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Synthesis, characterisation and ligand properties of a new amphiphilic triphenylphosphine analogue †

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{4-[Bis(2-diethylaminoethyl)aminomethyl]diphenyl}phosphine, N3P, an analogue of triphenylphosphine (TPP) with amphiphilic character, was synthesized and characterised. Its metal complexes [Rh(CO)(N3P)(acac)] and *cis*-[$PtCl_2(N3P)_2$] have been prepared and the crystal structure of the former determined. The feasibility of catalysts formed *in situ* from [$Rh(CO)_2$(acac)] and N3P in the hydroformylation of 1-hexene under homogeneous and biphasic conditions is also demonstrated.

Introduction

Aqueous phase organometallic catalysis has undergone a rapid development over the last few years.[1–3] A simplified process design,[4] an easier catalyst separation and recovery and environmental benefits of using water as a solvent are the main impetus for research in this field. Most of the work carried out so far has dealt with metal complexes carrying ligands modified with non-charged hydrophilic[5] or charged anionic[6–9] or cationic[10–13] substituents which render the complexes water-soluble. Catalysts based on water-soluble ligands simplify process design and facilitate catalyst recovery/recycling when applied in neat water, in biphasic (water/organic) solvent systems or as so-called supported aqueous phase catalyst (SAPC).[14] Yet, independent of the mode of application, for substrates of high hydrophobicity there is an inherent drawback with water-soluble catalysts with regard to reaction rates: the rate is largely controlled by the rate of phase-boundary mass transfer. This problem can partly be solved by addition of co-solvents or surfactants which both facilitate transfer of the substrate into the aqueous catalyst phase but which also inevitably hamper the recovery/recycling of the catalyst.

On the other hand, amphiphilic ligands and complexes thereof which by simple pH adjustments can be transferred between an organic and an aqueous solvent phase may present a better solution to both catalyst separation and slow phase boundary mass transfer. Amphiphilicity of the catalysts enables the reaction to be run homogeneously in an organic solvent, thus avoiding mass-transfer problems and at the same time offers good separability since the catalyst is easily extracted into an aqueous phase after completed reaction. Although less well studied than the more traditional biphasic approach, recently the amphiphilic concept has attained some interest and a number of amphiphilic phosphines have been synthesized and evaluated in catalysis.[15–17] Water-soluble or amphiphilic ligands can conceptually be considered as being composed of different modules, *viz.* a module providing functionality *vis-à-vis* water as a solvent and another module providing functionality *vis-à-vis* the metal ion and the particular application in mind. As indicated by the water solubility of mono- and tri-sulfonated triphenylphosphine (10 g and 1100 g^{-1} respectively) the solubility is largely governed by the charge to molecular mass ratio and two different strategies can be followed to achieve a high water solubility: protonation/deprotonation of a number of chargeable substituents[4–6] or protonation/deprotonation of a single, multiply chargeable substituent. The two strategies might impose different impacts on the electronic and steric properties and also affect the surfactant properties of the parent ligand. The present work follows the second strategy and describes the synthesis and characterisation of the amphiphilic phosphine ligand {4-[bis(2-diethylaminoethyl)aminomethyl]-phenyl}diphenylphosphine (N3P) which can be regarded as a good model for the polyethyleneimine based ligand previously studied in our group.[18] It also describes new rhodium and platinum complexes employing N3P as a ligand, as well as an initial study of their properties in the homogeneous and biphasic hydroformylation of 1-hexene.

Results and discussion

Ligand synthesis, characterisation and properties

Previously we have used a modular concept to assemble water-soluble phosphine ligands, *i.e.* simple coupling of functionalised triarylphosphines to water-soluble polymers.[19] Following a similar protocol, our initial attempt to prepare the target molecule N3P involved the reductive coupling of 4-diphenylphosphinobenzaldehyde to the central nitrogen in bis(2-diethylaminoethyl)amine (TEDETA) as outlined in Scheme 1, route a. Although the method is feasible it is a multistep synthesis and gives a low overall yield. We therefore turned to the more direct approach outlined in Scheme 1, route b. This procedure involves N-alkylation of the amine with *p*-bromobenzyl bromide and from thereon classic phosphine synthesis methodology.[20] Besides better yield and less steps involved, the main advantage of route b is that the amine **1** can be obtained pure by simple distillation and this simplifies the purification of the final product.

Protonation of the nitrogen atoms on N3P renders it highly water-soluble and both the phosphine itself and the metal complexes employing N3P as a ligand are easily extracted from an organic into an acidic aqueous phase. This is demonstrated by the phase distribution between an acidified aqueous phase and diethyl ether displayed in Fig. 1; at a pH <2.5 the phosphine is nearly quantitatively located in the aqueous phase, while at pH >7 it is mainly contained in the organic phase. Deviations from complete phase transfer at high and low pH are mainly due to the surface active properties of the ligand; some ligand remains dissolved in the wrong phase because of micelle/micro emulsion formation.

Methylation of the amine nitrogen atoms should render the

† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/4187/

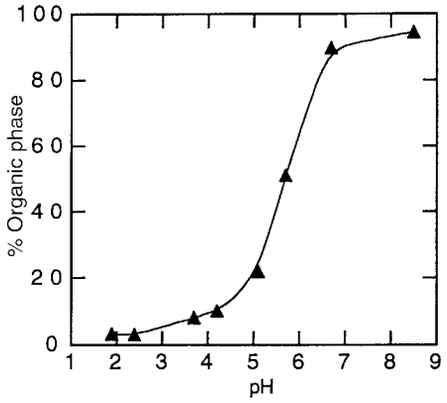
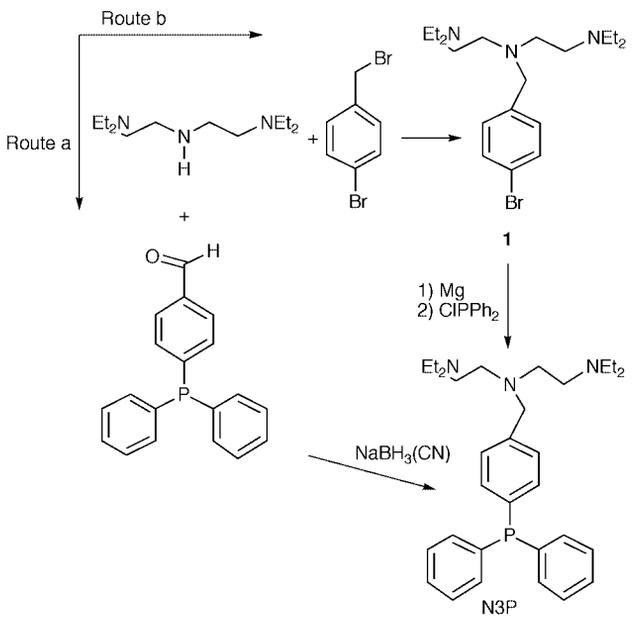


Fig. 1 Extraction curve for N3P.



Scheme 1 Synthesis of N3P, methods a and b.

phosphine N3P water-soluble without alterations in the pH, albeit with ruin of its amphiphilic character. Thus, attempts were made to N-alkylate N3P by methyl iodide to enable the use of the quaternary ammonium salt in a comparative study. We have, however, been unable to methylate the amine nitrogen atoms selectively in the presence of the tervalent phosphine group. An alternative synthetic route to aminomethylated phosphine, employing diphenylphosphinoyl chloride, where the phosphorus atom is oxidised, was therefore investigated. This synthesis went smoothly and final reduction of the oxide by trichlorosilane afforded the N-methylated phosphine in good yield. However, once isolated it showed a rather unexpected solution behaviour involving migration of the methyl group from nitrogen to phosphorus, which precludes its use as a complexing agent. This methyl migration reaction can conveniently be monitored by ^{31}P NMR; a 50 mM methanol solution of the aminomethylated phosphine showed only the quaternised phosphine after 5 h at 35 °C. A similar methyl migration reaction has been observed for aminomethylated phosphines[21] but not for the amphos (2-diphenylphosphinoethyltrimethylammonium) ligand.[22] We believe this to be an effect of closely spaced charges on the quaternised nitrogen atoms which lowers the stability of the quaternised central nitrogen atom. This effect is reflected in the pK_a values of analogous triamines, for which the pK_a of the central nitrogen atom is about 6 units lower than that for the terminal ones.[23]

Triphenylphosphine and its derivatives are strong Lewis bases and weak Brønsted bases. Using protonation of the

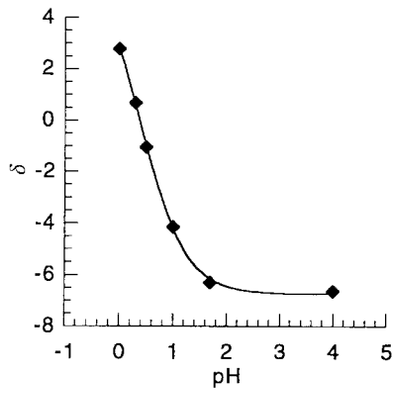


Fig. 2 The ^{31}P shift of N3P plotted against pH.

amine groups as a means to achieve water solubility, the pK_a of the phosphorus atom becomes of interest since it might affect the complexing properties of the phosphine group, *i.e.* the two competing reactions $R_3P + M^+ \longrightarrow R_3P{-}M^+$ and $R_3P + H^+ \longrightarrow R_3P{-}H^+$. This issue also becomes important in the extraction of amphiphilic phosphines from an organic phase to an acidic aqueous phase where a pH close to, or below, the pK_a of the phosphine might affect catalyst recovery.

Acidity constants are commonly determined by titrations. We have, however, determined the pK_a of the phosphorus atom of N3P by measuring the phosphine ^{31}P NMR shift as a function of pH. Owing to deshielding, protonation of the phosphorus atom changes the shift of the phosphine to lower field. The rapid interchange of protons between phosphorus atoms makes partial protonation seen, not as two separate peaks (protonated and free phosphine), but as one peak, its chemical shift being a weighted mean of the two extremes. Plotting the shift against pH results in the curve depicted in Fig. 2.

The assumption that the observed shift (δ) is a weighted mean of the shifts of protonated and free phosphine can be expressed in mathematical terms as in eqn. (1) where x denotes

$$\delta = x_b\delta_b + x_a\delta_a \quad (1)$$

the mol fraction and indices a and b denote acid and base forms respectively. The acidity constant and the total concentration are defined as in eqns. (2) and (3) and eqns. (1), (2) and (3) can

$$[b][H^+]/[a] = K_a \quad (2)$$

$$C_{total} = [a] + [b] \quad (3)$$

be combined to give (4). If the assumption holds, this equation

$$\delta = \frac{\delta_b 10^{-pK_a} + \delta_a 10^{-pH}}{10^{-pH} + 10^{-pK_a}} \quad (4)$$

should give a least-squares fit to the experimental data. Fig. 2 shows a plot of the ^{31}P shift of N3P *versus* pH. The pK_a corresponds to the pH at the inflexion point of the curve, and for the phosphine N3P an experimental pK_a value of 0.35 ± 0.03 (R = 0.999) was obtained.

On cannot exclude that part of the observed shift change in the ^{31}P resonance is caused by protonation of the amine groups, which takes place at a higher pH than that of the phosphine group. Such an effect would thus make the devised NMR method unsuited for determining the pK_a of the phosphine moiety and we have therefore validated the method independently, *i.e.* by UV/VIS spectroscopy.[24] Unprotonated phosphines generally show an absorption peak around 250–260 nm and for N3P the absorption peak is located at 260 nm. Upon lowering the pH the intensity of this peak decreased and another absorption (a peak with two shoulders) appeared at 270 nm. By

plotting the intensity of the absorption of the unprotonated phosphine against pH and fitting the data by an equation similar to (4) a pK_a value of 0.40 ± 0.05 (R = 0.990) was obtained, in good agreement with the value obtained by the ^{31}P NMR method. The negligible influence on the ^{31}P shift upon protonation of the amine groups in the side-chain and hence a further validation of the NMR method is also evident from the shape of the pH *vs.* δ curve which is flat in the region of amine protonation.

Since triphenylphosphine (TPP) has a pK_a value of 2.73,[25] the pK_a value of around 0.4 for N3P is substantially lower than one would expect from mere structural considerations. The low pK_a observed is most likely due to the inductive (−I) effect of the benzylic nitrogen, enhanced by inductive effects of the two terminal nitrogen atoms. Hessler *et al.*[26] found a similar effect in $\{[HMe_2N(CH_2)_2]_3PH\}^{4+}$ $4Cl^-$ (pK_a =1.4) compared to PEt_3 (pK_a = 8.7), and Aquino and Macartney[24] determined acidity constants for a number of water-soluble phosphines by UV/VIS spectroscopy, with similar results.[24]

The steric properties of phosphines can be estimated by the cone angle concept.[27] One way to estimate the cone angle is by measuring the ^{31}P NMR shift of the phosphines (L) in *trans*-$[PdCl_2(L)_2]$.[28] For this purpose the ^{31}P NMR shift of $[PdCl_2(N3P)_2]$ formed *in situ* from $[PdCl_2(PhCN)_2]$ and N3P has been measured. This complex exhibits a resonance at δ 24.7, very close to that of the corresponding TPP complex (δ 23.9). The latter resonance corresponds to a Tolman cone angle of 145° and the close similarity in ^{31}P resonance frequencies can be taken as a good indication that the side chain has no significant effect on the bulkiness of N3P as a complexing agent. This is also expected for a *para* substituted TPP derivative like N3P.

Rhodium and platinum complexes of N3P

Ligand substitution reactions in organic solvent, starting from the respective precursor complexes $[Rh(CO)_2(acac)]$ and $[PtCl_2(EtCN)_2]$, afforded [Rh(CO)(N3P)(acac)] and *cis*-$[PtCl_2(N3P)_2]$ straightforwardly. These two complexes were targeted because their TPP analogues are known to be catalyst precursors in the hydroformylation of alkenes.[29] Besides its dual Brønsted functionality, the N3P ligand with a phosphorus donor site and a triamine side-chain also contains a set of Lewis basic groups, which might complicate its complex forming properties. Despite the potential tridentate nature of the side-chain and the threefold excess of nitrogen over phosphorus, no indication of amine co-ordination has been found for either of the two precursor complexes and both products were isolated in high yield. The rhodium complex yielded crystals suitable for structure determination, whereas we have not been able to grow X-ray quality crystals of the platinum complex. Both complexes have, however, been fully characterised by elemental analysis and spectroscopic means. A doublet at δ 48.7 ($^1J_{RhP}$ 175 Hz) in the ^{31}P NMR spectrum of [Rh(CO)(N3P)(acac)] and a CO stretching frequency at 1974 cm^{-1} are in good agreement with data for the TPP counterpart. Likewise, a doublet at δ 14.7 ($^1J_{PtP}$ 3677 Hz) in the ^{31}P NMR spectrum of $[PtCl_2(N3P)_2]$ is characteristic of a phosphine ligand *trans* to Cl^- which has a weak *trans* influence, *i.e.* a *cis*-configurated complex.

Further attempts to elucidate the chemistry of the two complexes under conditions resembling those in actual hydroformylation experiments revealed the following; on addition of an excess (10:1) of N3P to a methanol solution of [Rh(CO)(N3P)(acac)] the doublet in the ^{31}P spectrum of the parent compound disappeared and a broad peak appeared at δ 23.6. On cooling to −30 °C the broad peak resolved to a doublet ($^1J_{RhP}$ 115 Hz) of unknown origin. No change in the spectrum could be seen on further cooling to −80 °C. On bubbling syngas (H_2:CO 1:1) through the solution the doublet at δ 23.6 decreased and a new doublet appeared at δ 41.0 ($^1J_{RhP}$ 155 Hz). Based on the spectroscopic features of the analogous TPP complex, which resonates at δ 39.8 ($^1J_{RhP}$ 155 Hz, in $CD_3C_6D_5$),[30] the complex formed after reaction with syngas can safely be assigned the formula $[RhH(CO)(N3P)_3]$, which has a trigonal bipyramidal structure and is considered to be the resting state of the catalyst. Further support for the identity of the complex was provided by its ^{1}H NMR (−30 °C) spectrum which showed a quartet at δ −9.8 ($^2J_{PH}$ 13 Hz) with a $^1J_{RhH}$ too small to be detected (<1 Hz).[31]

Table 1 Selected bond distances (Å) and angles (°) for [Rh(CO)L(acac)] (L = N3P or TPP)

	L = N3P	L = TPP
Rh–O(1)	2.034(4)	2.029(5)
Rh–O(2)	2.070(4)	2.087(4)
Rh–C(1)	1.765(8)	1.801(8)
Rh–P	2.2352(12)	2.244(2)
C(1)–O(3)	1.172(7)	1.153(11)
C(3)–O(1)	1.286(6)	1.274(7)
C(5)–O(2)	1.274(8)	1.275(8)
O(1)–Rh–O(2)	88.30(16)	87.9(2)
O(1)–Rh–P	91.61(10)	92.0(1)
C(1)–Rh–P	89.17(19)	87.8(2)
O(2)–Rh–C(1)	90.9(2)	92.4(2)
Rh–C(1)–O(3)	178.0(6)	176.8(9)
Rh–P–C(7)	115.21(13)	114.8(2)
Rh–P–C(13)	115.57(14)	114.7(2)
Rh–P–C(19)	114.51(14)	114.4(2)

An analogous rhodium hydride complex has been shown to be unstable in strongly acidic solutions,[15] and the complex formed from the N3P ligand is no exception in this respect. NMR tube experiments showed that on bubbling syngas through a D_2O solution of N3P and $[Rh(CO)_2(acac)]$ (pH ≈ 3, CH_3SO_3H) no peaks corresponding to the active hydrido complex could be detected. At higher pH the system behaved differently. By carrying out the same experiment, but setting the pH to ≈5 by addition of KOH, a doublet at δ 41 ($^1J_{RhP}$ 153 Hz) corresponding to the complex $[RhH(CO)(N3P)_3]$ appeared in the spectrum. A pH value of 5 can be regarded as a compromise between two conflicting properties, *viz.* the stability of the active hydrido complex and the water solubility. Thus, these NMR experiments indicate that two-phase (water/organic) catalysis, employing N3P as ligand, should be possible given that pH is carefully controlled. This was later confirmed by the hydroformylation experiments (see below).

Hydroformylation activity of the platinum complex $[PtCl_2(N3P)_2]$ requires the addition of $SnCl_2$. All attempts to modify the complex with $SnCl_2$, for the purpose of catalysis, yielded only a yellow-orange compound with very low solubility in common solvents. Assuming that the addition of $SnCl_2$ leads to the expected formation of a complex containing a Pt–$SnCl_3$ moiety one would, because of the high *trans* influence of $SnCl_3^-$, expect a noticeable shift change in the ^{31}P NMR spectrum. Since no such change was observed, despite the use of a large excess of $SnCl_2$, we suggest that the added Sn^{II} mainly participates in complex formation with the tridentate amine chain of the ligand and that this interaction precludes catalytic activity for the N3P–Pt–Sn based system.

Crystal structure of [Rh(CO)(N3P)(acac)]

The crystal structure of [Rh(CO)(N3P)(acac)] revealed the expected square planar co-ordination of the rhodium atom. Deviations from planar geometry are minor, the largest being 0.020(3) Å for C1. Not unexpectedly the crystal showed disorder in the side-chain. In Table 1, with atom numbering according to Fig. 3, selected bond distances and angles in [Rh(CO)(L)(acac)] (L = TPP[32] or N3P) are compared. The close resemblance in bond angles and distances of the two complexes shows that the side-chain does not affect the co-

Table 2 Hydroformylations of 1-hexene at 80 °C, $p(CO/H_2)$ 20 bar, [Rh] = 0.8 mM, [phosphine] = 8 mM, [substrate] = 0.8 M, All entries are mean values of 3 runs. Run 2 employed recycled catalyst from run 1

Type	Solvent	Phosphine	Reaction time/h	Yield (%)	n/i[a]	TOF
Homogeneous	Toluene	N3P				
Run 1			1	57	2.8	736
Run 2 (rec.)			1	48	2.8	622
		TPP	1	58	2.8	741
Biphasic	Water–toluene	N3P	16	32	2.8	10

[a] Normal to branched ratio.

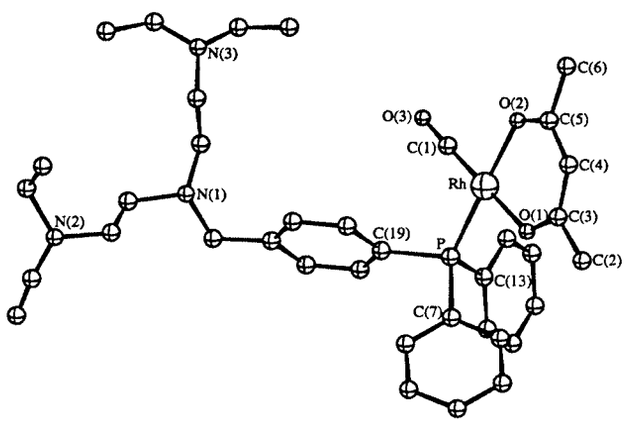


Fig. 3 Crystal structure of [Rh(CO)(N3P)(acac)].

ordination properties of the phosphine to any great extent. Furthermore, the crystal structure reveals no secondary metal–amine interaction as the shortest Rh···N distance found is 6.2 Å.

Hydroformylation activity

Results from hydroformylation experiments employing a catalyst formed *in situ* by mixing the appropriate ligand (N3P or TPP), the precursor complex $[Rh(CO)_2(acac)]$ (Rh : P = 1 : 10) in toluene and with 1-hexene as the substrate are displayed in Table 2. The data given are mean values of a series of experiments. The substrate, 1-hexene, was selected because its low water solubility renders it well suited for demonstrating the advantage of catalysts based on amphiphilic ligands over biphasic catalysis. Moreover, 1-hexene is a substrate for which traditional continuous distillation of the product is not attainable because of severe catalyst decomposition at the temperature required to boil off the product.

First, it is noticeable that under the conditions employed the activity of the N3P-based catalyst is virtually the same as that of the TPP-based catalysts, despite the amino groups on the side-chain in N3P, functional groups which may lower the hydroformylation activity. Secondly, the regioselectivity is the same for the two sytems and in addition to the cone angle discussed above this is yet another indication that the steric properties of N3P are very similar to those of TPP. The presence of amines in hydroformylation reactions is known to promote alcohol formation,[33] and to suppress isomerisation of the alkene.[34] However, only a small amount (<0.5%) of heptanol was detected in the product mixture, and hydrogenated and isomerised products together amount to less than 3.5%.

The N3P based catalyst can be recycled straightforwardly by extraction, but the recycled catalyst loses some of its original activity (85% retained based on TOF). We have not monitored the loss of rhodium in the extraction procedure but previous studies[17] of similar systems have shown a close resemblance in both ligand and catalyst recovery so the rhodium loss is probably only small. The loss in activity is thus mainly due to deactivation processes known to occur in similar systems (*e.g.* orthometallation or formation of phosphido bridged dinuclear species)[35] and those caused by the pH alterations in the extraction procedure.

The experiments employing a biphasic water/toluene solvent system were performed in an analogous manner with a catalyst formed *in situ* from $[Rh(CO)_2(acac)]$ and a tenfold excess of N3P, the pH of the aqueous phase being set to 5 with methanesulfonic acid. The selected pH of the water phase is a compromise between stability of the active hydrido complex and phase-distribution characteristics. From Fig. 1 it is obvious that complete water solubility really requires a pH < 2.5 and at pH 5 the N3P(aq) : N3P(org) ratio is roughly 4 : 1. Despite this the toluene phase was still uncoloured after the reaction thus indicating that the rhodium complex remains in the aqueous phase. The discrepancy between expected and visually observed phase distribution of the catalyst can be accounted for by considering charge to molecular mass ratio as the important parameter in determining water solubility; $[RhH(CO)(L)_2]$ is the active catalyst formed under hydroformylation conditions and this complex carries two phosphine ligands, hence it has a higher water solubility than N3P alone because of a higher charge to molecular mass ratio. Visual inspection can, of course, never reveal smaller amounts of catalyst in the organic phase, and we cannot preclude catalysis taking place in the organic phase.

The reaction rate under biphasic conditions is very low, giving only about 1.4% of the TOF of the same catalyst system in neat toluene (Table 2). This low reaction rate reflects a low rate of phase transfer of 1-hexene between toluene and water under the experimental conditions employed.

All attempts to use $[PtCl_2(N3P)_2]$ as a catalyst precursor in hydroformylation of 1-hexene failed. After 24 h at 100 °C, 50 bar using the unmodified complex no product could be detected. Addition of the co-catalyst $SnCl_2$ caused precipitation of a yellow solid, and applying this solid as a slurry in the hydroformylation reaction gave no product formation.

Conclusion

The phosphine N3P is an amphiphilic phosphine with high solubility in acidic aqueous solutions. For a soft metal centre, such as Rh^I or Pt^{II}, the ligand binds *via* its P-donor site without interference from the amine functions. Metal complexes employing N3P as a ligand are easily extracted from an organic phase to an acidic aqueous phase. The pK_a of the phosphorus atom, as determined by ^{31}P NMR, is approximately 0.4, thus enabling extractions even at very low pH without concomitant protonation of the phosphine moiety. Rhodium complexes of N3P employed as catalysts in the hydroformylation of 1-hexene exhibit features closely resembling those of TPP complexes. Recycling of the catalyst based on the N3P ligand by extractions is possible with relatively high retention of its initial activity.

Experimental

General procedures

All chemicals were from commercial sources except *cis*-$[PtCl_2(EtCN)_2]$,[36] 4-(diphenylphosphino)benzaldehyde[37] and

N,*N*,*N*″,*N*″-tetraethyldiethylenetriamine (TEDETA),[38] which were synthesized according to literature procedures. Solvents and chlorodiphenylphosphine were distilled prior to use, otherwise the chemicals were used as received. Solvents used in the synthesis and manipulation of the phosphines were thoroughly degassed with N_2 or Ar prior to use.

The NMR spectra were recorded at 21 °C on a Varian Unity 300 MHz spectrometer with an observation frequency of 121 MHz for ^{31}P (referenced to 85% H_3PO_4) and of 300 MHz for ^{1}H (referenced to $SiMe_4$), IR Spectra on a Nicolette FT-IR spectrometer as Nujol mulls or KBr plates and UV/VIS spectra on a Milton Roy 3000 spectrophotometer. The pH measurements for the NMR experiments were carried out using a standard glass electrode, calibrated with standard buffer solutions at pH 1 and 4.

Hydroformylation reactions

The hydroformylations were performed in a glass vessel contained in a Roth 50 ml stainless steel autoclave with a 1:1 $CO:H_2$ gas mixture at 20 bar pressure. In the homogeneous experiments 0.04 mmol phosphine and 0.004 mmol rhodium precursor together with the internal standard (3-methylnaphthalene) were dissolved in 5 ml of toluene in the glass vessel. Syngas was then bubbled through the solution for 10 min after which 500 μl 1-hexene were added. The glass vessel was placed in the autoclave together with a magnetic stirring bar. The autoclave was closed and pressurised/depressurised 3 times before finally setting the pressure and temperature.

Recycling of the catalysts

After two hours of reaction time the autoclave was cooled to 0 °C and depressurised. The reaction solution was transferred to an argon filled Schlenk tube after which the catalyst was extracted with 3 × 2 ml of acidified water (pH ≈ 1 with methanesulfonic acid). The now uncoloured organic phase was separated and the pH in the combined aqueous phases was set to 12 with a KOH solution. The aqueous phase was extracted with 3 × 1.7 ml toluene and the combined toluene phases used in another catalytic run. The ratio of the TOF in the two runs is taken as a measure of the retained activity.

Biphasic catalysis

The compound N3P (20 mg, 0.04 mmol) was added to a solution of 8 μl methanesulfonic acid in 5 ml of water in a glass vessel under Ar. After stirring for a few minutes, 1.0 mg (0.004 mmol) $[Rh(CO)_2(acac)]$ was added. After dissolution of the solids the pH was set to ≈5 with KOH after which the internal standard and the substrate (500 μl) dissolved in toluene (5 ml) were added. The resulting two phase mixture was then treated in exactly the same manner as for homogeneous runs.

Crystal data and data collection

The data were collected at room temperature on a Siemens SMART CCD diffractometer. The structure was solved by direct methods using the SHELXTL PLUS program package.[39]

Crystal data. $C_{37}H_{51}N_3O_3PRh$, $M = 719.27$, triclinic, space group $P\bar{1}$, $a = 8.937(2)$, $b = 14.420(3)$, $c = 15.427(3)$ Å, $\alpha = 82.42(3)$, $\beta = 88.44(3)$, $\gamma = 75.80(3)°$, $V = 1910.4(7)$ Å^3, $T = 273$ K, Mo-Kα radiation, $\lambda = 0.7107$ Å, $Z = 2$, $D_c = 1.253$ Mg m^3, $F(000) = 758$, yellow plate with dimensions 0.25 × 0.14 × 0.04 mm, $\mu = 0.525$ mm^{-1}, 15771 reflections measured, 10954 unique, used in refinements, $R_{int} = 0.0433$, $R = 0.059$, $R' = 0.120$).

CCDC reference number 186/1701.

See http://www.rsc.org/suppdata/dt/1999/4187/ for crystallographic files in .cif format.

Syntheses

N3P. *Method a.* *N*,*N*,*N*″,*N*″-tetraethyldiethylenetriamine (7.3 g, 34 mmol) was dissolved in methanol (150 ml). The pH of the solution was adjusted to ≈6 with methanesulfonic acid. 4-(Diphenylphosphino)benzaldehyde (5.0 g, 17.2 mmol) was added together with $NaBH_3(CN)$ (0.76 g, 12 mmol). The mixture was stirred at room temperature for 16 h after which the solvent was evaporated and the residue taken up in 1 M HCl (100 ml) and extracted with CH_2Cl_2 (2 × 25 ml). The pH of the aqueous phase was set to ≈12 with KOH after which it was extracted with benzene (2 × 50 ml). The combined benzene phases were dried over $MgSO_4$ and evaporated. Yield 6.1 g (72%) crude product which can be purified by chromatography as in method b.

Method b. *N*,*N*,*N*″,*N*″-Tetraethyldiethylenetriamine (51.0 g, 0.23 mol) was added dropwise with stirring to a solution of 4-bromobenzyl bromide (57.0 g, 0.23 mol) dissolved in absolute ethanol (400 ml) in a three-necked flask. The reaction mixture was stirred for 15 min and then refluxed for 2 h. After cooling, the ethanol was evaporated and the residue taken up in benzene, washed with 10% KOH and saturated NaCl solution and then dried over $MgSO_4$. The benzene was removed and the crude product **1** distilled at 180–185 °C/3 mbar. Yield 74 g (84%) pale yellowish oil. ^{1}H NMR δ ($CDCl_3$): δ 1.0 (t); 2.5 (m); 3.6 (s); 7.1 (d, aromatic) and 7.4 (d, aromatic).

A three-necked flask containing magnesium (2.1 g, 86 mmol) and dried and degassed THF (200 ml) under argon was equipped with a dropping funnel charged with compound **1** (30.0 g, 78 mmol). After addition of a crystal of I_2 and a few ml of **1** to initiate the Grignard reaction, the rest of the contents was added in small portions. When all **1** had been added the reaction solution was stirred for 30 min and then refluxed for 1 h. After cooling to 0 °C chlorodiphenylphosphine (17.2 g, 78 mmol) was slowly added dropwise to the deep red solution. The solution was stirred for 30 min at 0 °C and then refluxed for 16 h. After cooling to room temperature the reaction was quenched with 10% NH_4Cl solution (40 ml) . The solvent was evaporated and the residue taken up in acidified (HCl) water and washed three times with CH_2Cl_2. The pH of the aqueous phase was set to 12 with KOH solution and washed three times with diethyl ether. The ether phases were combined, washed with saturated NaCl solution and dried over $MgSO_4$ after which the ether was evaporated, leaving a yellow oil. Yield: 31 g (82%). The crude N3P was further purified by column chromatography (silica gel 60, ethyl acetate–triethylamine 10:1). ^{1}H NMR ($CDCl_3$): δ 1.0 (t); 2.5 (m); 3.6 (s); and 7.3 (m, aromatic). ^{31}P NMR ($CDCl_3$): δ −5.1 (s). Calc. for $C_{31}H_{44}N_3P$: C, 76.1; H, 9.0; N, 8.6; P, 6.3. Found: C, 76.3; H, 9.1; N, 8.8; P, 6.4%.

Methylation of N3P, formation of methyl iodide salt. The phosphine oxide of N3P was synthesized in a similar way to N3P (method b), using diphenylphosphinoyl chloride instead of chlorodiphenylphosphine, yielding a yellowish oil (77%). The oxide was dissolved in methanol and 5 equivalents of methyl iodide were added dropwise. The reaction mixture was stirred for 16 h and evaporated. The residue was dissolved in acetonitrile, an excess (5 equivalents) of $SiCl_3H$ added dropwise and the mixture refluxed for 17 h followed by removal of remaining $SiCl_3H$ by distillation. Water was added and the solid product was filtered off and discharged. The remaining solution was evaporated leaving a yellow solid. Recrystallisation from acetonitrile–diethyl ether yielded a white powder. ^{1}H NMR ($CDCl_3$): δ 1.3 (t); 2.2 (s); 3.0 (s); 3.5 (q); 3.6 (t); 3.8 (t); 4.4 (s); and 7.3–7.8 (m, aromatic). ^{31}P NMR (D_2O): δ −3.9 (s).

[Rh(CO)(N3P)(acac)]. The compound N3P (100 mg, 0.2 mmol) was dissolved in CH_2Cl_2 (5 ml), $[Rh(CO)_2(acac)]$ (53 mg, 0.2 mmol) in CH_2Cl_2 (5 ml) added dropwise and the solution stirred at room temperature for 30 min. After evaporation the residue was taken up in *n*-pentane (5 ml). Storing at −30 °C overnight yielded 130 mg (90%) of yellow crystals. ^{1}H NMR ($CDCl_3$): δ 1.0 (t); 1.6 (s); 2.1 (s); 2.5(m); 3.6 (s); 5.4 (s) and 7.3–

7.6 (m, aromatic). ^{31}P NMR ($CDCl_3$): δ 48.7 (d) $^1J_{RhP}$ 175 Hz. IR (KBr, cm^{-1}): ν(CO) 1974. Calc. for $C_{37}H_{51}N_3O_3PRh$: C, 61.8; H, 7.1; N, 5.8; O, 6.7; P, 4.3. Found: C, 61.6; H, 7.3; N, 5.8; O, 7.0; P, 4.6%.

***cis*-[$PtCl_2$(N3P)$_2$].** A solution of *cis*-[$PtCl_2(EtCN)_2$] (125 mg, 0.33 mmol) in CH_2Cl_2 (5 ml) was added to N3P (350 mg, 0.72 mmol) in CH_2Cl_2 (5 ml). The mixture was stirred at room temperature for 16 h. After the solvent had been removed, the oily residue was stirred with *n*-pentane. A white solid precipitated which was washed with pentane and dried in vacuum. Yield: 370 mg (90%). ^{31}P NMR ($CDCl_3$): δ 14.7 (d), $^1J_{RhP}$ 3677 Hz. Calc. for $C_{62}H_{88}Cl_2N_6P_2Pt$: C, 59.8; H, 7.1; Cl, 5.7; N, 6.7; P, 5.0. Found: C, 59.3; H, 7.1; Cl, 5.8; N, 6.7; P, 5.1%.

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