Aminophobanes: hydrolytic stability, tautomerism and application in Cr-catalysed ethene oligomerisation†

Mairi F. Haddow,†a Judit Jaltai,a Martin Hanton,†b Paul G. Pringle,*a Laura E. Rush,a Hazel A. Sparkesa and Christopher H. Woodallb

9-Amino-9-phosphabicyclo[3.3.1]nonanes, (PhobPNHR; R = Me or iPr) are readily prepared by aminolysis of PhobPCl and are significantly less susceptible to hydrolysis than the acyclic analogues Cy2PNHR. Treatment of Cy2PNHMe with Cy2PCl readily gave Cy2PNMePCy2. By contrast, treatment of PhobPCl with PhobPNHMe in the presence of Et3N does not afford PhobPNMePPhob but instead the salt [PhobP(=NMeH)PPhob]Cl is formed which, upon addition of [PtCl3(NC(C6H5)Bu)2] gives the zwitterionic complex [PtCl3(PPhob(=NMeH)PPhob)]. The neutral PhobP(=NMe)PPhob is accessible from PhobNMeLi and is converted to the chelate [PdCl2(PhobPNMePPhob)] by addition of [PdCl2(cod)]. The anomalous preference of the PhobP group for the formation of PPN products is discussed. The unsymmetrical diphenyl ligands PhobPNMePAr2 (Ar = Ph, o-Tol) are prepared, converted to [Cr(CO)4(PhobPNMePAr2)] and shown to form Cr-catalysts for ethene oligomerisation, producing a pattern of higher alkenes that corresponds to a Schulz-Flory distribution overlaid on selective tri/tetramerisation.

Introduction

Significant differences between the donor properties of phosphacycles and their acyclic analogues are to be expected because of the effects that ring constraints can have on the frontier orbital energies and the steric properties of the P-donor.1 The molecular manifestations of these ring effects include stability (thermodynamic and kinetic) and structural rigidity which can be desirable qualities when considering the design of ligands. As a result, the coordination chemistry of phosphacycles and their applications in catalysis have attracted much academic and industrial attention.2 Phobanes (PhobPZ, in Chart 1) are examples of rigid phosphacycles which have found important applications in homogeneous catalysis3,4 most notably in Co-catalysed hydroformylation.5 We are interested in heterophobanes (PhobPZ where Z = a non-hydrocarbyl group) as ligands and particularly the effect that the phobyl group has on the reactivity of the P–Z bond. For example, fluorophobane (PhobPF) was shown to be a rare example of a fluorophosphine that is thermodynamically more stable to disproportionation and kinetically more stable to hydrolysis than acyclic fluorophosphine analogues; moreover PhobPF shows promise as a ligand for hydroformylation and hydrocyanation catalysis.6 Aminodiphosphines R2PNPR2 (known as PNP ligands, Chart 1) are excellent ligands for Cr-catalysed ethene tri/tetramerisation. As illustrated in Table 1, the characteristics of the R and R′ groups in R2PNPR2 have a decisive effect on the chemoselectivity, productivity and therefore the potential industrial utility of the oligomerisation catalyst.7,8 Increased steric bulk serves to lower the ratio of 1-octene to 1-hexene obtained, whilst changing from aryl to alkyl substituents on phosphorus dramatically reduces activity and increases polymer formation. The data in Table 1 highlight the impact of process conditions such as solvent, temperature and pressure upon the catalysis.

The industrial interest in PNP ligands9 makes it important to have reliable methods for their preparation. As summarised in Scheme 1, the most general route to PNP ligands is the reaction of a primary amine with a chlorophosphine in the presence of a base.10 The monophos R2PNHR′ species are presumed intermediates and when R or R′ is bulky, they are...
readily isolated and are potential intermediates to unsymmetrical PNP ligands. When the substituents in either of the reactants R2PCl or R′NH2 are bulky, a complication is the formation of the phosphinimine PPN compounds (Scheme 1); Maumela et al.10 have shown that when R = Ph and R′ = t-Bu, the PPN product is the kinetic product whose isomerisation to the thermodynamic PNP product is catalysed by Ph2PCl.

We were interested in investigating PNP ligands such as La-Ld where a phobyl group has been incorporated (Chart 2). It is shown here that the monophosphines La and Lb are readily prepared but their conversions to Lc and Ld has not been achieved. However the mixed diphosphines Lf and Lg are accessible and are shown to be ligands for Cr-catalysed ethene tri/tetramerisation.

Results and discussion

Stereoelectronically, a Cy3P group can be viewed as an acyclic analogue of a PhobP group since ostensibly, they are similarly bulky dialkylphosphino groups. However, we have shown previously that the rigidity of the PhobP moiety leads to a larger steric profile than expected12 and the approximately 90° C–P–C bridgehead angle in PhobP has the effect of lowering the HOMO and LUMO energies.13 Ligands L4–L7 (Chart 3) were targeted in the belief that a comparison of their chemistry with the phobane analogues La–Ld (Chart 2) would provide insight into the effect of the bicycle.

Monodentate aminophobanes

The monophosphines La and Lb were readily prepared by amination of PhobPCl. The relative lability of La and Lb to hydrolysis (eqn (1)) was gauged by treatment of La, Lb, Lc and Ld with aqueous solutions under the same conditions and monitoring the formation of R2P(=O)H by 31P NMR spectroscopy. All four aminophosphines eventually underwent complete hydrolysis but at different rates. Comparison of the extents of hydrolysis

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*a Catalysis data taken from ref. 7 and 8. All wt% values are of total product slate. C6 and C8 refer to the entire C6 and C8 fractions and 1-C6 and 1-C8 refer to the proportion of the linear α-olefin within that fraction. b Catalysis conditions: 33 μmol CrCl3[THF]3; 2 eq. ligand; 300 eq. MMAO-3A; 100 mL toluene. c Catalysis conditions: 33 μmol Cr(acac)3; 2 eq. ligand; 300 eq. MMAO-3A; 100 mL toluene. d Catalysis conditions: 2.5 μmol Cr(acac)3; 1.2 eq. ligand; 300 eq. MMAO-3A; 100 mL methylcyclohexane.
after 16 h (Table 2) shows that the NHPr group provides more protection from hydrolysis than the less bulky NHMe. Moreover, the bicyclic compounds PhobPNHR are significantly kinetically stabilised to hydrolysis with respect to the acyclic Cy2PNHR analogues. The resistance to hydrolysis of PhobPNHR is consonant with the phobyl moiety behaving as a bulky group.12

The donor properties of La and Lb can be compared quantitatively with L1 and L2 from the νCO values for their trans-[RhCl(CO)(L)2] complexes.14 The rhodium complexes were made in situ (see Scheme 2) and the recorded νCO values (Table 2) are consistent with La and Lb being slightly poorer σ-donors/better π-acceptors than their acyclic analogues L1 and L2, as expected.13

Ligands La and Lb form trans-dichloroplatinum(II) complexes 1a and 1b, and trans-tetracarbonylchromium(0) complexes 2a and 2b (Scheme 2). The crystal structures of 1b and 2b have been determined and are shown in Fig. 1 and 2. In addition, the crystal structure of trans-[PtCl2(L)]2 (3) , an acyclic analogue of 1b has been determined (Fig. 3).

In aminophobane complex 1b and its acyclic analogue 3, the Pt metal centre is square planar. The Pt sits on a crystallographic inversion centre and the asymmetric unit consists of half of the complete molecule, consequently the N–P–P–N torsion angles are 180° in both cases, i.e. the anti conformer is adopted, as in other trans-[PtCl2(PhobPZ)] complexes.6,12,15 The cone angle of Lb in 1b is 111.8° and of L2 in 3 is larger at 115.8°. In the structure of 2b, the asymmetric unit contains one complete molecule. The cone angle of Lb in 2b is 109.2° which is smaller than in 1b, the compression probably reflecting the greater crowding in the octahedral complex. The N–P–P–N torsion angle in 2b is 108.3(1)° indicating the amino
groups are gauche to each other, a conformation not previously observed in PhobPZ complexes.

Bidentate aminophobanes

The previously reported diphosphinoamine \( \text{L}_4 \) is readily prepared from \( \text{MeNH}_2 \) and \( \text{Cy}_2\text{PCl} \) in the presence of \( \text{Et}_3\text{N} \) (Scheme 3). The intermediate in this reaction is presumably \( \text{Cy}_2\text{PNHMe} \) (\( \text{L}_4 \)) and indeed treatment of the isolated \( \text{L}_4 \) with \( \text{Cy}_2\text{PCl} \) in the presence of \( \text{Et}_3\text{N} \) gave the expected diphosphinoamine \( \text{L}_c \). Instead, a PPN species \( (J_{PP} = 407 \text{ Hz}) \) was the exclusive product; this was initially assigned structure \( \text{L'}_c \) but its \(^1\text{H} \) NMR spectrum (which showed a multiplet at 7.01 ppm integrating for 1H) and mass spectrum \( (M^+ \text{ at } [\text{L'}_c + 1]) \) led to its assignment as the HCl adduct \( \text{L'}_c \cdot \text{HCl} \) (Scheme 4). This was supported by its reaction with \( [\text{PtCl}_2(\text{NC} \cdot \text{HCl})] \) which yielded crystals of the insoluble, zwitterionic complex \( [\text{PtCl}_2(\text{L'}_c \cdot \text{H})] \) \( (5) \) whose X-ray crystal structure is shown in Fig. 5. The conditions under which \( \text{L'}_c \cdot \text{HCl} \) was formed (Scheme 4) indicate that the iminophosphine \( \text{L'}_c \) is more basic than either \( \text{NEt}_3 \) or N-methylpyrrolidine.

The crystal structure of \( \text{L}_c \) has a square planar Pt with an rms deviation of the atoms from the square plane of \(-0.03 \text{ Å} \). The PPN ligand is rotated away from the PtCl₃ plane with torsion angles Cl₁–P₁–P₁–Cl₂ of \(-102.4(1)° \) and Cl₃–Pt₁–P₁–P₂ of \( 75.6(1)° \).

Treatment of PhobPNMeH with \( ^6\text{BuLi} \) at \(-78 \text{ °C} \) followed by PhobPCl gave a PPN species with a \( J_{PP} = 327 \text{ Hz} \) (significantly smaller than the \( J_{PP} \text{ of 407 Hz} \) for \( \text{L'}_c \cdot \text{HCl} \)) that is assigned to the neutral \( \text{L'}_c \) which has been isolated. No reaction occurred upon addition of PhobPCl to \( \text{L'}_c \) in \( \text{CH}_2\text{Cl}_2 \), conditions that might have been expected to tautomerise \( \text{L'}_c \) to \( \text{L}_c \).

It has previously been shown that some neutral PPN compounds rearrange when they react with \( [\text{ML}_2(\text{cod})] \) \( (\text{M} = \text{Pd} \) or \( \text{Pt})^{17} \) or \( [\text{NiBr}_2(\text{dme})]^{18} \) to give PNP chelate complexes. Reaction

![Fig. 3](image-url)  
Crystal structure of \( \text{trans-[PtCl}_2(\text{Cy}_2\text{PNHPr})_2] \) (3). All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pt(1)–P(1) 2.3178(7), Pt(1)–Cl(1) 2.3193(7), P(1)–N(1) 1.681(3), P(1)–P(1)–N(1) 113.91(10).

![Fig. 4](image-url)  
Crystal structure of complex \( [\text{PtCl}_2(\text{L}_4)] \) (4). Only one of the three unique molecules is shown and all hydrogen atoms and six molecules of \( \text{CHCl}_3 \) have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pt(1)–P(2) 2.206(6), Pt(1)–P(1) 2.257(6), Pt(1)–Cl(1) 2.363(5), Pt(1)–Cl(2) 2.376(7), P(1)–N(1) 1.745(17), P(2)–N(1) 1.668(18), P(2)–P(1)–P(1) 71.1(3), N(1)–P(1)–Pt(1) 92.8(6), N(1)–P(2)–Pt(2) 96.9(9), P(2)–N(1)–P(1) 99.0(8).
of \([\text{PdCl}_2(\text{cod})]\) with \(L'\) gave the chelate \([\text{PdCl}_2(Lc)]\) (6) whose crystal structure has been determined and is shown in Fig. 6.

The asymmetric unit contains one molecule of 6, with the \(\text{PdP}_2\text{Cl}_2\) fragment being essentially planar (rms \(\sim 0.07\) Å) although the overall geometry is a distorted square planar due to the constraints of the 4-membered PNP chelate. As seen in the structure of analogue 4, the \(\text{Pd}1–\text{P1}–\text{N1}–\text{P2}\) ring is also essentially planar with an rms deviation for the atoms of 0.01 Å.

From the homodiphos products obtained in the reactions of \(L_a\) and \(L_1\) with \(\text{R}_2\text{PCl}\) (see Schemes 3 and 4), it appears that the PhobP group differs from \(\text{Cy}_2\text{P}\) and \(\text{Ar}_2\text{P}\) groups in promoting PPN over PNP formation; this raised the question of what would happen when the syntheses of the heterodiphos PNP ligands PhobPNMePR_2 where \(R = \text{Cy} (L_e), \text{Ph} (L_f)\) or \(\text{o-Tol} (L_g)\) were attempted?

The reaction between PhobPNMe and \(\text{Cy}_2\text{PCl}\) was followed by \(^{31}\text{P}\) NMR spectroscopy and it was unambiguously shown that a PPN product was formed which, on the basis of its \(J_{PP}\) of 358 Hz, was tentatively assigned to the protonated species \(L'_e\cdot\text{HCl}\) (Scheme 5); addition of \(\text{Et}_3\text{N}\) led to multiple P-containing species but there was no evidence for the formation of the neutral PPN (\(L'_e\)) or PNP (\(L_f\)) species. The reaction between PhobPCI and \(\text{Cy}_2\text{PNHMe}\) was also monitored and in this case, \(^{31}\text{P}\) NMR spectroscopy revealed that a PPN product was formed (\(J_{PP} = 403\) Hz) which was assigned to the cationic species \(L''_e\cdot\text{HCl}\) (Scheme 5), an isomer of \(L'_e\cdot\text{HCl}\). It therefore appears that the PPN-promoting effect of the PhobP group dominates over the PNP-preference of the \(\text{Cy}_2\text{P}\) group.

The unsymmetrical PNP ligands \(L_g\) and \(L_k\) (\(J_{PP} = 80\) Hz in both) featuring PhobP groups were successfully prepared upon treatment of PhobPNMe with \(\text{Ar}_2\text{PCl}\) (\(Ar = \text{Ph}\) or \(\text{o-Tol}\)) in the presence of \(\text{Et}_3\text{N}\) (eqn (2)). It therefore appears that the PPN formation promoted by the PhobP group is superseded by the PNP preference of the \(\text{Ar}_2\text{P}\) groups.
The reaction of PhobPNHMe with Tol2PCl was monitored by $^{31}\text{P}$ NMR spectroscopy. A PPN species ($J_{PP} = 331$ Hz), tentatively assigned to $L'_g\cdot\text{HCl}$ (Scheme 6) was formed rapidly which, upon treatment with NEt$_3$, was transformed to $L_g$ ($J_{PP} = 80$ Hz).

Treatment of the bulky $R_2\text{PNH}^\text{Pr}$ ($L_b$ or $L_2$) with $R_2\text{PCl}$ ($R_2\text{P} = \text{Cy}_2\text{P}$ or PhobP) under the conditions that converted $R_2\text{PNHMe}$ to the corresponding $L_3$ (Scheme 3) or $L'_c\cdot\text{HCl}/L'_c$ (Scheme 4) gave, according to in situ $^{31}\text{P}$ NMR spectroscopy, mixtures of unidentified products as well as the reactants.

Under the conditions that smoothly led to the mixed PNP ligands $L_f$ and $L_g$ (eqn (2)), $L_b$ reacted with Ar$_2\text{PCl}$ to give PPN species whose structures were assigned to the protonated $L'_h\cdot\text{HCl}$ and $L'_i\cdot\text{HCl}$ (eqn (3)) on the basis of the large $J_{PP}$ values of 338 and 359 Hz respectively. Crystals of $L'_h\cdot\text{HCl}$ were obtained and the crystal structure shown in Fig. 7 confirms the PPN assignment. The N⋯Cl distance of 3.101(1) Å indicates the presence of hydrogen-bonding between the N–H and Cl.

### PPN versus PNP preferences

The $N$- and $P$-substituents determine whether PNP ($A$) or PPN ($A'$) species are formed in the reaction of amines with chlorophosphines (Scheme 7). In some cases, it has been shown$^{10,19}$ that the PPN can be converted to the PNP tautomer using a $R_2\text{PCl}$ catalyst and we have observed PPN species as transients en route to the PNP products (e.g. $\text{Cy}_2\text{PNMePCy}_2$ see Scheme 3) showing that the PNP is the thermodynamic product. In other cases (e.g. $\text{Cy}_2\text{PN(SO}_2\text{Ar})\text{PCy}_2$) the neutral PPN tautomer appears to be the thermodynamic product.$^{17,18,20}$ An additional element observed in this work is the formation of a protonated $A'\cdot\text{HCl}$ product that is resistant to deprotonation by amines.

A pathway from chlorophosphine and primary amine to PNP/PPN products that encompasses these empirical observations is shown in Scheme 7. Nucleophilic attack by amine on chlorophosphine with loss of HCl would give the intermediate aminophosphine (step i). Reaction of a second chlorophosphine at the P site of the aminophosphine would give the salt $A'\cdot\text{HCl}$ (step ii) which can eliminate HCl to give the neutral $A'$ (step iii) and finally rearrangement to give PNP (step iv).

The formation of a PPN species when PhobPCl reacts with PhobPNHMe or PhobPNMeLi instead of PhobPNMePPhob...
contrasts with the smooth formation of Cy$_2$PNMePCy$_2$ via a PPN intermediate; furthermore, PhobP(==NMe)PPhob does not isomerise to the PNP tautomer in the presence of PhobPCl. At present, it is not known whether these observations are due to PhobP(==NMe)PPhob being the thermodynamically preferred tautomer or slow kinetics of interconversion and therefore further investigation of this system is warranted.

**Oligomerisation catalysis**

The unsymmetrical PNP ligands L$_f$ and L$_g$ have been screened for Cr-catalysed ethene oligomerisation (see below) and it was therefore appropriate to explore their Cr coordination chemistry. The reaction of [Cr(CO)$_4$(nbd)] with L$_f$ or L$_g$ gave the corresponding Cr(0) complexes 7 and 8 (eqn (4)) which have been fully characterised and their crystal structures have been determined (Fig. 8 and 9).

In combination with chromium, the ligands L$_f$ and L$_g$ gave moderate activities towards ethylene oligomerisation but the formation of polymer was high, as can be seen from Table 3. Within the liquid fraction, it is clear that a degree of selective oligomerisation to 1-hexene and 1-octene did occur (particularly for L$_g$) but concurrently with Schulz-Flory selectivity (Fig. 10). The 1-octene to 1-hexene ratios obtained for both ligands is high.

**Conclusions**

The monodentate aminophobanes PhobPNHR (R = Me or tPr) have been readily prepared and are more resistant to hydrolysis than their Cy$_2$PNHR analogues consistent with the PhobP group having a greater effective steric bulk than Cy$_2$P. Attempts to make the free ligand PhobPNMePPhob have been thwarted by formation of PPN species which resist tautomerisation although a rearrangement takes place in the presence of [PdCl$_2$(cod)] to give the desired PNP–Pd chelate. The readily prepared mixed diphos ligands PhobPNMePAr$_2$ (Ar = Ph or o-Tol) in combination with Cr, catalysed the oligomerisation of ethylene with a partial selectivity to tri/tetramerisation, the remainder of the selectivity appearing to be Schulz-Flory in nature; the activities were moderate, but the polymer formation was high.

**Experimental**

Unless otherwise stated, all reactions were carried out under a dry nitrogen atmosphere using standard Schlenk-line techniques. Dry N$_2$-saturated solvents were collected from a Grubbs system in flame and vacuum-dried glassware. MeOH was dried over 3 Å molecular sieves, pentane was dried over 4 Å molecular sieves and both were deoxygenated by N$_2$ saturation. The starting materials PhobPCl, [Cr(CO)$_4$(η$_5$-norbornadiene)], [PtCl$_2$(NCBu)$_3$], [PdCl$_2$(cod)], were prepared by literature methods. All other reagents were used as received from Aldrich, Strem or Lancaster. The aminophosphines were stored under nitrogen at room temperature. NMR spectra were recorded on a Jeol Delta 270, Jeol Eclipse 300, Jeol Eclipse 400, Varian 400 or Lambda 300. Infrared spectroscopy was carried out.

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**Fig. 8** Crystal structure of complex [Cr(CO)$_4$(L$_f$)] (7). All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Cr(1)–P(3) 2.3163 (16), Cr(1)–P(2) 2.3474 (16), P(2)–N(1) 1.7145 (5), P(3)–N(1) 1.7015 (5), P(3)–Cr(1)–P(2) 68.29 (5), N(1)–P(3)–Cr(1) 94.6817, N(1)–P(2)–Cr(1) 96.03 (5), C(17)–P(2)–C(16) 96.03 (5), C(7)–P(3)–C(11) 103.5 (2).

**Fig. 9** Crystal structure of [Cr(CO)$_4$(L$_g$)] (8). All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Cr(1)–P(1) 2.3477 (6), Cr(1)–P(2) 2.3669 (6), P(1)–N(1) 1.7146 (7), P(2)–N(1) 1.7035 (7), P(3)–Cr(1)–P(2) 68.04 (4), P(2)–N(1)–P(1) 101.01 (9), N(1)–P(1)–Cr(1) 94.67 (6), N(1)–P(2)–Cr(1) 94.29 (6), C(16)–P(1)–C(13) 95.66 (10), C(7)–P(2)–C(4) 105.17 (9).
Table 3 Ethene oligomerisation resultsa

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a Conditions: Cr(acac)3 (2.5 µmol), 1.2 eq. L, 960 eq. MMAO-3A (800 eq. added to pre-activation, 160 eq. added to autoclave vessel), PhCl solvent (70 mL), 53 bar ethylene, 60 °C. The wt% values for the carbon number fractions refer to the liquid fraction.

Preparation of PhobPNHIPr (Lb)

A solution of PhobPCl (0.530 g, 3.03 mmol) in CH2Cl2 (2.0 mL) was added in portions to a solution of iPrNH2 (1.54 mL, 20.1 mmol) in THF (9.0 mL). The resulting suspension was stirred at room temperature for 16 h and then the solvent was evaporated to dryness to give a white solid (0.57 g, 63%).31P{1H} NMR (121 MHz; CDCl3) δ 1.60 (14H, m, phobane), 2.20 (14H, m, phobane), 1.14 (6H, d, JHP = 2.0 Hz, CH3N). 1H NMR (270 MHz; CDCl3) δ 1.48-2.20 (14H, m, phobane), 2.67 (3H, d, JHF = 15.0 Hz, CH3N). 13C{1H} NMR (67 MHz; CDCl3) δ 21.5 (d, JCP = 2.0 Hz, CH2), 22.9 (d, JCP = 4.6 Hz, CH3), 23.7 (d, JCP = 3.1 Hz, CH3), 28.1 (d, JCP = 10.9 Hz, CH3N), 31.2 (d, JCP = 14.0 Hz, CH3), 33.0 (d, JCP = 26.9 Hz, CH). Elemental analysis: Found (Calc. for C11H22NP 199.1496 (199.1490). MS (ESI: m/z 171 (M+)).

Preparation of [PhobP(NHMe)(PPhob)]Cl (Lc·HCl)

A solution of PhobPCI (0.530 g, 3.03 mmol) in CH2Cl2 (2.0 mL) was added in portions to a solution of Lc (0.510 g, 3.00 mmol) and N-methylpyrrolidine (2.40, 28.2 mmol) in CH2Cl2 (2 mL). The reaction mixture was stirred for 3 h and then the solvent was removed under reduced pressure. The resulting white solid was recrystallised from hot MeCN to afford white crystals (0.43 g, 45%).31P{1H} NMR (121 MHz; CDCl3) δ 46.5 (d, JFP = 407 Hz), –24.2 (d, JFP = 407 Hz).1H NMR (400 MHz; CDCl3) δ 1.60–2.54 (28H, m, phobane), 2.66 (3H, dd, JHF = 12.3 Hz, JHP = 5.68 Hz, CH3N), 7.01 (1H, m, HCl). 13C{1H} NMR (100 MHz; CDCl3) δ 20.4 (d, JCP = 6.9 Hz), 20.7 (d, JCP = 6.9 Hz), 20.8 (d, JCP = 6.9 Hz), 21.2 (d, JCP = 1.5 Hz), 21.9 (d, JCP = 6.9 Hz), 24.9 (d, JCP = 6.1 Hz), 25.1 (d, JCP = 6.1 Hz), 26.2 (d, JCP = 6.1 Hz), 26.9 (d, JCP = 6.1 Hz), 27.3 (d, JCP = 6.1 Hz), 27.5 (dd, JCP = 9.2 Hz, JCP = 1.5 Hz) 27.7 (d, JCP = 3.8 Hz), 28.9 (t, JCP = 3.84 Hz), 32.7 (d, JCP = 14.6 Hz), 32.9 (d, JCP = 15.3 Hz). Elemental analysis: Found (Calc. for C17H32ClNP2) C, 59.1 %; H, 10.4 (10.6) %; N, 8.1 (8.1); MS (ESI: m/z 2301 (M+) / 2307 (M+)).
(58.7); N, 3.8 (4.0); H, 9.4 (9.3) %. HRMS (El): Found (Calc. for C_{17}H_{32}NP_{2}) 312.0044 (312.0043).

**Preparation of PhobP(═NMe)PPhob (L_{1})**

To the solution of L_{a} (0.45 g, 2.6 mmol) in THF (3.0 mL), a 1.6 M solution of BuLi (4.5 mL, 7.20 mmol) in hexane was added at −78 °C over 5 min. The reaction mixture was stirred at −78 °C for 40 min. PhobPCI (0.45 g, 2.6 mmol) in THF (2 mL) was added in portions to the cooled reaction mixture. The mixture was allowed to warm to room temperature and stirred for 2 h. The solvent was then removed under reduced pressure and the residue was triturated with diethyl ether (10 mL). The solid was filtered off and dried. Satisfactory elemental analysis was not obtained and the product was used without further purification (0.52 g, 65%) 31P{ 1H} NMR (121 MHz; CDCl3) δ 30.7 (d, J_{PP} = 320 Hz), −32.3 (d, J_{PP} = 320 Hz). 1H NMR (300 MHz, CDCl3) δ 1.25-2.52 (14H, m, phobane), 2.62 (3H, dd, J_{HH} = 14.5 Hz, J_{HF} = 5.7 Hz, CH3N).

**Preparation of PhobPNMePPhob (L_{2})**

Aminophobane L_{a} (0.280 g, 1.64 mmol) and NET_{3} (0.220 g, 2.17 mmol) were dissolved in MeCN (1 mL). To this stirred mixture, PhbPCI (0.380 g, 2.12 mmol) was added dropwise over 5 min. The reaction mixture was stirred for 2 h to give a white solid, which was filtered off and recrystallised from hot MeCN to afford white needles (0.44 g, 69%). 31P{ 1H} NMR (121 MHz; CDCl3) δ 57.6 (d, J_{PP} = 80 Hz), 51.1 (d, J_{PP} = 80 Hz). 1H NMR (270 MHz; CD2Cl2) δ 1.21-2.24 (14H, m, phobane), 2.32 (3H, dd, J_{HF} = 4.3 Hz, J_{HH} = 8.5 Hz, CH3N), 7.05-7.22, 7.55-7.69 (10H, 2 m, ArH). 13C{ 1H} NMR (100 MHz; CD2Cl2) δ 21.0 (d, J_{CP} = 1.5 Hz, CH2), 23.2 (d, J_{CP} = 2.6 Hz, CH2), 28.7 (dd, J_{CP} = 20.7 Hz, J_{CC} = 11.9 Hz, CH2N), 30.2 (d, J_{CP} = 17.1 Hz, CH3), 33.0 (dd, J_{CC} = 16.6 Hz, J_{CP} = 7.2 Hz, CH2), 24.1 (t, J_{CC} = 3.1 Hz, CH2), 128.2 (d, J_{CC} = 5.7 Hz, CH2), 128.4 (s, CH) 132.2 (d, J_{CP} = 19.2 Hz, CH2), 138.4 (dd, J_{CC} = 16.6 Hz, J_{CP} = 1.0 Hz, C). Elemental analysis: Found (Calc. for C_{21}H_{27}NP_{2}) C, 71.8 (70.9); N, 4.5 (4.0); H, 7.8 (7.6) %. HRMS (El): Found (Calc. for C_{21}H_{27}NP_{2}) 355.1613 (355.1612).

**Preparation of PhobPNMeP(o-Tol)2 (L_{3})**

Aminophobane L_{a} (0.200 g, 1.16 mmol) and NET_{3} (0.240 g, 2.32 mmol) were dissolved in MeCN (1 mL). To this stirred mixture, PhbPCI (0.380 g, 2.12 mmol) was added dropwise over 5 min. The reaction mixture was stirred for 16 h to give the white solid product, which was filtered off and recrystallised from hot MeCN to afford white needles (0.17 g, 38%). 31P{ 1H} NMR (161 MHz; CDCl3) δ 338 Hz, 39.1 (d, J_{PP} = 338 Hz). 1H NMR (400 MHz; CDCl3) δ 0.94 (6H, d, J_{HH} = 6.2 Hz, CH3), 1.35 (1H, d, J_{HH} = 6.4 Hz, CH), 1.74-2.94 (14H, m, phobane), 7.64-7.77 (10H, 2 m, ArH). 13C{ 1H} NMR (100 MHz; CDCl3) δ 20.5 (d, J_{CP} = 5.4 Hz), 20.9 (d, J_{CP} = 4.6 Hz), 25.1 (d, J_{CP} = 4.6 Hz), 26.6 (d, J_{CP} = 5.3 Hz), 27.7 (d, J_{CP} = 2.3 Hz), 28.1 (s), 46.6 (s), 128.5 (d, J_{CP} = 8.5 Hz), 130.2 (d, J_{CP} = 7.6 Hz), 131.4 (s), 134.9 (d, J_{CP} = 2.3 Hz). HRMS (El): Found (Calc. for C_{23}H_{29}NP_{2}) 384.2004 (384.1999).

A solution of L_{b} (0.83 g, 4.2 mmol) and N-methylpyrrolidine (0.39 g, 4.2 mmol) in CH2Cl2 (5 mL). The reaction mixture was stirred for 1 h and the solvent was then removed under reduced pressure. The resulting white solid was recrystallised from hot MeCN to yield white crystals (0.71 g, 62%). 31P{ 1H} NMR (121 MHz; CDCl3) δ 30.7 (d, J_{PP} = 320 Hz), 32.3 (d, J_{PP} = 320 Hz). 1H NMR (400 MHz; CD2Cl2) δ 9.7 (1H, d, J_{HH} = 10.4 Hz, CH), 2.87-3.31 (14H, m, phobane), 7.22, 7.69 (10H, 2 m, ArH). 13C{ 1H} NMR (100 MHz; CD2Cl2) δ 28.1 (d, J_{CP} = 3.8 Hz), 28.9 (d, J_{CP} = 4.6 Hz), 25.6 (d, J_{CP} = 4.6 Hz), 26.8 (d, J_{CP} = 10.9 Hz), 28.5 (d, J_{CP} = 3.8 Hz), 29.9 (d, J_{CP} = 4.6 Hz), 45.6 (d, J_{CP} = 4.6 Hz), 123.8 (dd, J_{CP} = 14.0 Hz, J_{CP} = 3.8 Hz), 126.7 (s), 130.4 (d, J_{CP} = 7.8 Hz), 133.9 (d, J_{CP} = 7.0 Hz), 142.3 (dd, J_{CP} = 31.9 Hz, J_{CP} = 7.0 Hz). Elemental analysis: Found (Calc. for C_{23}H_{23}ClNP_{2}) C, 67.0 (67.0); N, 3.5 (3.1); H, 8.5 (8.1)%.

**Preparation of Cy2PNMePCy2 (L_{4})**

Cy2PCI (2.79 g, 11.9 mmol) was dissolved in CH2Cl2 (6.0 mL). To this, a 2 M THF solution of MeNH2 (3.0 mL, 6.0 mmol) and NET_{3} (1.30 g, 12.8 mmol) were added dropwise over 5 min. The resulting suspension was stirred for 16 h. The solvent was then removed under reduced pressure and the residue was dissolved in toluene (30 mL). The [Et3NH]Cl salt was filtered off to give a clear solution. The solvent was then removed under reduced pressure to give the crude product, which was recrystallised from hot acetonitrile (0.77 g, 32%). 31P{ 1H} NMR (121 MHz; CDCl3) δ 86.8. 1H NMR (300 MHz; CDCl3) δ 1.10-1.60 (14H, m, CH and CH2), 2.64 (s, CH3), 27.2 (s, CH3), 29.5 (t, J_{CP} = 9.2 Hz, CH3N). 13C{ 1H} NMR (300 MHz; CDCl3) δ 49.3 (d, J_{CP} = 539 Hz), −39.8 (d, J_{CP} = 359 Hz).
Preparation of trans-[PtCl₂(PhobPNMe)] (1a)
PhobPNMe (0.069 g, 0.45 mmol) was dissolved in CH₂Cl₂ (2.0 mL). [PtCl₂(NC'Bu)] (0.086 g, 0.23 mmol) was added and the resulting yellow solution was stirred for 2 h. The solvent was reduced to ca. 1 mL and then hexane (4 mL) was added to give the yellow precipitated product (0.080 g, 57%). ³¹P{¹H} NMR (121 MHz; CDCl₃) δ 46.3 (Jₚₚ = 2638 Hz). ¹H NMR (300 MHz; CDCl₃) δ 1.52–2.16 (28H, m, phobane), 2.98 (6H, t, Jₚₚ = 6.6 Hz, CH₃N). ¹³C{¹H} NMR (75 MHz; CDCl₃) δ 1.21 (s), 22.1 (s), 24.2 (t, Jₚₚ = 6.6 Hz), 25.8 (s), 29.2 (s), 30.8 (s). Elemental analysis: Found [Calc. for C₁₈H₃₆Cl₂N₂P₂Pt] C, 35.4 (35.5); N, 4.6 (5.0%). HRMS (ESI): Found (Calc. for C₂₂H₄₄Cl₂N₂P₂Pt) C, 39.7 (39.7); N, 3.9 (4.2); H, 6.6 (6.6)%. 

Preparation of trans-[PtCl₂(PhobPNHMe)] (1a)
PhobPNHMe (0.069 g, 0.45 mmol) was dissolved in CH₂Cl₂ (2.0 mL). [PtCl₂(NC'Bu)] (0.086 g, 0.23 mmol) was added and the resulting yellow solution was stirred for 2 h. The solvent was reduced to ca. 1 mL and then hexane (4 mL) was added to give the yellow precipitated product (0.080 g, 57%). ³¹P{¹H} NMR (121 MHz; CDCl₃) δ 46.3 (Jₚₚ = 2638 Hz). ¹H NMR (300 MHz; CDCl₃) δ 1.52–2.16 (28H, m, phobane), 2.98 (6H, t, Jₚₚ = 6.6 Hz, CH₃N). ¹³C{¹H} NMR (75 MHz; CDCl₃) δ 1.21 (s), 22.1 (s), 24.2 (t, Jₚₚ = 6.6 Hz), 25.8 (s), 29.2 (s), 30.8 (s). Elemental analysis: Found [Calc. for C₁₈H₃₆Cl₂N₂P₂Pt] C, 35.4 (35.5); N, 4.6 (5.0%). HRMS (ESI): Found (Calc. for C₂₂H₄₄Cl₂N₂P₂Pt) C, 39.7 (39.7); N, 3.9 (4.2); H, 6.6 (6.6)%. 

Preparation of trans-[Cr(CO)₄(PhobPNMePPh₂)] (7)
To a solution of L₄ (0.03 g, 0.095 mmol) in toluene (3 mL), [PdCl₂(cod)] (0.031 g, 0.099 mmol) in toluene (3 mL) was added and stirred for 2 h to give a yellow solution. Warming this solution to 40 °C led to the slow formation of yellow crystals of the product suitable for X-ray crystallography. Satisfactory elemental analysis was not obtained and the crystals were insoluble in common organic solvents which precluded further characterisation by NMR spectroscopy.

Preparation of [PdCl₂(PhobPNMePPh₂)] (5)
A mixture of L₄·HCl (0.025 g, 0.070 mmol) and [PtCl₂(NC'Bu)] (0.034 g, 0.070 mmol) was dissolved in CH₂Cl₂ (5 mL) and stirred for 2 h to give a yellow solution. Warming this solution to 50 °C for 5 min. The clear reaction mixture was then cooled to room temperature and the resulting yellow precipitate was filtered off and washed with hexane (0.010 g, 20%). Crystals suitable for X-ray crystallography were grown from CDCl₃ although satisfactory elemental analysis was not obtained. ³¹P{¹H} NMR (121 MHz; CDCl₃) δ 37.1 (Jₚₚ = 3211 Hz). ¹H NMR (300 MHz; CDCl₃) δ 1.20–1.97 (44H, m, CH and CH₃), 2.72 (3H, t, Jₚₚ = 9.4 Hz, CH₃N). ¹³C{¹H} NMR (75 MHz; CDCl₃) δ 25.7 (s), 26.9 (m) 27.9 (s), 38.0 (t, Jₚₚ = 15.2 Hz). Elemental analysis: Found [Calc. for C₁₈H₃₆Cl₂N₂P₂Pt] C, 43.3 (43.5); N, 2.3 (2.0); H, 6.8 (6.9)%. HRMS (EI): Found (Calc. for C₂₅H₂₇ClN₂P₂Pt) 653.2529 (653.2520).

Preparation of trans-[Cr(CO)₄(PhobPNMePPh₂)] (7)
To a solution of L₄ (0.030 g, 0.070 mmol) in CH₂Cl₂ (2 mL), [Cr(CO)₄(η⁵-norbornadiene)] (0.018 g, 0.070 mmol) was added and stirred for 2 h to give a yellow solution. Warming this solution to 50 °C led to the slow formation of yellow crystals of the product suitable for X-ray crystallography. Satisfactory elemental analysis was not obtained and the crystals were insoluble in common organic solvents which precluded further characterisation by NMR spectroscopy.

Preparation of [PtCl₂(PhobPNMePPh₂)] (5)
A mixture of L₄·HCl (0.025 g, 0.070 mmol) and [PtCl₂(NC'Bu)] (0.034 g, 0.070 mmol) was dissolved in CH₂Cl₂ (5 mL) and stirred for 2 h to give a yellow solution. Warming this solution to 40 °C led to the slow formation of yellow crystals of the product suitable for X-ray crystallography. Satisfactory elemental analysis was not obtained and the crystals were insoluble in common organic solvents which precluded further characterisation by NMR spectroscopy.

Preparation of [PdCl₂(PhobPNMePPh₂)] (5)
A mixture of L₄·HCl (0.025 g, 0.070 mmol) and [PtCl₂(NC'Bu)] (0.034 g, 0.070 mmol) was dissolved in CH₂Cl₂ (5 mL) and stirred for 2 h to give a yellow solution. Warming this solution to 40 °C led to the slow formation of yellow crystals of the product suitable for X-ray crystallography. Satisfactory elemental analysis was not obtained and the crystals were insoluble in common organic solvents which precluded further characterisation by NMR spectroscopy.
### Table 4 Crystal data and structure refinement for all structures in the paper

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Identification code 6·HCl

8

1.404
0.26 × 0.26 × 0.26
3.68 to 55.08
3.68 to 55.08
–

6

1.144.0
0.24 × 0.2 × 0.15
11.404 0.327 0.630 0.599
5.90 to 35.0
5.90 to 35.0
–

Table 4 (Contd.)

To a solution of L$_8$ (0.030 g, 0.060 mmol) in CH$_2$Cl$_2$ (2 mL), [Cr(CO)$_4$(η$^4$-norbornadiene)] (0.017 g, 0.060 mmol) in CH$_2$Cl$_2$ (2 mL) was added. The resulting yellow solution was stirred for 24 h. The solvent was then removed under reduced pressure to yield a yellow solid, which was washed with hexane (5 mL) (0.021 g, 30%). $^3$P NMR (121 MHz, CDCl$_3$) δ 104.1 (d, J$_{HP}$ = 27 Hz), 104.6 (d, J$_{HP}$ = 27 Hz). $^1$H NMR (300 MHz, CDCl$_3$) δ 1.24 (6H, s, CH$_3$), 1.52–2.65 (14H, m, phobane). 2.97 (3H, dd, J$_{HF}$ = 7.4 Hz, J$_{HF}$ = 8.1 Hz, CH$_3$N), 7.11–7.56 (8H, m, HAr).

HRMS (EI): Found (Calc. for C$_{27}$H$_{31}$CrNO$_4$P$_2$) 547.1133 (547.1133). IR (in CH$_2$Cl$_2$): ν(CO) 2003, 1908, 1885, 1873 cm$^{-1}$.

**Preparation of [Cr(CO)$_4$(PhobPNMeP(o-Tol)$_2$)] (8)**

Oligomerisation catalysis

A rigorously cleaned autoclave was heated (130 °C) under vacuum for 60 min, then cooled to reaction temperature and back-filled with Ar (1 bar). Solvent was then added via syringe. The autoclave was pressurised with ethylene to 10 bar and vented. On a Schlenk line, a pre-activated catalyst solution was prepared by stirring the Cr source, ligand and modified methylluminoxane (MMAO) together for 24 h. The solvent was then removed under reduced pressure to yield a yellow solid, which was washed with hexane (5 mL) (0.021 g, 30%). $^3$P NMR (121 MHz, CDCl$_3$) δ 104.1 (d, J$_{HP}$ = 27 Hz), 104.6 (d, J$_{HP}$ = 27 Hz). $^1$H NMR (300 MHz, CDCl$_3$) δ 1.24 (6H, s, CH$_3$), 1.52–2.65 (14H, m, phobane). 2.97 (3H, dd, J$_{HF}$ = 7.4 Hz, J$_{HF}$ = 8.1 Hz, CH$_3$N), 7.11–7.56 (8H, m, HAr).

HRMS (EI): Found (Calc. for C$_{27}$H$_{31}$CrNO$_4$P$_2$) 547.1133 (547.1133). IR (in CH$_2$Cl$_2$): ν(CO) 2003, 1908, 1885, 1873 cm$^{-1}$.

Crystal structure determinations

X-ray diffraction experiments for 1b, 3, 4, 5, and 6 and L$_8$-HCl were carried out at 100 K and for 2b at 173 K on a Bruker APEX II diffractometer using Mo-K$_x$ radiation ($\lambda$ = 0.71073 Å). 7 was collected at 120 K on a Bruker Nonius FR591 rotating anode using Mo-K$_x$ radiation ($\lambda$ = 0.71073 Å) and 8 was collected on E11 of Station I19 of Diamond Light Source ($\lambda$ = 0.71073 Å) at 120 K. Data collections were performed using a CCD area detector from a single crystal mounted on a glass fibre.
sities were integrated using SAINT with a multi-scan absorption correction performed using SADABS. All structures were solved using SHELXS and refined against all $F^2$ using SHELXL and OLEX2. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were located geometrically and refined using a riding model. The structure of 4 was refined as a racemic twin and restraints were applied to the thermal displacement parameters to maintain sensible values. Crystal structure and refinement data are given in Table 4. The structures are shown in Fig. 1–8 with thermal ellipsoids drawn at the 50% probability level.

Acknowledgements

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References