extraction at pH 1	51	1027	144	12	99	10.9
3	L^3	Titration: 7 × extraction at pH 4–4.5	34	1150	47	4	100	2.5
4		Single extraction at pH 1	49	1029	161	13	100	10.0
5	L^4	Titration: 7 × extraction at pH 5	11	8[e]	1108	91	99	72.1
6		Single extraction at pH 1.8[f]	13	7[g]	2180	92	100	55.6

The 95% confidence interval of the mean measured values is ± 4.5% for contents > 10 μg, otherwise ± 10%. [a] Rhodium recovered in the new organic layer as a percentage of the total amount measured. [b] Mass balance defined as the total amount of rhodium measured as a percentage of the starting amount (= 1235 μg). [c] Defined as the turnover frequency of the recovered rhodium as a percentage of the original turnover frequency measured in the first run (see text). [d] Rhodium content of the toluene layer and persistent emulsion. [e] Persistent emulsion contained 97 μg Rh. [f] Experiment on larger scale (same absolute concentrations) with a total rhodium amount of 2375 μg. [g] Persistent emulsion contained 175 μg Rh.

phase. The catalytic activity of the toluene layer was accordingly low, but the selectivity of the hydroformylation was identical to that of the first run. A duplicate experiment gave identical results.

Compound L^2. The recycling experiment using L^2 proved similar to that with L^1. However, during acidic extraction no emulsion was formed which is reflected in the low rhodium loss of 51 μg. An NMR experiment showed that the active complex $[RhH(CO)_2L^2]$, which was characterised earlier, decomposes in the acidic environment. The ^{31}P NMR spectrum of the acidic aqueous layer exhibited no doublet at δ 36, but very broad signals in the region δ 0–20.

Compound L^3. Titration with a H_2SO_4 solution of pH 1.8 resulted in a bright yellow aqueous layer at pH 4–4.5. Seven extractions gave a colourless toluene layer with a low rhodium contamination of 34 μg without emulsion. Upon addition of a saturated $NaHCO_3$ solution, however, a greenish precipitate was formed while the aqueous layer remained yellow. The rhodium recovery was only 4% and the retention of activity accordingly low. Single extraction of the autoclave content with a H_2SO_4 solution of pH 1 resulted in an almost quantitative extraction. The colourless toluene phase contained only 49 μg rhodium. The subsequent neutralisation procedure gave rise to the same observations as during the titration experiment, and a rhodium recovery of only 13%.

Compound L^4. Upon titration with a H_2SO_4 solution of pH 1.8 rhodium was partially extracted at pH 5. At this pH about 40% of the free phosphine is extracted (Fig. 3). After seven extractions a yellow aqueous phase and a colourless toluene layer were obtained. Phase separation was complicated by an emulsion between the organic and aqueous layer. Since this emulsion contained up to 150 μg rhodium (12%) it was taken along with the aqueous extractions. Neutralisation to pH 7 was also accompanied by substantial emulsion formation. This emulsion, which contained 8% of the total rhodium amount and is stable for more than 24 h, was not taken along with the toluene extractions. The low rhodium contaminations of both the first organic and aqueous layer only account for 1.5% of the total rhodium amount. Both the rhodium recovery (91%) and retention of activity (72%) were high. Single extraction with a H_2SO_4 solution of pH 1.8 also resulted in quantitative extraction of rhodium. The observations are similar to those described above. Although the rhodium recovery equals that of the titration experiment the retention of activity is significantly lower.

Rhodium can be recycled to the extent of 92% when compound L^4 is used. The rhodium contaminations in the extracted toluene and aqueous layers were remarkably low. Only the formed emulsions, probably due to the surface-active properties of the amphiphilic phosphine, contained significant amounts of rhodium. The originally highly selective and active rhodium hydrides can be regenerated up to 72% activity (entry 5). Single extraction of rhodium and the excess of phosphine at pH 1.8 and successive extractions at pH 5 gave similar rhodium recovery percentages. The higher retention of activity in the latter case strongly suggests that extraction in a mild acidic environment decreases the extent of irreversible decomposition. This is in agreement with the earlier results found for the modified PPh_3 ligands.[37]

In contrast with compound L^4, L^1–L^3 are inappropriate for application to rhodium recovery. Acidic extraction is efficient, except for L^1 which tends to stabilise emulsions. Treatment with basic solutions leads to extensive, irreversible decomposition. The decomposition reactions of the rhodium complexes have not been elucidated but NMR analysis established that the excess of phosphine does not decompose and is recycled. Presumably, the presence of a pyridyl nitrogen atom, whether positioned in a bipyridine backbone or a pyridyl ring, gives rise to irreversible decomposition of the rhodium hydride species to trivalent rhodium species which cannot be extracted from the aqueous layer. The small amount of rhodium which is re-extracted in toluene can be largely regenerated to the active hydride, since the same high selectivity is observed as in the first hydroformylation.

Conclusion

The novel amphiphilic diphosphines give rise to hydroformylation catalysts which are highly active and selective. For the pyridyl-modified ligands, reaction rates up to two times faster than that of bisbi were observed, with the same selectivity. The ligand functionalised with the diethylamino groups allows the separation of the product aldehydes from the rhodium catalyst, and the recovery of rhodium up to 92%. The recycled rhodium effected hydroformylation of a new batch of oct-1-ene with the same high selectivity and a reduced activity (72%). While the recovery of rhodium can be improved sufficiently by more washing steps at lower pH, we also learned that regeneration of catalysts recycled under more acidic conditions is far less complete. Catalyst regeneration is therefore a key issue. This is unexpected since usually the formation of rhodium hydrides occurs smoothly under basic conditions. Modification of other potent hydroformylation ligands is currently in progress.

Experimental

General

All reactions were carried out in flame-dried glassware using standard Schlenk techniques under an argon atmosphere. Toluene, tetrahydrofuran (thf) and diethyl ether were distilled from sodium–benzophenone, CH_2Cl_2 was dried over P_2O_5 and distilled from CaH_2. All solvents used in the preparation or handling of phosphines were degassed prior to use. Solvents and reagents were distilled prior to use. All chemicals were obtained from Janssen and Aldrich Chemical Co. The compounds bisbi,[47] 2,2′-bis(bromomethyl)-1,1′-biphenyl **Ia**,[47] [4-(diethylaminomethyl)phenyl]phenylphosphine oxide **IV**,[54] phenyl(3-pyridyl)phosphine[54] and $[RhH(CO)(PPh_3)_3]$[68] were prepared according to literature procedures. For column chromatography both silica gel 60 (Merck, 230–400 mesh) and aluminium oxide (neutral activity, 50–200 μm, Janssen) were used. Proton (300 MHz, $SiMe_4$ as standard), ^{31}P (121.5 MHz, H_3PO_4 as standard) and ^{13}C (75.5 MHz, $SiMe_4$ as standard) NMR spectra were measured on a Bruker AMX 300 spectrometer in $CDCl_3$ unless otherwise stated, IR spectra on a Nicolet 510 FT-IR spectrophotometer. Melting points were determined on a Gallenkamp MFB-595 apparatus. Gas chromatography–mass spectrometry was measured on a HP 5890/5971 spectrometer. For exact mass determination a JEOL JMS-SX/SX102A spectrometer was used.

Hydroformylation reactions were carried out in a laboratory-made stainless-steel autoclave (200 cm^3). Gas chromatographic analyses were run on a Carlo Erba GC 6000 Vega Series apparatus (split/splitless injector, J & W Scientific, DB1 30 m column, film thickness 3.0 μm, carrier gas 70 kPa He, flame ionisation detector) equipped with a HP 3396 integrator. Syngas 3.0 was obtained from UCAR. The oct-1-ene was freshly filtered over a short column of aluminium oxide (neutral activity, 50–200 μm, Janssen) to remove hydroperoxides. The UV spectra were measured on a Varian Cary 4 single-beam apparatus. The pH values were measured on a Corning 240 pH-meter. The ICP-AES measurements were done using a sequential Jarrell Ash upgraded (model 2.5) Atomscan model 2400 ICP scanning monochromator. Sulfuric acid calibration solutions of rhodium were prepared by dilution of a rhodium standard ($RhCl_3$ in 20% HCl) from Johnson Matthey. Elemental analyses were performed by the Department of Micro Analyses at the University of Groningen and by our Department using a Vario EL from Elementar Analysensysteme GmbH (Foss Electric Benelux) in the CHNS mode (thermal conductivity detector). The NMR simulation was done with geNMR 3.5M software.[69] The following notation was used in the NMR assignments; bipyridine/biphenyl ring ($C^{1'-6'}$), PPh (C_{i-p}), $P(C_6H_4NEt_2)$ ($C_{i'-p'}$) and $P(C_5H_4N\text{-}3)$ (C^{2-6}).

Preparations

2,2′-Bis[phenyl(3-pyridyl)phosphinomethyl]-1,1′-biphenyl L¹. A solution of phenyl(3-pyridyl)phosphine (11.67 mmol, 2.18 g) in thf (50 cm^3) was cooled to −78 °C. A 2.5 mol dm^{-3} solution of *n*-butyllithium in hexane (11.67 mmol, 4.7 cm^3) was added in 30 min and stirring was continued at room temperature for 1 h. The resulting deep red-brown solution was added dropwise to a solution of compound **Ia** (5.84 mmol, 1.98 g) in thf (15 cm^3) at −78 °C. The reaction mixture was then allowed to warm to room temperature overnight. The reaction mixture was concentrated and 4 mol dm^{-3} NaOH solution (20 cm^3) was added. The aqueous layer was extracted with toluene (3 × 40 cm^3). The toluene phase was dried over Na_2SO_4 and the solvent evaporated. No further purification was needed. The yellowish oil solidified into a yellow-white solid within 2 d. Yield 91% (5.10 mmol, 2.81 g) of the diastereomeric mixture. NMR: ^1H, δ 8.49 (m, 2 H, aromatic), 8.25 (m, 1 H, aromatic), 7.61–6.73 (m, 23 H, aromatic), and 3.34–3.09 (m, 4 H, CH_2); $^{31}P\text{-}\{^1H\}$, δ −15.87 (d, 1 P, J = 1.2), −15.93 (1 P), −16.50 (1 P) and −16.53 (d, 1 P, J = 1.2); ^{13}C, δ 153.3 (dm, J = 22.7, C^2), 152.9 (dd, J = 21.9, 3.0, C^2), 149.4 (C^6), 149.1 (C^6), 140.5 (d, J = 3.8, $C^{1'}$), 140.2 (d, J = 16.6, C^4), 139.7 (d, J = 13.6, C^4), 136.6–136.1 (m, C_i, C^3), 134.8–134.3 (m, C_i, C^3), 133.1 (dd, J = 20.4, 3.8, C_o), 132.6 (d, J = 18.9, C_o), 130.4, 130.3, 129.5 (d, J = 9.1), 129.1, 128.9, 128.4 (dd, J = 7.6, 7.5 Hz), 127.3, 125.9, 123.1 (br s, C^5) and 32.8 (m, CH_2). Exact mass (FAB): 553.1863 (M + H) (calc. for $C_{36}H_{31}N_2P_2$: 553.1963) (Found: C, 78.40; H, 5.55; N, 4.95. Calc. for $C_{36}H_{30}N_2P_2$: C, 78.25; H, 5.50; N, 5.05%). M.p. 92.5–95.5 °C.

2,2′-Bis(chloromethyl)-3,3′-bipyridine IIIa. A stirred mixture of 2,2′-dimethyl-3,3′-bipyridine **II** (10 mmol, 1.84 g), *N*-chlorosuccinimide (25 mmol, 3.34 g) and benzoyl peroxide (35 mg) in CCl_4 (220 cm^3) was refluxed for 24 h. During this period extra portions (about 10 mg) of benzoyl peroxide were added. The reaction mixture was cooled in an ice-bath, filtered and the filtrate concentrated *in vacuo*. The resulting brown oil was purified by column chromatography (silica gel, 10% thf–CH_2Cl_2) yielding a light orange crystalline product. Yield 38% (3.8 mmol, 0.95 g). NMR: ^1H, δ 8.75 (dd, 2 H, J = 4.8, 1.8, $H^{6'}$), 7.68 (dd, 2 H, J = 7.8, 1.8, $H^{4'}$), 7.41 (dd, 2 H, J = 7.8, 4.8, $H^{5'}$) and AB (4.52 + 4.38, 4 H, J = 11.0 Hz, CH_2); ^{13}C, δ 154.7 ($C^{2'}$), 150.7 ($C^{6'}$), 138.8 ($C^{4'}$), 133.7 ($C^{3'}$), 123.8 ($C^{5'}$) and 45.5 (CH_2). GC-MS: m/z 252 [M^+(^{35}Cl, ^{35}Cl), 100], 254 [M^+ + 2(^{35}Cl, ^{37}Cl), 64] and 256 [M^+ + 4(^{37}Cl, ^{37}Cl), 10%]. M.p. 67–68 °C.

2,2′-Bis(diphenylphosphinomethyl)-3,3′-bipyridine L². A solution of diphenylphosphine (8.6 mmol, 1.5 cm^3) in thf (25 cm^3) was cooled to −78 °C. A 2.5 mol dm^{-3} solution of *n*-butyllithium in hexane (8.6 mmol, 3.44 cm^3) was added in 30 min. Stirring was continued for 1 h. The resulting orange solution was added dropwise to a solution of compound **IIIa** (4.3 mmol, 1.09 g) in thf (40 cm^3) at −78 °C within 45 min. The reaction mixture was allowed to warm to room temperature overnight. The solvents were evaporated and 2 mol dm^{-3} NaOH solution (20 cm^3) was added. The aqueous layer was extracted with toluene (2 × 30 cm^3) and the toluene phase evaporated resulting in a cream solid. No further purification was needed. Yield 95% (4.1 mmol, 2.25 g). NMR: ^1H, δ 8.55 (dd, 2 H, J = 4.9, 1.7, $H^{6'}$), 7.37–7.23 (m, 12 H, aromatic), 7.19 (quasi t, 4 H, J = 7.4, aromatic), 7.10 (distorted t. 4 H, J = 6.9, aromatic), 7.00 (dd, 2 H, J = 7.6, 4.7, aromatic), 6.87 (distorted d. 2 H, J = 7.6, aromatic), AB [3.46 (d, $^1J_{HH}$ = 13.7) +3.26 (dd, $^1J_{HH}$ = 13.7, through-space J_{PH} = 2.6 Hz), 4 H, CH_2]; $^{31}P\text{-}\{^1H\}$, δ −10.6; ^{13}C, δ 156.7 (d, J = 6.8, $C^{2'}$), 149.5 ($C^{6'}$), 138.8 (dd, J = 15.9, 14.4, C_i), 138.4 ($C^{4'}$), 134.7 (d, J = 5.3, $C^{3'}$), 133.4 (dd, J = 20.4, 19.6, C_o), 129.1 (C_p), 128.9 (m, C_m), 121.4 (C^5) and 37.1 (d, J = 16.0 Hz, CH_2). Exact mass (FAB): m/z 553.1791 (M + H) (calc. for $C_{36}H_{31}N_2P_2$: 553.1963) (Found: C, 78.05; H, 5.60; N, 5.20. Calc. for $C_{36}H_{30}N_2P_2$: C, 78.25; H, 5.50; N, 5.05%). M.p. 136–138 °C.

2,2′-Bis[phenyl(3-pyridyl)phosphinomethyl]-3,3′-bipyridine L³. A solution of phenyl(3-pyridyl)phosphine (8.4 mmol, 1.57 g) in thf (20 cm^3) was cooled to −78 °C. A 2.5 mol dm^{-3} solution of *n*-butyllithium in hexane (8.4 mmol, 3.36 cm^3) was added in 30 min. Stirring was continued for 1 h. The resulting deep red-brown solution was added dropwise to a solution of compound **IIIa** (4.2 mmol, 1.06 g) in thf (40 cm^3) at −78 °C within 45 min. The brown reaction mixture was allowed to warm to room temperature overnight. The solvents were evaporated and 2 mol dm^{-3} NaOH solution (20 cm^3) was added. The aqueous layer was extracted with toluene (2 × 30 cm^3). The toluene phase was evaporated resulting in a brownish solid. After washing with hexane (2 × 10 cm^3) a pure beige solid was obtained. Yield 96% (3.97 mmol, 2.2 g) of the diastereomeric mixture. NMR: ^1H, δ 8.51 (m, 4 H, aromatic), 8.32 (m, 1 H, aromatic),

7.60 (m, 1 H, aromatic), 7.42–6.99 (m, 18 H, aromatic), 3.51–3.42 (m, 2 H, CH_2) and 3.34–3.24 (m, 2 H, CH_2); ^{31}P-{^1H}, δ −17.50 (d, 1 P, J = 1.5), −17.54 (1 P), −17.83 (d, 1 P, J = 1.5) and −17.90 (1 P); ^{13}C, δ 156.1 (t, J = 6.8, $C^{2'}$), 153.9 (d, J = 23.4, C^2), 150.0, 149.6, 140.6 (dd, J = 13.6, 13.3), 138.3 (d, J = 19.6), 137.3–137.0 (m, C^3, C_i), 135.2 (dd, J = 16.2, 16.4, C^3, C_i), 134.5 (d, J = 5.2, $C^{3'}$), 133.4 (dd, J = 20.4, 20.1 Hz, C_o), 129.7 (C_p), 129.2 (m, C_m), 123.9 (C^5), 121.7 ($C^{5'}$), and 36.7 (m, CH_2). Exact mass (FAB): 555.1907 (M + H) (calc. for $C_{34}H_{29}N_4P_2$: 555.1868) (Found: C, 72.95; H, 5.50; N, 9.70. Calc. for $C_{34}H_{28}N_4P_2$: C, 73.65; H, 5.10; N, 10.10%). M.p. 126–128 °C.

2,2′Bis-{[4-(diethylaminomethyl)phenyl]phenylphosphorylmethyl}-1,1′-biphenyl V. A solution of compound **IV** (12.0 mmol, 3.40 g) in thf (50 cm^3) was slowly added to a suspension of sodium hydride (12.6 mmol, 0.38 g) in thf (10 cm^3) at room temperature. The yellow reaction mixture was cooled to −30 °C and a solution of **Ia** (6.0 mmol, 2.04 g) in thf (30 cm^3) was added in 0.5 h. The reaction mixture was allowed to warm to room temperature and refluxed for 1.5 h. The solvents were then evaporated and aqueous 2 mol dm^{-3} NaOH (50 cm^3) was added. The aqueous layer was extracted with toluene (3 × 40 cm^3). The organic phase was evaporated and the resulting oil purified by column chromatography (silica gel, 60% ethyl acetate–35% hexane–5% NEt_3). Yield 65% of a yellowish oil (3.7 mmol, 2.81 g). NMR: ^1H, δ 7.60–7.01 (m, 24 H, aromatic), 6.43 (t, 1 H, J = 7.6, aromatic), 6.35 (t, 1 H, J = 8.2, aromatic), 3.55 (br s, 4 H, CH_2N), 3.36–3.23 (m, 4 H, CH_2P), 2.52 (m, 8 H, CH_2CH_3), and 1.04 (m, 12 H, CH_3); ^{31}P-{^1H}, δ 30.0; ^{13}C, δ 144.2 (d, J = 22.6, C^4), 140.3 (d, J = 5.3, C^4), 132.2 (d, J = 105.7, C_i), 131.5, 131.0, 130.8 (m), 130.2, 129.5 (m, C^4), 128.7, 128.6–128.2 (m), 127.3, 126.5, 57.0 (CH_2N), 46.6 (CH_2CH_3), 33.8 (d, J = 68.0 Hz, CH_2P) and 11.5 (CH_3). M.p. 51–54 °C.

2,2′-Bis{[4-(diethylaminomethyl)phenyl]phenylphosphinomethyl}-1,1′-biphenyl L⁴. Compound **V** (0.50 mmol, 0.37 g) was dissolved in toluene (20 cm^3) and NEt_3 (5.0 mmol, 0.7 cm^3) was added. At 0 °C trichlorosilane (5.0 mmol, 0.68 cm^3) was added dropwise. The reaction mixture was stirred overnight and then refluxed for 3 h. Aqueous 20% KOH (30 cm^3) was added at 0 °C. After stirring for 45 min the organic phase was separated and the aqueous layer washed with toluene (20 cm^3). The combined organic phases were dried on $MgSO_4$ and evaporated. No further purification was necessary. Yield 84% of a yellowish oil (0.43 mmol, 0.31 g). NMR: ^1H, δ 7.33–6.91 (m, 26 H, aromatic), 3.56 (s, 2 H, CH_2N), 3.55 (s, 2 H, CH_2N), AB [3.24 (d, $^1J_{HH}$ = 13.3) +3.13 (dd, $^1J_{HH}$ = 13.3, through-space J_{PH} = 2.9), 4 H, CH_2], 2.53 (br q, 8 H, J = 7.1, CH_2CH_3) and 1.06 (t, 12 H, J = 7.0, CH_3); ^{31}P-{^1H} δ − 10.53, −10.57, −10.62 and −10.68; ^{13}C δ 141.4 (d, J = 3.8, $C^{1'}$), 141.0 ($C_{p'}$), 139.4 (d, J = 16.6, $C_{i/i'}$), 139.0 (d, J = 16.6, $C_{i/i'}$), 136.9 (d, J = 16.1, $C_{i/i'}$), 136.6 (d, J = 15.9, $C_{i/i'}$), 136.8–136.2 (m, $C^{2'}$), 133.7 (d, J = 18.9, $C_{o/o'}$), 133.2 (d, J = 18.1, $C_{o/o'}$), 131.0, 130.3 (d, J = 10.6, $C^{3'}$), 129.5–128.6 (m), 127.6, 126.2, 57.8 (CH_2N), 47.3 (CH_2CH_3), 34.2 (d, J = 16.6 Hz, CH_2P) and 12.3 (CH_3). Exact mass (FAB): m/z 721.3788 (M + H) (Calc. for $C_{48}H_{55}N_2P_2$: 721.3841) (Found: C, 80.25; H, 7.70; N, 3.75. Calc. for $C_{48}H_{54}N_2P_2$: C, 79.95; H, 7.55; N, 3.90%).

Rhodium complexes. In the synthesis of [RhH(CO)(PPh_3)(L–L)] complexes, diphosphine (0.05 mmol) and [RhH(CO)(PPh_3)$_3$] (0.05 mmol) were dissolved in [$^2H_8$]toluene (1.1 cm^3) and stirred at room temperature overnight. In the synthesis of [$RhH(CO)_2$(L–L)] complexes a high-pressure NMR tube was filled with diphosphine (0.06 mmol), [Rh(acac)$(CO)_2$] (0.05 mmol) and [$^2H_8$]toluene (1.2 cm^3). The tube was pressurised to 15 bar syngas and put in an oil-bath at 60 °C for 16 h. No attempts were made to isolate any of the complexes. The NMR spectra are discussed in the Results section. Infrared spectra were measured under atmospheric pressure; broad non-resolved bands were found at 1940–1990 and 1945–1990 cm^{-1} respectively for [$RhH(CO)_2L^2$] and [$RhH(CO)_2L^1$].

Catalysis

In a typical experiment the autoclave was filled with a mixture of a 4 mmol dm^{-3} solution of [Rh(acac)$(CO)_2$] in toluene (0.004 mmol, 1 cm^3), the phosphine (0.04 mmol) and toluene (19 cm^3), under an atmosphere of argon. The autoclave was pressurised with syngas ($CO:H_2$ = 1:1) to 20 bar and the temperature raised to 80 °C in approximately 1 h. Subsequently, oct-1-ene (20 mmol, 3.14 cm^3) and decane (3 mmol, 0.6 cm^3) as internal standard were added under pressure. The samples were quenched with triphenylphosphite to deactivate the catalyst and analysed by gas chromatography. In the hydroformylation experiment in neat oct-1-ene, [Rh(acac)$(CO)_2$] (0.004 mmol, 1 cm^3), L^1 (0.04 mmol) and toluene (1 cm^3) were first pressurised with syngas ($CO:H_2$ = 1:1) to 20 bar and the temperature was raised to 80 °C in approximately 1 h prior to the addition of oct-1-ene (0.134 mol, 21 cm^3) and decane (3 mmol, 0.6 cm^3).

Distribution measurements of the free phosphines

In a typical experiment an accurate solution of the phosphine in Et_2O was prepared. The UV spectra of several dilutions of this stock solution were measured. A wavelength was selected near or at the maximum, and the corresponding absorption coefficient was determined (Table 8). In water, the absorption coefficient at a selected wavelength of the phosphine was determined by following the same procedure for an aqueous solution of the phosphine in 1 mol dm^{-3} H_2SO_4. Next, a series of flasks was filled with diluted aqueous H_2SO_4 solutions of different pH values. An equivalent volume of the organic stock solution was added and each biphasic system was shaken, after which the phases were allowed to separate. Samples were taken from both layers and by using UV spectrometry the concentrations were determined. Finally, the effective pH value of the aqueous layer was measured. Owing to the high volatility of Et_2O and oxygen-sensitive phosphines, all procedures were carried out under argon with syringes and closed glassware.

Rhodium recycling experiments

In a typical titration experiment the autoclave was filled with a mixture of a 4 mmol dm^{-3} solution of [Rh(acac)$(CO)_2$] in toluene (0.012 mmol, 3 cm^3), the phosphine (0.12 mmol) and toluene (12 cm^3). The autoclave was pressurised with syngas ($CO:H_2$ = 1:1) to 20 bar and the temperature was raised to 80 °C in approximately 1 h. Oct-1-ene (20 mmol, 3.14 cm^3) and decane (3 mmol, 0.6 cm^3) were added under pressure. A small sample was taken after 30 min. Next, the autoclave was cooled with ice to below 10 °C and the content was siphoned into a separatory funnel containing demineralised water (15 cm^3). The autoclave was washed twice with toluene (5 cm^3). The combined toluene phases and the aqueous phase were then titrated with a H_2SO_4 solution (L^1 and L^2, pH 0; L^3 and L^4, pH 1.8) until the typical yellow colour of rhodium was partly transferred to the aqueous layer. After phase separation the titration procedure was repeated with smaller volumes of both water and H_2SO_4 solution until the toluene layer, containing the decane, octene and nonanals, was colourless. When emulsions were taken along with the aqueous extractions (in the case of L^4), the amount of toluene which was thus also transferred to the aqueous layer did not exceed 0.5 cm^3. The bright yellow aqueous layers were poured into a Schlenk flask and fresh toluene (20 cm^3) was added. With saturated aqueous $NaHCO_3$ solution the acidic solution was neutralised (L^1 and

Table 8 Selected wavelengths and corresponding absorption coefficients

	Organic solution		Aqueous solution	
Phosphine	λ/nm	10^{-4} ε/dm^3 mol^{-1} cm^{-1}	λ	10^{-4} ε/dm^3 mol^{-1} cm^{-1}
L^1	250	1.97	240	2.51
L^2	255	2.10	268	1.69
L^3	255	2.26	268	1.91
L^4	254	2.12	265	0.98

L^2, to pH 6–6.5; L^3 and L^4, to pH 6.5–7), under rapid stirring. After 45 min the toluene layer was removed and syringed into another flask. The aqueous phase was successively extracted with toluene (2 × 10 and 2 × 5 cm^3) until the aqueous phase was colourless and almost clear. The combined orange-yellow toluene phases were concentrated to 15 cm^3. The autoclave was washed with toluene (20 cm^3) before it was filled with the recycled reaction mixture and pressurised again to 20 bar syngas at 80 °C in 1 h. Oct-1-ene was added and samples were taken when approximately the same extent of conversion was reached as in the first run, as judged from the pressure drop.

In the single-extraction experiment the autoclave content was directly siphoned into a H_2SO_4 solution of appropriate pH (25 cm^3). After phase separation, the separatory funnel and the organic phase were washed with 5 cm^3 of the same aqueous solution.

Rhodium measurements by ICP-AES

The first and the final toluene layer in each recycling experiment (plus the samples taken in the hydroformylation runs), the neutralised aqueous layer, and possibly formed precipitates/emulsions were subjected to rhodium analysis. Analyses by ICP-AES were only done for aqueous samples. Therefore the organic layers were pretreated. After gentle evaporation, the organic residue (and rhodium) was completely oxidised by boiling sulfuric acid (96%) and subsequently added nitric acid (65%). Demineralised water was carefully added to obtain a clear aqueous solution of 50 cm^3. The rhodium atomic spectral lines at 343.489 and 369.236 nm were measured. The concentration detection limits were 0.011 and 0.013 μg cm^{-3}, respectively. The 95%-confidence intervals of the mean measured values were established by applying Student's t-test.

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