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Bis(phosphine) derivatives of diamines

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Abstract

The synthesis, oxidation and coordination chemistry of new bis(aminophosphines) based on diamines is demonstrated. $Ph_2PN(CH_2Ph)CH_2CH_2(CH_2Ph)NPPh_2$, $^iPr_2PN(CH_2Ph)CH_2CH_2(CH_2Ph)NP^iPr_2$, $Ph_2PNH(C_{10}H_6)_2NHPPh_2$, $Ph_2PNH(C_{10}H_6)(C_6H_4)NHPPh_2$ were prepared and tested in the hydroformylation of hex-1-to give aldehydes with poor selectivity (up to l:b = 2.5:1) to the desired linear products. Modelling calculations were performed for all ligands. R_2 groups enlarge the natural bite angle when going from $R_2 = Ph_2$ to $R_2 = {}^iPr_2$ which are more bulky. Most of the ligands seem to be rigid (with flexibility ranges of 25°–46°). Four demonstrative X-ray structures are reported.

Keywords: Ligand; Catalysis; X-ray structure; Complex

1. Introduction

Hydroformylation of alkenes is a very important catalytic reaction in industry and great effort has been devoted to obtaining highly active and selective catalysts [1–6]. This is a very important area of investigation since it has been extensively reported that selective catalytic processes are affected by many factors such as the configuration that the ligand may have, i.e., its bite angle and its range of flexibility and the electronic properties of the ligands when binding the precursor metal species [7–12]. These factors influence the direction of approach of the substrate to the active catalyst and therefore the selectivity of the reaction.

By altering the substituents on the phosphorus atoms and keeping the same diamine backbone (piperazine and homopiperazine) [13,14] we were able to conduct a systematic study on the electronic and steric effects of a wide range of the bis(aminophosphines) derivatives of piperazine and homopiperazine. In recent work [13–22], we studied synthesis of new P–N containing ligands and the effect of the electronic properties of different ligands on the regioselectivity of rhodium catalysed hydroformylation of alkenes. Continuing our studies on the preparation of potentially active ligands for homogeneous catalysis, we investigated the synthesis, oxidation and coordination chemistry of new bis(aminophosphines) based on simple diamines in anticipation that the resulting phosphines will have different steric and electronic properties. Here, we report the synthesis of two new phosphines together with hydroformylation studies and four demonstrative X-ray structures.

2. Results and discussion

Reaction of *N*,*N*′-dibenzylethylenediamine with two equivalents of R_2PCl gives **1** and **2** (Eq. (1)). **1** was first prepared by Payne and Stephan [23] and later by Balakrishna et al. [24]. However, they did not report IR or FAB^+ mass spectrometry data and neither did they study its oxidation chemistry nor its activity in homogeneous catalysis. Therefore, we considered it to be of interest to study this compound further, including the preparation of its diselenide derivative and the study of its activity in rhodium catalysed hydroformylation of alkenes whilst **2** offers a steric and electronic variant in this regard.

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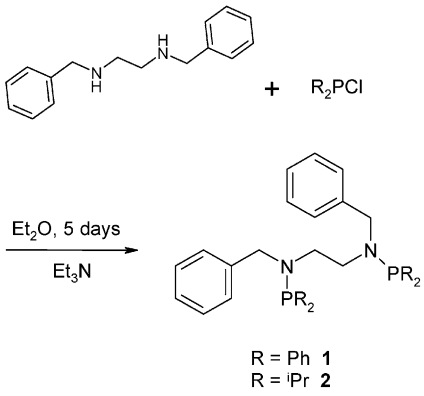


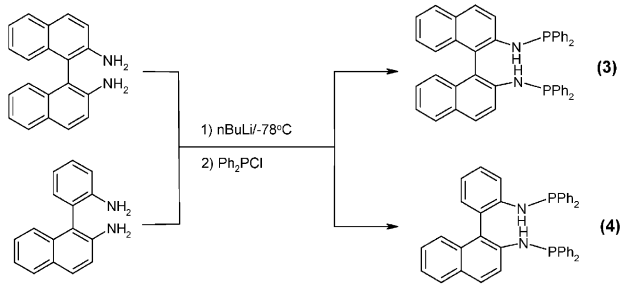
(1)

FAB$^+$ mass spectrometry confirms the proposed identity of the ligands by showing the expected parent-ion peaks and elemental analysis data is in agreement with calculated values.

The $^{31}P\{^1H\}$ NMR spectrum of **2** displays a singlet at δ (P) 89.1 ppm, the large downfield shift when compared to **1** (δ (P) 66.5 ppm) reflecting the close proximity of the phosphorus centres to the isopropyl substituents in **2** instead of the phenyl groups in **1**.

Crystals of compound **2** (Fig. 1) suitable for X-ray analysis were obtained by recrystallisation of the compound from hot toluene. The molecular structure shows that the P–N bonds adopt a *trans* orientation relative to one another. The molecule has a centre of symmetry and, thus, the bond lengths and angles are equal for the two halves of the molecule. P–N bond lengths are typical for this type of compound. The phosphorus atoms adopt a flattened tetrahedral geometry with C–P–N angles somewhat less than 109°, whilst the nitrogen centres have trigonal character (P–N–C angles are closer to 120° than 109°) though the P–N bond is quite long.

Reaction of (S)-(−)-1,1′-binaphthyl-2,2′-diamine and 1-(2-aminophenyl)-2-naphthalene with two equivalents of Ph_2PCl, after deprotonation by *n*BuLi, proceeds in thf to give $Ph_2PNH(C_{10}H_6)_2NHPPh_2$ (**3**) (BDPAB) and $Ph_2PNH(C_{10}H_6)(C_6H_4)NHPPh_2$ (**4**), respectively (Eq. (2))



(2)

The $^{31}P\{^1H\}$ NMR spectrum of **3** comprises a singlet at δ (P) 27.7 ppm. The identity of this compound is supported by FAB$^+$ mass spectrometry (m/z 652 [M$^+$]) and the IR spectrum, because a band associated with a ν(N–H) stretch (3330 cm^{-1}) is observed. ^1H NMR and elemental analysis data are in agreement with the literature. It presents interesting characteristics such as its structural rigidity and chirality and, although it is not a new bis(aminophosphine) [25,26], we considered it important to study it because its, the ligand had not been tested in the rhodium catalysed hydroformylation of alkenes. Recrystallisation from hot toluene gives **3** as colourless crystals. The X-ray structure (Fig. 2) reveals

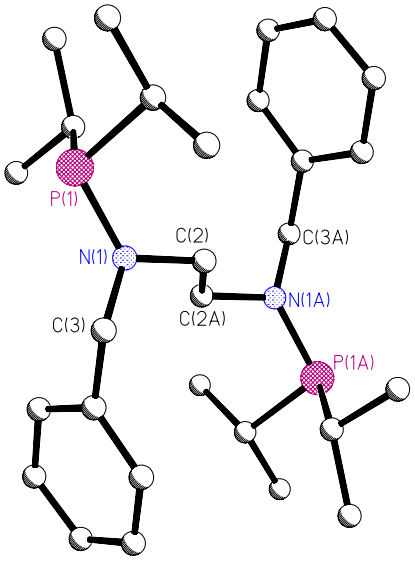


Fig. 1. Solid state structure of $^iPr_2PN(CH_2Ph)CH_2CH_2(CH_2Ph)NP^iPr_2$ **2**. Selected bond lengths (Å) and angles (°) N(1)–P(1) 1.704(2), P(1)–C(13) 1.850(3), P(1)–C(10) 1.856(3), N(1)–C(3) 1.466(3), C(3)–N(1)–C(2) 114.9(2), C(3)–N(1)–P(1) 116.26(17), C(2)–N(1)–P(1) 123.11(17), N(1)–P(1)–C(13) 100.49(13), N(1)–P(1)–C(10) 105.72(12), C(13)–P(1)–C(10) 102.85(17).

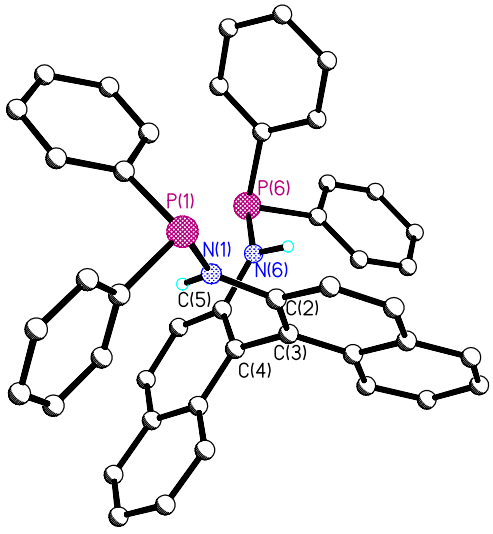


Fig. 2. Solid state structure of $Ph_2PNH(C_{10}H_6)_2NHPPh_2$ **3**. Selected bond lengths (Å) and angles (°) P(1)–N(1) 1.7043(19), P(1)–C(25) 1.836(2), P(1)–C(19) 1.835(2), N(1)–C(2) 1.402(3), C(5)–N(6) 1.403(3), N(6)–C(6) 1.7115(18), N(1)–P(1)–C(25) 103.32(10), N(1)–P(1)–C(19) 99.54(10), C(25)–P(1)–C(19) 101.25(10), C(2)–N(1)–P(1) 125.33(16) C(5)–N(6)–P(6) 126.38(15), N(6)–P(6)–C(7) 99.73(9), N(6)–P(6)-C(13) 102.33(10), C(7)–P(6)–C(13) 99.68(10).

an interesting orientation of the naphthyl rings of the amine backbone relative to one another with a dihedral angle of 98° P–N bond lengths are typical for this type of compound. The two nitrogen atoms in the molecule adopt a geometry close to trigonal whilst, like **2** the phosphorus centres are flattened from tetrahedral.

The magnitude of P–Se J values can be used to assess the donor ability of phosphines [32,33] with better donors having lower $^1J\{^{77}Se–^{31}P\}$ values, as a consequence of the degree of s character in the phosphorus lone pair, etc., i.e., larger coupling constants imply more s character and a poorer donor. Reaction of **1** and **2** with two equivalents of elemental selenium in toluene proceeds smoothly to give $Ph_2P(Se)N(CH_2Ph)CH_2CH_2(CH_2Ph)NP(Se)Ph_2$ (**5**) and $^iPr_2P(Se)N(CH_2Ph)CH_2CH_2(CH_2Ph)NP(Se)^iPr_2$ (**6**). The $^{31}P\{^1H\}$ NMR spectra of **5** and **6** consist of singlets at δ (P) 70.8 and δ (P) 104.1 ppm, respectively, shifted-downfield from the free ligand in both cases, with $^1J(^{77}Se–^{31}P)$ coupling constants of 777 and 741 Hz, respectively, which are in accord with values previously reported for similar selenides [27–31] and suggest that as expected **2**, with electron donating alkyl groups, is the better donor system.

5 and **6** show, in their IR spectra, bands that can be assigned to ν(P–N) [943 cm^{-1} for **5** and 936 cm^{-1} for **6**] and ν(P–Se) at 557 cm^{-1} for **5** and 594 cm^{-1} for **6**.

Slow diffusion of diethyl ether into a dichloromethane solution of **6** gives the product as colourless crystals suitable for X-ray analysis (Fig. 3). The molecular structure shows that the P=Se bonds adopt a *trans* orientation relative to one another. The P–N bond is significantly shorter in this P(V) compound compared to the parent P(III) system which is somewhat counter-intuitive and suggests that in **2** there may be some antibonding π character in the P–N linkage. The P=Se bond lengths are typical for this type of compound. The phosphorus atoms are close to tetrahedral – implying that the selenium atom in **6** is less stereochemically active than the lone pair in **2**.

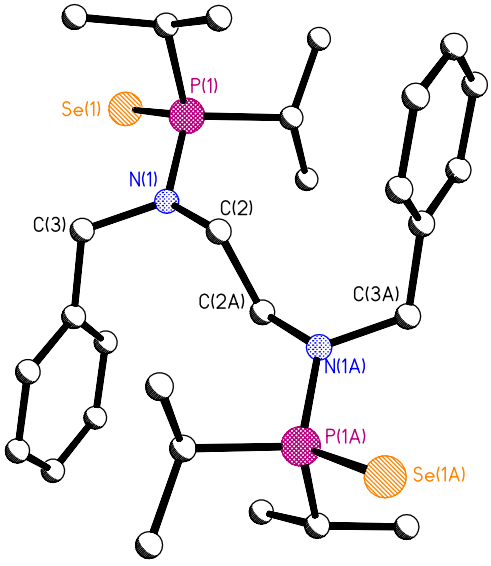
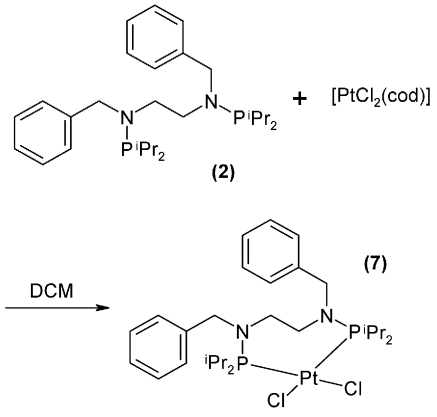


Fig. 3. Solid state structure of $^iPr_2P(Se)N(CH_2Ph)CH_2CH_2(CH_2Ph)NP(Se)^iPr_2$ **6.** Selected bond lengths (Å) and angles (°): Se(1)–P(1) 2.1115(10), P(1)–N(1) 1.679(3), P(1)–C(10) 1.822(4), P(1)–C(13) 1.853(4), N(1)–C(3) 1.477(4), N(1)–C(2) 1.475(4), N(1)–P(1)–C(10) 105.63(18), N(1)–P(1)–C(13) 109.80(17), C(10)–P(1)–C(13) 107.1(2), N(1)–P(1)–Se(1) 111.94(11), C(10)–P(1)–Se(1)111.31(15), C(13)–P(1)–Se(1) 110.86(13), C(3)–N(1)–C(2) 114.3(3), C(3)–N(1)–P(1) 118.9(2), C(2)–N(1)–P(1) 121.2(2).

Reaction of **2** with equimolar quantities of $[PtCl_2(cod)]$ in dichloromethane gives the seven-membered, *P P′* chelate *cis*-$[PtCl_2\{^iPr_2PN(CH_2Ph)CH_2CH_2N(CH_2Ph)P^iPr_2\}]$ **7**.



as a colourless solid in good yield (82%).

The $^{31}P\{^1H\}$ NMR spectrum of **7** consists of a singlet (δ (P) 86.7 ppm) with a $^1J(^{195}Pt–^{31}P)$ coupling constants of 4106 Hz. The analogous platinum complex with ligand **1** shows a very similar $^1J(^{195}Pt–^{31}P)$ (4048 Hz) and a singlet (δ (P) 59.1 ppm) at almost 27 ppm upfield because of the presence of phenyl groups on the phosphorus atoms instead of the more electron donating isopropyl groups present in **7**.

FAB^+ mass spectrometry does not show the parent-ion peak and shows instead fragmentation patterns consistent with the loss of one or two chloride ions (m/z) 702/3 [M–Cl^-] and 666/8 [M–$2Cl^-$] and the IR spectrum of **7** shows bands for ν(P–N) (887 cm^{-1}) and ν(Pt–Cl) (337 and 326 cm^{-1}) which supports the *cis* geometry of **7**.

Recrystallisation from hot toluene gives **7** as colourless crystals suitable for X-ray analysis. The X-ray structure of **7** (Fig. 4 and Table 2) reveal that the ligand is bound in a bidentate coordination mode to the platinum centre with *cis* geometry. The complex forms a seven-membered Pt–P–N–C–C–N–P ring and the metal has distorted square planar geometry because the bite angle of the ligand is larger than the ideal 90° and Cl–Pt–Cl is smaller than 90°. The P–N distances are typical of a single bond and are, as was the case for **6**, shorter than that in **2** (see Fig. 4).

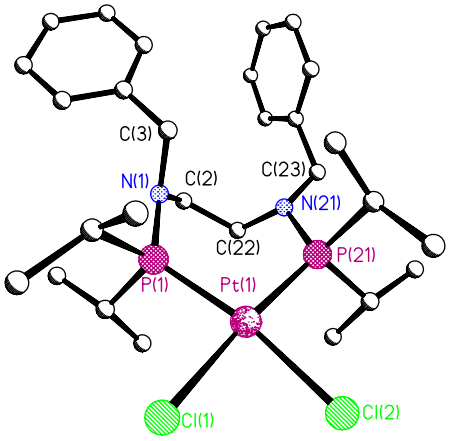


Fig. 4. Solid state structure of *cis*-[$PtCl_2\{^iPr_2PN(CH_2Ph)CH_2CH_2N(CH_2Ph)P^iPr_2\}$] **7**. Selected bond lengths (Å) and angles (°): Pt(1)–P(21) 2.2531(8), Pt(1)–P(1) 2.2594(8), Pt(1)–Cl(1) 2.3724(8), Pt(1)–Cl(2) 2.3777(8), P(1)–N(1) 1.6843(19), P(1)–C(10) 1.844(3), P(1)–C(13) 1.888(2), N(1)–C(3) 1.467(3), N(1)–C(2) 1.489(3), P(21)–Pt(1)–P(1) 100.64(3), P(21)–Pt(1)–Cl(1) 174.60(3), P(1)–Pt(1)-Cl(1) 84.74(3), P(21)–Pt(1)–Cl(2) 88.64(3), P(1)–Pt(1)–Cl(2) 170.44(2), Cl(1)–Pt(1)–Cl(2) 86.01(3), N(1)–P(1)–C(10) 103.84(12), N(1)–P(1)–C(13) 101.26(11), C(10)–P(1)–C(13) 106.58(12), N(1)–P(1)–Pt(1) 123.57(8), C(10)–P(1)–Pt(1) 107.82(9), C(13)–P(1)–Pt(1) 112.42(9), C(3)–N(1)–C(2) 112.06(19), C(3)–N(1)–P(1) 122.52(16),C(2)–N(1)–P(1) 119.13(17).

Ligands **1–4** were tested in the rhodium catalysed hydroformylation of hex-1-ene using a simple batch autoclave (Table 1) Generally the linear:branched selectivity is not particular impressive. We conducted simple molecular modelling calculations (Spartan Pro) of the natural bite angle (β_n) according to the method of Casey and co-workers [34,35] as well as the flexibility range of the ligand (Table 1) since van Leeuwen has proposed that ligands with a natural bite angle of 112°–120° favour equatorial–equatorial coordination during the catalytic cycle and thus give better l:b ratios. We have found a relatively poor correlation between natural bite angle (which specifically ignores metal orbital electronic effects) and the real bite angles, although generally the so-called natural bite angle is somewhat larger than either calculated or measured 'real' bite angle [36,37]. The results obtained with the ligands **1–4** which have natural bite angles in the range 108.9°–127.7° do not support the hypothesis that there is a correlation between bite angle and selectivity (see Table 2).

This work illustrates the usefulness of P–N containing ligands in hydroformylation, in particular the ease of the simple P–N bond forming reaction enables rapid screening of different ligand bite angles and electronic properties. Further work is in progress.

Table 1
Hydroformylation of oct-1-ene catalysed by rhodium complexes with batch autoclave test unit at 100 °C and 20 bar CO/H_2 (1:1); all reactions gave 100% conversion

Compound	Formula	Time (h)	Selectivity to aldehyde %	l:b	β_n	Flexibility range
1	$Ph_2PN(CH_2Ph)CH_2CH_2(CH_2Ph)NPPh_2$	22.2	79.8	1.9:1	108.9	28
2	$^iPr_2PN(CH_2Ph)CH_2CH_2(CH_2Ph)NP^iPr_2$	5	78.4	1.2:1	127.7	25
3	$Ph_2PNH(C_{10}H_6)_2NHPPh_2$	13.9	94.5	1.8:1	120	46
4	$Ph_2PNH(C_{10}H_6)(C_6H_4)NHPPh_2$	13.9	86.1	2.3:1	115.5	33

β is the natural bite angle [35].

Table 2
Details of the X-ray data collections and refinements

Compound (local ID number)	**2**	**3**	**6**	**7**
Empirical formula	$C_{28}H_{46}N_2P_2$	$C_{44}H_{34}N_2P_2$	$C_{28}H_{46}N_2P_2Se_2$	$C_{28}H_{46}N_2P_2Cl_2Pt$
M	472.6	652.7	630.5	738.6
Crystal system	triclinic	triclinic	orthorhombic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	*Pbca*	$P2(1)/n$
a (Å)	8.392(2)	10.4672(19)	16.1838(7)	10.308(2)
b (Å)	9.344(4)	11.128(2)	13.6979(6)	22.822(4)
c (Å)	11.192(5)	15.555(3)	14.2025(7)	13.710(3)
α (°)	87.53(4)	89.499(3)		
β (°)	76.43(3)	85.136(3)		110.145(2)
γ (°)	61.64(2)	71.093(3)		
U (Å^3)	748	1708	3148	3028
Z	1	2	4	4
D_c (g cm^{-3})	1.049	1.269	1.330	1.620
μ (mm^{-1})	0.162	0.162	2.468	4.936
T (K)	293	125	293	125
Reflections measured	2263	8538	12,551	13,700
Independent reflections (R_{int})	1561(0.0174)	4776(0.0245)	2229(0.1166)	3924(0.1381)
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0464, 0.1174	0.0389, 0.0951	0.0352, 0.0841	0.0531, 0.1147

3. Experimental

General conditions for the syntheses and catalytic studies were as previously described [13,14].

$Ph_2PN(CH_2Ph)CH_2CH_2(CH_2Ph)NPPh_2$ ***1*** was prepared following the procedure of Balakrishna et al. [24].

A dry and degassed Et_2O (20 ml) solution of chlorodiphenylphosphine (3.2 ml, 3.95 g, 17.95 mmol) was added dropwise over a period of 30 min to a stirred solution of *N*,*N*′-dibenzylethylenediamine (2.050 g, 8.51 mmol) and triethylamine (2.4 ml, 1.72 g, 16.99 mmol) in dry and degassed Et_2O (20 ml) at 0 °C. Stirring was continued overnight, during which time a white precipitate separated from the colourless solution. This precipitate was isolated by suction filtration and consecutively washed with water, methanol and diethyl ether. The product was dried under *vacuum* to give a white solid which was crystallised from CH_2Cl_2–hexane. Yield: 4.25 g, 82%; Microanalysis: Found: (*Anal.* Calc.) C, 78.6 (78.9); H, 6.7 (6.3); N, 4.7 (4.6)%; $^{31}P\{H\}$ NMR ($CDCl_3$): 66.5 (s) ppm; Selected IR data (KBr): *v*(PN) 916 cm^{-1}; FAB^+ MS: *m*/*z* 610 $[M+H]^+$, 632 $[M+Na^+]$.

$(^iPr)_2PN(CH_2Ph)CH_2CH_2(CH_2Ph)NP(^iPr)_2$ ***2***. A dry and degassed Et_2O (10 ml) solution of chlorodiisopropylphosphine (3.5 ml, 3.386 g, 22.00 mmol) was added dropwise over a period of 30 min to a stirred solution of *N*,*N*′-dibenzylethylenediamine (2.5 ml, 2.644 g, 11.00 mmol) and triethylamine (3.1 ml, 2.23 g, 22.00 mmol) in dry and degassed Et_2O (40 ml). Stirring was continued for 5 days. The solution was evaporated to dryness in vacuo and thf (30 ml) was added. Triethylammonium hydrochloride separated from the colourless solution. This precipitate was removed by suction filtration under nitrogen. The filtrate was evaporated to dryness in vacuo to give a yellowish oil. Crystallisation from hot toluene gave white crystals.: Yield: 2.391 g, 46%; Microanalysis: Found: (*Anal.* Calc.) C, 70.7 (71.2); H, 10.3 (9.8); N 5.8 (5.9)%; $^{31}P\{H\}$ NMR ($CDCl_3$): 89.1 (s) ppm; FAB^+ MS: *m*/*z* 473 $[M+H^+]$.

$Ph_2PNH(C_{10}H_6)_2NHPPh_2$ ***3*** was prepared following the method of Miyano et al. [25,26].

A dry and degassed thf (10 ml) solution of (S)-(−)-1,1′-binaphthyl-2,2′-diamine (0.446 g, 1.57 mmol) was cooled to −78 °C in an acetone–dry Ice bath. To the cooled solution was added dropwise a hexane solution of BuLi (1.3 ml, 2.5 mol dm^{-3}, 3.28 mmol) over 30 min. After the addition the mixture was stirred at −78 °C for 1 h and another 30 additional min at room temperature. The reaction solution was cooled to −78 °C again and to it was added dropwise a solution of diphenylchlorophosphine (0.6 ml, 0.709 g, 3.21 mmol) in thf (10 ml) over 1 h. Stirring was continued for another 1 h at −78 °C. Then the cooling bath was removed and the mixture was stirred overnight at room temperature. The solution was evaporated to dryness in vacuo and dichloromethane (30 ml) was added. Lithium chloride, which precipitated, was removed by filtration under nitrogen and then the volatiles were evaporated in vacuo to leave a white solid. Recrystallisation from ethanol–benzene gave white crystals. $^{31}P\{H\}$ NMR ($CDCl_3$): 27.7 (s) ppm. IR, Mass Spectroscopy, ^1H NMR and elemental analysis are in agreement with literature data.

$Ph_2PNH(C_{10}H_6)(C_6H_4)NHPPh_2$ ***4***. A dry and degassed thf (25 ml) solution of 1-(2-aminophenyl)-2-naphthylamine (0.998 g, 4.26 mmol) was cooled to −78 °C in an acetone–dry Ice bath. To the cooled solution was added dropwise a hexane solution of BuLi (3.6 ml, 2.5 mol dm^{-3}, 8.91 mmol) over 50 min. After the addition, the mixture was stirred at −78 °C for 1 h and another 30 additional min at room temperature. The reaction solution was cooled to −78 °C again and to it was added dropwise a solution of diphenylchlorophosphine (1.6 ml, 1.928 g, 8.74 mmol) dissolved in thf (10 ml) over 1 h. Stirring was continued for another 1 h at −78 °C. Then the cooling bath was removed and the mixture was stirred overnight at room temperature. The solution was evaporated to dryness in vacuo and dichloromethane (30 ml) was added. Lithium chloride, which precipitated, was removed by filtration under nitrogen and then the volatiles were evaporated in vacuo to leave a white solid. Yield: 2.362 g, 92%; Microanalysis: Found: (*Anal.* Calc.) C, 79.4 (79.7); H, 5.2 (5.4); N, 4.6 (4.7)%; ^1H NMR: δ 7.86–6.86 ppm (m, 20 H, aromatic), 4.3 ppm (d, 1 H, $^2J(PH) = 78.3$ Hz, NH), 4.7 ppm (d, 1 H, $^2J(PH) = 78.3$ Hz, NH); $^{31}P\{H\}$ NMR ($CDCl_3$): 28.8 (s), 28.1 (s) ppm; Selected IR data (KBr): *v*(NH) 3367 and 3322 cm^{-1}, *v*(PN) 891 and 889 cm^{-1}; FAB^+ MS: *m*/*z* 603 $[M+H^+]$.

$Ph_2P(Se)N(CH_2Ph)CH_2CH_2(CH_2Ph)NP(Se)Ph_2$ ***5***. To a dry and degassed toluene (10 ml) solution of selenium (0.026 g, 0.33 mmol) was added solid $Ph_2PN(CH_2Ph)$ $CH_2CH_2(CH_2Ph)NPPh_2$ (0.100 g, 0.16 mmol). The solution was heated to reflux for ca. 2–3 h and allowed to cool to room temperature. The solution was evaporated to dryness in vacuo and the solid was dissolved in dichloromethane (2 ml). The dichloromethane solution was filtered through Celite and diethyl ether (20 ml) was added. The white product was collected by suction filtration and washed with diethyl ether (2×10 ml). Yield: 0.108 g, 88%; Microanalysis: Found: (Anal. Calc.) C, 62.9 (62.7); H, 4.6 (5.0); N, 3.6 (3.6)%; $^{31}P\{H\}$ NMR ($CDCl_3$): 70.8 (s) ppm, $^1J(^{77}Se–^{31}P)$ 777 Hz; Selected IR data (KBr): *v*(PN) 943 cm^{-1}, *v*(PSe) 557 cm^{-1}; FAB^+ MS: *m*/*z* 768 $[M+H^+]$.

$(^iPr)_2P(Se)N(CH_2Ph)CH_2CH_2$ $(CH_2Ph)NP(Se)(^iPr)_2$ ***6***. To a dry and degassed toluene (5 ml) solution of selenium (0.055 g, 0.70 mmol) was added $(^iPr)_2PN(CH_2Ph)CH_2CH_2(CH_2Ph)NP(^iPr)_2$ (0.165 g, 0.35 mmol) in toluene (5 ml). The solution was heated to reflux for ca. 2–3 h and allowed to cool to room temperature. The solution was evaporated to dryness in vacuo and the solid was dissolved in dichloromethane

(2 ml). The dichloromethane solution was filtered through Celite and diethyl ether (20 ml) was added. The white product was collected by suction filtration and washed with diethyl ether (2 × 10 ml). Recrystallisation from Toluene–hexane gave crystals. Yield: 0.159 g, 72%; Microanalysis: Found: (*Anal*. Calc.) C, 53.8 (53.3); H, 7.7 (7.4); N, 4.4 (4.4)%; $^{31}P\{H\}$ NMR ($CDCl_3$): 104.1 (s) ppm, $^{1}J(^{77}Se–^{31}P)$ 741 Hz; Selected IR data (KBr): ν(PN) 936 cm^{-1}, ν(PSe) 594 cm^{-1}; FAB^+ MS: *m/z* 630/2 [M], 655 [M+Na^+].

cis-[PtCl$_2${(^{i}Pr)$_2$PN(CH$_2$Ph)CH$_2$ CH$_2$(CH$_2$Ph)NP(^{i}Pr)$_2$}] 7. To a dichloromethane (10 ml) solution of [$PtCl_2$(cod)] (0.195 g, 0.52 mmol) was added (^{i}Pr)$_2$PN(CH$_2$Ph)CH$_2$CH$_2$(CH$_2$Ph)NP(^{i}Pr)$_2$ (0.246 g, 0.52 mmol) in dichloromethane (5 ml) and the colourless solution stirred for ca. 2–3 h. The solution was concentrated under reduced pressure to ca. 1 ml and diethyl ether (10 ml) added. The white product was collected by suction filtration and washed with diethyl ether (2 × 10 ml). Yield: 0.315 g, 82%; $^{31}P\{H\}$ NMR ($CDCl_3$): 86.7 (s) ppm, $^{1}J(^{195}Pt–^{31}P)$ 4106 Hz; Selected IR data (KBr): ν(PN) 887 cm^{-1}, ν(PtCl) 337 and 326 cm^{-1}; FAB^+MS: *m/z* 702/3 [M–Cl^-], 666/8 [M–2Cl^-].

Catalytic studies [Rh(acac)(CO)$_2$] (0.01 mol dm^{-3}), phosphine (0.023 mol dm^{-3}), hex-1-ene(1 cm^3) were reacted in toluene (4 cm^3) at 100 °C and 20 bar CO/H_2 (1:1) for time stated in Table 1. The rhodium complex, phosphine and toluene were heated at 100 °C and 14 bar CO/H2 (1:1) for 45 min, to allow the active catalyst to form before injection of the hex-1-ene and pressurising to 20 bar.

Crystallography was performed using a Bruker SMART diffractometer; full hemisphere of data with 0.3° 'slices', room temperature, Mo Kα radiation and empirical absorption corrections. All of the non-H atoms were refined anisotropically with the hydrogen atoms being refined in idealised geometries. All calculations employed the SHELXTL program system [38].

4. Supplementary materials

Crystallographic data for the structural analyses has been deposited with the Cambridge Crystallographic data centre, CCDC Nos. 221581–221584 Copies of this information may be obtained free of charge from The Director CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (Fax +44 1223 336-033 or E-mail deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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