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

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9-Amino-9-phosphabicyclo[3.3.1]nonanes, (PhobPNHR′; R = Me or ^{i}Pr) are readily prepared by aminolysis of PhobPCl and are significantly less susceptible to hydrolysis than the acyclic analogues Cy_2PNHR'. Treatment of Cy_2PNHMe with Cy_2PCl readily gave $Cy_2PNMePCy_2$. By contrast, treatment of PhobPCl with PhobPNHMe in the presence of Et_3N does not afford PhobPNMePPhob but instead the salt [PhobP(=NMeH)PPhob]Cl is formed which, upon addition of $[PtCl_2(NC^tBu)_2]$ gives the zwitterionic complex $[PtCl_3(PhobP(=NMeH)PPhob)]$. The neutral PhobP(=NMe)PPhob is accessible from PhobNMeLi and is converted to the chelate $[PdCl_2(PhobPNMePPhob)]$ by addition of $[PdCl_2(cod)]$. The anomalous preference of the PhobP group for the formation of PPN products is discussed. The unsymmetrical diphos ligands $PhobPNMePAr_2$ (Ar = Ph, *o*-Tol) are prepared, converted to $[Cr(CO)_4(PhobPNMePAr_2)]$ 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 catalysis[3,4] 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]

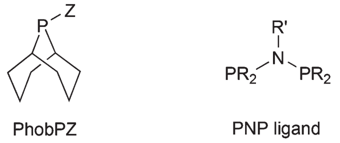

Chart 1

Aminodiphosphines $R_2PNR'PR_2$ (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 $R_2PNR'PR_2$ 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 ligands[9] 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 R_2PNHR' species are presumed intermediates and when R or R′ is bulky, they are

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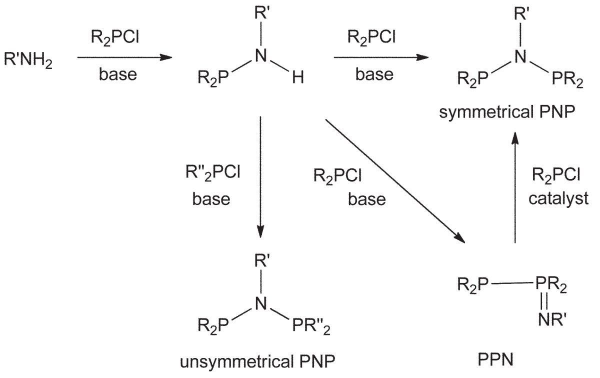
Table 1 Catalytic data for Cr–PNP based tri/tetramerisation[a]

Ligand	P/bar	T/°C	TON/kg per g Cr	TOF/kg per g Cr per h	1-C_8 : 1-C_6	C_6 /wt% (% 1-C_6)	C_8 /wt% (% 1-C_8)	C_{10+}/wt%	PE/wt %
$Ph_2PNMePPh_2$ [b]	30	65	27	54	5.7	24.8 (39.4)	59.0 (94.1)	n/r	1.4
$Ph_2PN^iPrPPh_2$ [b]	30	65	12	24	2.1	32.7 (86.5)	60.6 (99.2)	n/r	0.3
$Ph_2PN^iPrPPh_2$ [c]	45	45	272	544	5.7	16.9 (70.3)	68.3 (98.8)	n/r	1.1
$Et_2PNMePEt_2$ [c]	45	45	4	8	4.1	16.8 (64.6)	45.2 (97.4)	n/r	13.6
$Ph_2PNMePPh_2$ [d]	45	60	482	964	9.5	16.4 (33.4)	54.0 (95.9)	24.8	4.9
$Ph_2PN^iPrPPh_2$ [d]	45	60	552	1104	5.4	16.8 (75.5)	69.5 (99.0)	12.6	0.9

[a] Catalysis data taken from ref. 7 and 8. All wt% values are of total product slate. C_6 and C_8 refers to the entire C_6 and C_8 fractions and 1-C_6 and 1-C_8 refer to the proportion of the linear α-olefin within that fraction. [b] Catalysis conditions: 33 μmol $CrCl_3(THF)_3$; 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.



Scheme 1

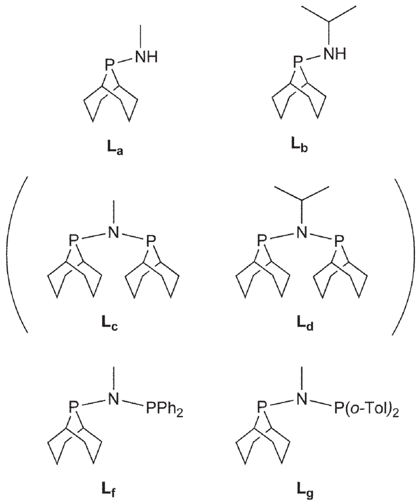


Chart 2 Aminophobanes targets; $\mathbf{L_c}$ and $\mathbf{L_d}$ (in parentheses) have not been observed.

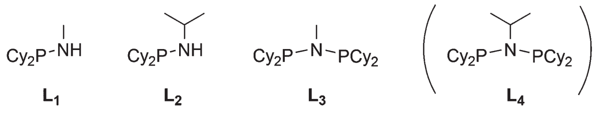


Chart 3 Aminodicyclohexylphosphines targets; $\mathbf{L_4}$ (in parentheses) has not been observed.

readily isolated and are potential intermediates to unsymmetrical PNP ligands.[11] When the substituents in either of the reactants R_2PCl or $R'NH_2$ 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 Ph_2PCl.

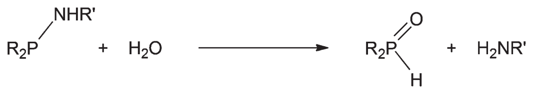
We were interested in investigating PNP ligands such as $\mathbf{L_a}$–$\mathbf{L_d}$ where a phobyl group has been incorporated (Chart 2). It is shown here that the monophosphines $\mathbf{L_a}$ and $\mathbf{L_b}$ are readily prepared but their conversions to $\mathbf{L_c}$ and $\mathbf{L_d}$ has not been achieved. However the mixed diphosphines $\mathbf{L_f}$ and $\mathbf{L_g}$ are accessible and are shown to be ligands for Cr-catalysed ethene tri/tetramerisation.

Results and discussion

Stereoelectronically, a Cy_2P 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 expected[12] and the approximately 90° C–P–C bridgehead angle in PhobP has the effect of lowering the HOMO and LUMO energies.[13] Ligands $\mathbf{L_1}$–$\mathbf{L_4}$ (Chart 3) were targeted in the belief that a comparison of their chemistry with the phobane analogues $\mathbf{L_a}$–$\mathbf{L_d}$ (Chart 2) would provide insight into the effect of the bicycle.

Monodentate aminophobanes

The monophobanes $\mathbf{L_a}$ and $\mathbf{L_b}$ were readily prepared by aminolysis of PhobPCl. The relative lability of $\mathbf{L_a}$ and $\mathbf{L_b}$ to hydrolysis (eqn (1)) was gauged by treatment of $\mathbf{L_a}$, $\mathbf{L_b}$, $\mathbf{L_1}$ and $\mathbf{L_2}$ with aqueous solutions under the same conditions and monitoring the formation of $R_2P({=}O)H$ by ^{31}P NMR spectroscopy. All four aminophosphines eventually underwent complete hydrolysis but at different rates. Comparison of the extents of hydrolysis after 16 h (Table 2) shows that the NH^{i}Pr 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 Cy_2PNHR analogues. The resistance to hydrolysis of PhobPNHR is consonant with the phobyl moiety behaving as a bulky group.[12]



$$R_2P{-}NHR' + H_2O \longrightarrow R_2P(=O)H + H_2NR' \qquad (1)$$

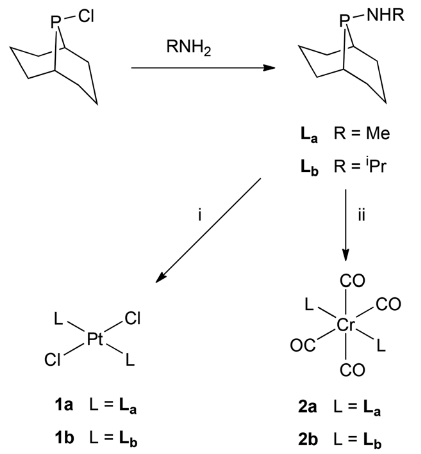
The donor properties of $\mathbf{L_a}$ and $\mathbf{L_b}$ can be compared quantitatively with $\mathbf{L_1}$ and $\mathbf{L_2}$ from the ν_{CO} values for their *trans*-[RhCl(CO)(L)$_2$] complexes.[14] The rhodium complexes were made *in situ* (see Scheme 2) and the recorded ν_{CO} values (Table 2) are consistent with $\mathbf{L_a}$ and $\mathbf{L_b}$ being slightly poorer σ-donors/better π-acceptors than their acyclic analogues $\mathbf{L_1}$ and $\mathbf{L_2}$, as expected.[13]

Ligands $\mathbf{L_a}$ and $\mathbf{L_b}$ 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*-[PtCl$_2$($\mathbf{L_2}$)$_2$] (**3**), an acyclic analogue of **1b** has been determined (Fig. 3).

Table 2 Comparison of some properties of aminophobanes and acyclic analogues

	% Hydrolysis at 16 h^a	ν_{CO} ^{b}/cm^{-1}
PhobPNHMe ($\mathbf{L_a}$)	5	1957
Cy_2PNHMe ($\mathbf{L_1}$)	100^c	1955
PhobPNH^{i}Pr ($\mathbf{L_b}$)	1	1954
Cy_2PNH^{i}Pr ($\mathbf{L_2}$)	64	1951

^{a} For the hydrolysis experiments, the aminophosphines (1.4 mmol) were dissolved in a 0.55 M solution of water in MeOH (25 mL) and stirred. The reactions were monitored by periodically taking aliquots of the solution and measuring the ^{31}P NMR spectrum. ^{b} The IR spectrum in the 2050–1850 cm^{-1} region was measured in CH_2Cl_2 for the *trans*-[RhCl(CO)(L)$_2$] complexes generated *in situ* by combining [$Rh_2Cl_2(CO)_4$] with 4 equiv. of L. ^{c} $\mathbf{L_1}$ was 50% hydrolysed after 0.5 h.



Scheme 2 Reagents: (i) [PtCl$_2$(NC^{t}Bu)$_2$] in CH_2Cl_2; (ii) [Cr(CO)$_4$(nbd)] (nbd = norbornadiene) in CH_2Cl_2.

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*-[PtCl$_2$(PhobPZ)$_2$] complexes.[6,12,15] The cone angle of $\mathbf{L_b}$ in **1b** is 111.8° and of $\mathbf{L_2}$ in **3** is larger at 115.8°. In the structure of **2b**, the asymmetric unit contains one complete molecule. The cone angle of $\mathbf{L_b}$ 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

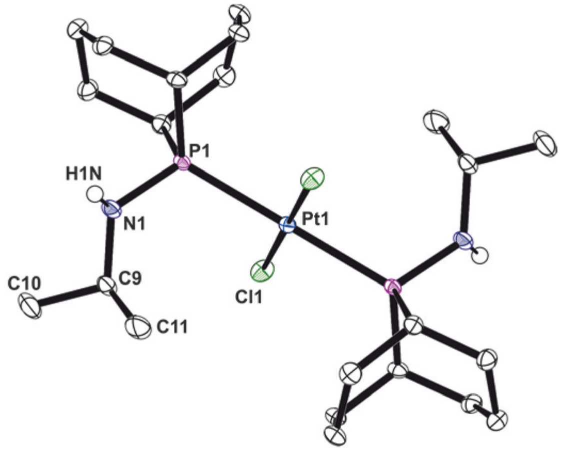


Fig. 1 Crystal structure of *trans*-[PtCl$_2$(PhobPNH^{i}Pr)$_2$] (**1b**). All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pt(1)–P(1) 2.3241(10), Pt(1)–Cl(1) 2.3102(8), P(1)–N(1) 1.6594(16), Pt(1)–P(1)–N(1) 109.40(6).

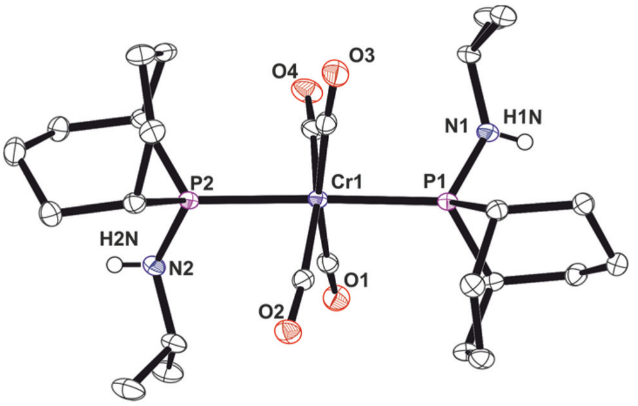


Fig. 2 Crystal structure of *trans*-[Cr(CO)$_4$(PhobPNH^{i}Pr)$_2$] (**2b**). All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Cr(1)–P(1) 2.3434(3), Cr(1)–P(2) 2.3499(3), P(1)–N(1) 1.6910(9), P(2)–N(2) 1.6934(10), 114.06(4), Cr(1)–P(1)–N(1) 114.20(2), Cr(1)–P(2)–N(2).

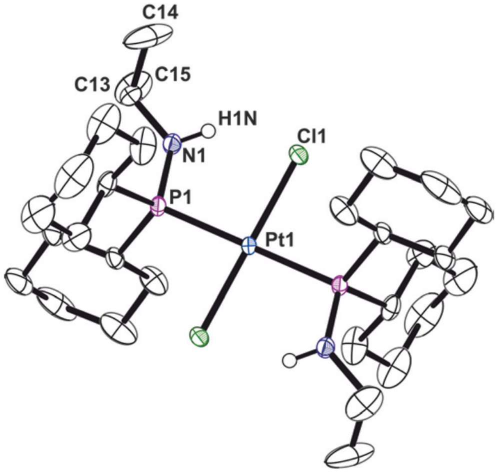
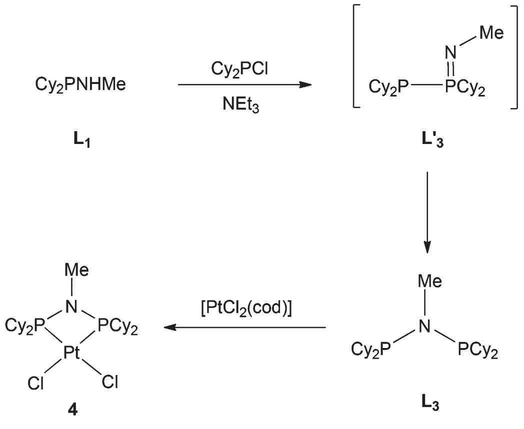


Fig. 3 Crystal structure of *trans*-[$PtCl_2(Cy_2PNH^iPr)_2$] (**3**). All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pt(1)–P(1) 2.3178(7), Pt(1)–Cl(1) 2.3193(7), P(1)–N(1) 1.681(3), Pt(1)–P(1)–N(1) 113.91(10).

groups are *gauche* to each other, a conformation not previously observed in PhobPZ complexes.

Bidentate aminophobanes

The previously reported[16] diphosphinoamine $\mathbf{L_3}$ is readily prepared from $MeNH_2$ and Cy_2PCl in the presence of Et_3N (Scheme 3). The intermediate in this reaction is presumably Cy_2PNHMe ($\mathbf{L_1}$) and indeed treatment of the isolated $\mathbf{L_1}$ with Cy_2PCl in the presence of Et_3N in CH_2Cl_2 gave $\mathbf{L_3}$ quantitatively according to ^{31}P NMR spectroscopy. The spectrum of the reaction mixture also revealed a transient PPN species (as evidenced by a large J_{PP} of 280 Hz) to which the tautomeric structure $\mathbf{L'_3}$ is assigned. The PPN species $\mathbf{L'_3}$ smoothly converted over 30 min to PNP ligand $\mathbf{L_3}$ whose structure was confirmed by its conversion to the chelate complex **4** (Scheme 3), the crystal structure of which has been determined (Fig. 4).



Scheme 3

The asymmetric unit consists of three independent molecules of **4** along with six chloroform molecules. Although the PtP_2Cl_2 fragment is approximately planar (rms deviation ~0.03 Å), the Pt has a distorted square planar geometry due to the constraints of the 4-membered PNP chelate. The three independent Pt–P–N–P rings are approximately planar with rms deviations of ~0.03 Å.

In contrast to the ready reaction of $\mathbf{L_1}$ with Cy_2PCl to give PNP ligand $\mathbf{L_3}$ (Scheme 3), the reaction of PhobPNHMe ($\mathbf{L_a}$) with PhobPCl in the presence of NEt_3 or *N*-methylpyrrolidine did not give the expected diphosphinoamine $\mathbf{L_c}$. Instead, a PPN species (J_{PP} = 407 Hz) was the exclusive product; this was initially assigned structure $\mathbf{L'_c}$ but its ^1H NMR spectrum (which showed a multiplet at 7.01 ppm integrating for 1H) and mass spectrum (M^+ at [$\mathbf{L'_c}$ + 1]) led to its assignment as the HCl adduct $\mathbf{L'_c}$·HCl (Scheme 4). This was supported by its reaction with [$PtCl_2(NC^tBu)_2$] which yielded crystals of the insoluble, zwitterionic complex [$PtCl_3(\mathbf{L'_c}\cdot H)$] (**5**) whose X-ray crystal structure is shown in Fig. 5. The conditions under which $\mathbf{L'_c}$·HCl was formed (Scheme 4) indicate that the iminophosphine $\mathbf{L'_c}$ is more basic than either NEt_3 or *N*-methylpyrrolidine.

The crystal structure of **5** has a square planar Pt with an rms deviation of the atoms from the square plane of ~0.03 Å. The PPN ligand is rotated away from the $PtCl_3$ plane with torsion angles Cl1–Pt1–P1–P2 of −102.4(1)° and Cl3–Pt1–P1–P2 of 75.6(1)°.

Treatment of PhobPNMeH with ^{n}BuLi at −78 °C followed by PhobPCl gave a PPN species with a J_{PP} = 327 Hz (significantly smaller than the J_{PP} of 407 Hz for $\mathbf{L'_c}$·HCl) that is assigned to the neutral $\mathbf{L_c'}$ which has been isolated. No reaction occurred upon addition of PhobPCl to $\mathbf{L'_c}$ in CH_2Cl_2, conditions that might have been expected to tautomerise $\mathbf{L'_c}$ to $\mathbf{L_c}$.[10]

It has previously been shown that some neutral PPN compounds rearrange when they react with [$MCl_2(cod)$] (M = Pd or Pt)[17] or [$NiBr_2(dme)$][18] to give PNP chelate complexes. Reaction

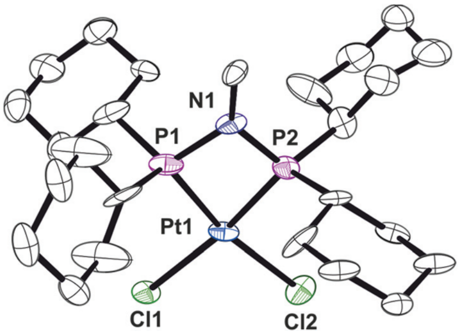
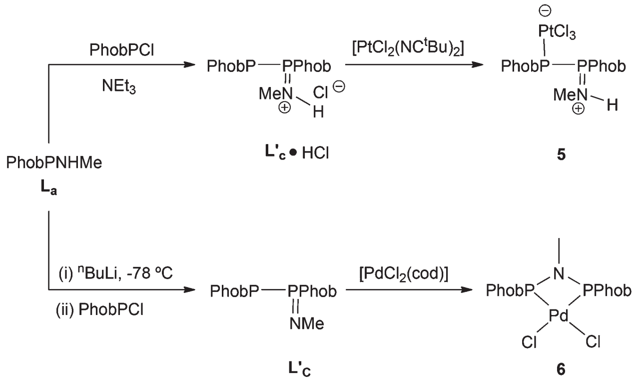


Fig. 4 Crystal structure of complex [$PtCl_2(\mathbf{L_3})$] (**4**). Only one of the three unique molecules is shown and all hydrogen atoms and six molecules of $CHCl_3$ have been omitted for clarity. Selected bond lengths (Å) and angles (°); Pt(1)–P(2) 2.206(6), Pt(1)–P(1) 2.257(6), Pt(1)–Cl(1) 2.363(5), Pt(1)–Cl(2) 2.376(7), P(1)–N(1) 1.745(17), P(2)–N(1) 1.668(18), P(2)–Pt(1)–P(1) 71.1(3), N(1)–P(1)–Pt(1) 92.8(6), N(1)–P(2)–Pt(1) 96.9(9), P(2)–N(1)–P(1) 99.0(8).



Scheme 4

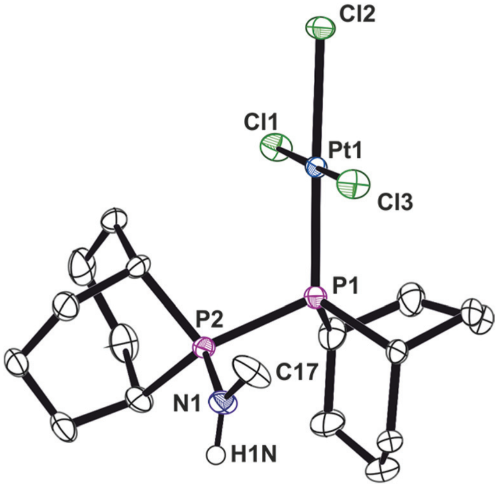


Fig. 5 Crystal structure of $[PtCl_3(L'_c{\cdot}H)]$ (**5**). All hydrogen (except H1N) atoms, a CH_2Cl_2 molecule (50% occupied) and one $C_2H_2Cl_4$ molecule have been omitted for clarity. Selected bond lengths (Å) and angles (°); Pt(1)–P(1) 2.2194(13), Pt(1)–Cl(1) 2.3085(12), Pt(1)–Cl(2) 2.3683(12), Pt(1)–Cl(3) 2.2988(12), P(1)–P(2) 2.2797(19), P(2)–N(1) 1.629(4), N(1)–C(17) 1.468(7), N(1)–H(1N) 0.8800, P(1)–Pt(1)–Cl(3) 88.86(5), P(1)–Pt(1)–Cl(1) 92.80(5), Cl(3)–Pt(1)–Cl(1)177.36(5), P(1)–Pt(1)–Cl(2) 177.89(5), Cl(3)–Pt(1)–Cl(2)89.39(5), Cl(1)–Pt(1)–Cl(2) 88.99(5), Pt(1)–P(1)–P(2) 108.26(6), N(1)–P(2)–P(1) 111.95(19).

of $[PdCl_2(cod)]$ with $\mathbf{L'_c}$ gave the chelate $[PdCl_2(\mathbf{L_c})]$ (**6**) whose crystal structure has been determined and is shown in Fig. 6.

The asymmetric unit contains one molecule of **6**, with the PdP_2Cl_2 fragment being essentially planar (rms ~ 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 Pd1–P1–N1–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 $\mathbf{L_a}$ and $\mathbf{L_1}$ with R_2PCl (see Schemes 3 and 4), it appears that the PhobP group differs from Cy_2P and Ar_2P 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 = Cy ($\mathbf{L_e}$), Ph ($\mathbf{L_f}$) or *o*-Tol ($\mathbf{L_g}$) were attempted?

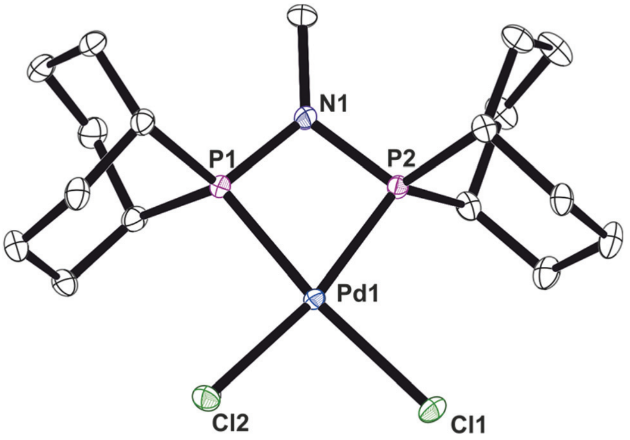
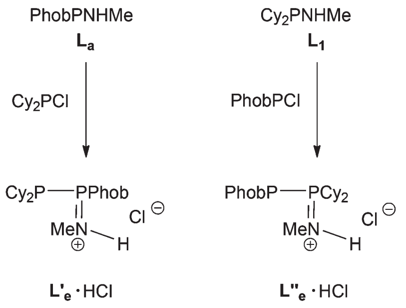


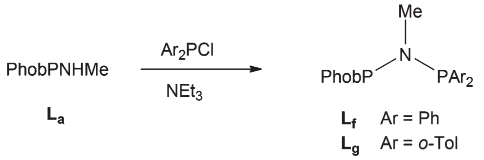
Fig. 6 Crystal structure of complex $[PdCl_2(L_c)]$ (**6**). All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°); Pd(1)–P(1) 2.2311(4), Pd(1)–P(2) 2.2353(4), Pd(1)–Cl(2) 2.3735(4), Pd(1)–Cl(1) 2.3748(4), P(1)–N(1) 1.6949(14), P(2)–N(1) 1.7016(14), P(1)–Pd(1)–P(2) 70.851(15).

The reaction between PhobPNHMe and Cy_2PCl was followed by ^{31}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 $\mathbf{L'_e}{\cdot}HCl$ (Scheme 5); addition of Et_3N led to multiple P-containing species but there was no evidence for the formation of the neutral PPN ($\mathbf{L'_e}$) or PNP ($\mathbf{L_e}$) species. The reaction between PhobPCl and Cy_2PNHMe was also monitored and in this case, ^{31}P NMR spectroscopy revealed that a PPN product was formed (J_{PP} = 403 Hz) which was assigned to the cationic species $\mathbf{L''_e}{\cdot}HCl$ (Scheme 5), an isomer of $\mathbf{L'_e}{\cdot}HCl$. It therefore appears that the PPN-promoting effect of the PhobP group dominates over the PNP-preference of the Cy_2P group.

The unsymmetrical PNP ligands $\mathbf{L_f}$ and $\mathbf{L_g}$ (J_{PP} = 80 Hz in both) featuring PhobP groups were successfully prepared upon treatment of PhobPNHMe with Ar_2PCl (Ar = Ph or *o*-Tol) in the presence of Et_3N (eqn (2)). It therefore appears that the PPN formation promoted by the PhobP group is superseded by the PNP preference of the Ar_2P groups.



Scheme 5

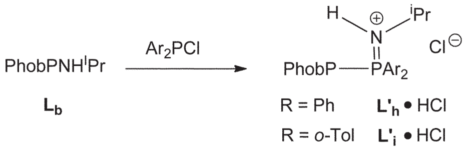


(2)

The reaction of PhobPNHMe with Tol_2PCl was monitored by ^{31}P NMR spectroscopy. A PPN species (J_{PP} = 331 Hz), tentatively assigned to $\mathbf{L'_g}$·HCl (Scheme 6) was formed rapidly which, upon treatment with NEt_3, was transformed to $\mathbf{L_g}$ (J_{PP} = 80 Hz).

Treatment of the bulky R_2PNH^iPr ($\mathbf{L_b}$ or $\mathbf{L_2}$) with R_2PCl (R_2P = Cy_2P or PhobP) under the conditions that converted R_2PNHMe to the corresponding $\mathbf{L_3}$ (Scheme 3) or $\mathbf{L'_c}$·HCl/$\mathbf{L'_c}$ (Scheme 4) gave, according to *in situ* ^{31}P NMR spectroscopy, mixtures of unidentified products as well as the reactants.

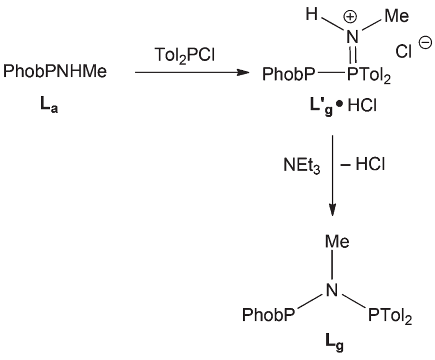
Under the conditions that smoothly led to the mixed PNP ligands $\mathbf{L_f}$ and $\mathbf{L_g}$ (eqn (2)), $\mathbf{L_b}$ reacted with Ar_2PCl to give PPN species whose structures were assigned to the protonated $\mathbf{L'_h}$·HCl and $\mathbf{L'_i}$·HCl (eqn (3)) on the basis of the large J_{PP} values of 338 and 359 Hz respectively. Crystals of $\mathbf{L'_h}$·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.



(3)

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_2PCl catalyst and we have observed PPN species as transients *en route* to the PNP products (*e.g.* $Cy_2PNMePCy_2$ see Scheme 3) showing that the PNP is the thermodynamic product. In other cases (*e.g.* $Cy_2PN\{SO_2Ar\}PCy_2$) 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′**·HCl product that is resistant to deprotonation by amines.



Scheme 6

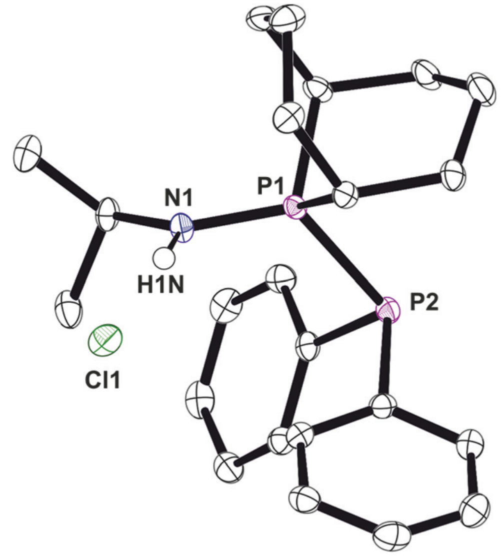
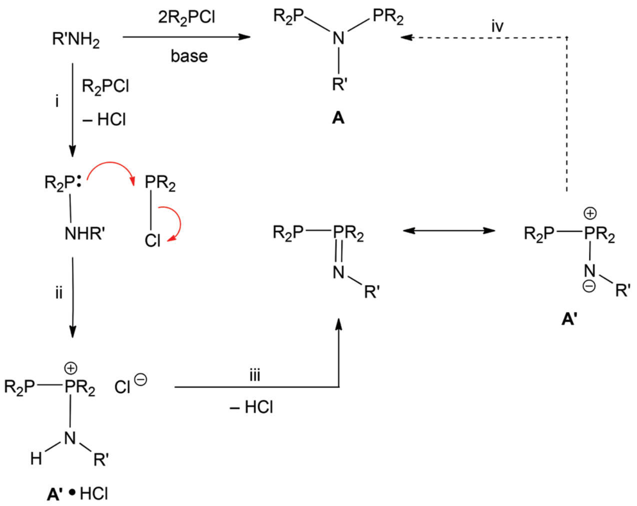


Fig. 7 Crystal structure of complex $\mathbf{L'_h}$·HCl. All hydrogen atoms, except on the N1, have been omitted for clarity. Selected bond lengths (Å) and angles (°); P(1)–N(1) 1.6241(0), P(1)–P(2) 2.2403(4), N(1)–H(1N) 0.863(16), N(1)–P(1)–P(2) 119.93(4).



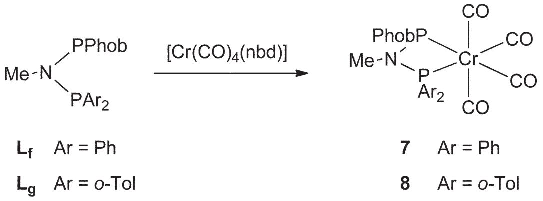
Scheme 7 Proposed pathway for the conversion of an amine to a PNP ligand. A dotted line is used for step iv since this step is not observed with the aminophobanes.

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′**·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 $Cy_2PNMePCy_2$ *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 $\mathbf{L_f}$ and $\mathbf{L_g}$ 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 $\mathbf{L_f}$ or $\mathbf{L_g}$ 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).



(4)

In combination with chromium, the ligands $\mathbf{L_f}$ and $\mathbf{L_g}$ 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 $\mathbf{L_g}$) but concurrently with Schulz-Flory selectivity (Fig. 10). The 1-octene to 1-hexene ratios obtained for both ligands is high.

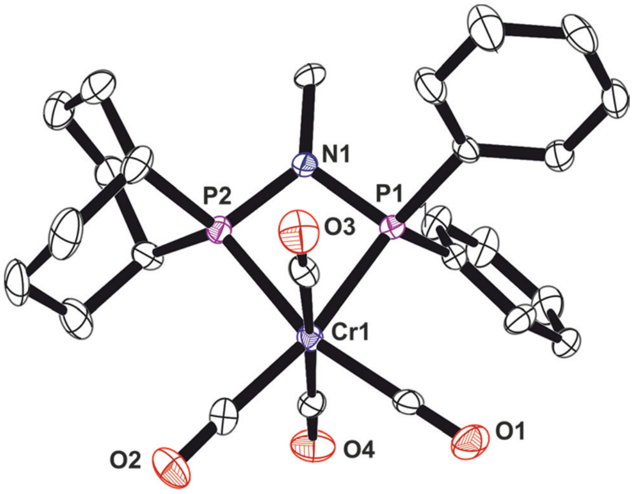


Fig. 8 Crystal structure of complex $[Cr(CO)_4(\mathbf{L_f})]$ (**7**). All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°); Cr(1)–P(3) 2.3163 (16), Cr(1)–P(2) 2.3474(16), P(2)–N(1) 1.714(5), P(3)–N(1) 1.701(5), P(3)–Cr(1)–P(2) 68.29(5), P(3)–N(1)–P(2) 100.1(2), N(1)–P(3)–Cr(1) 96.48(17), N(1)–P(2)–Cr(1) 94.99(16), C(17)–P(2)–C(16) 96.0(3), C(7)–P(3)–C(1) 103.5(2).

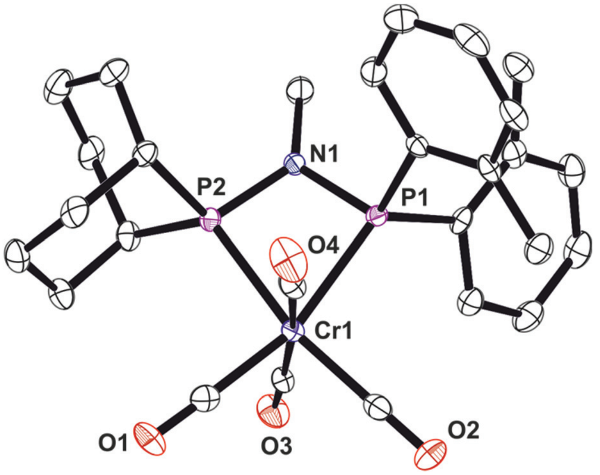


Fig. 9 Crystal structure of $[Cr(CO)_4(\mathbf{L_g})]$ (**8**). All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°); Cr(1)–P(1) 2.3477(6), Cr(1)–P(2) 2.3669(6), P(1)–N(1) 1.7146(17), P(2)–N(1) 1.7035(17), P(1)–Cr(1)–P(2) 68.04(4), P(2)–N(1)–P(1) 101.01(9), N(1)–P(1)–Cr(1) 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).

Conclusions

The monodentate aminophobanes PhobPNHR (R = Me or ^{i}Pr) have been readily prepared and are more resistant to hydrolysis than their Cy_2PNHR analogues consistent with the PhobP group having a greater effective steric bulk than Cy_2P. 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[21] 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,[13] $[Cr(CO)_4(\eta^4\text{-norbornadiene})]$,[22] $[PtCl_2(NC^tBu)_2]$,[23] $[PdCl_2(cod)]$,[24] 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

Table 3 Ethene oligomerisation results[a]

L	Rxn time/min	TON/kg per g Cr	TOF/kg per g Cr per h	Liquid product/wt%	Solid product (PE)/wt%	C_4/wt%	C_6/wt% (% 1-C_6)	C_8/wt% (% 1-C_8)	1-C_8 : 1-C_6	C_{10-14} /wt%	C_{15+}/wt%
$\mathbf{L_f}$	24.8	393	951	89.5	10.5	1.7	16.1 (20.7)	26.7 (93.0)	7.5	22.4	33.0
$\mathbf{L_g}$	16.7	31	110	56.6	43.4	1.8	16.3 (70.2)	61.1 (99.4)	5.3	7.2	13.6

[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.

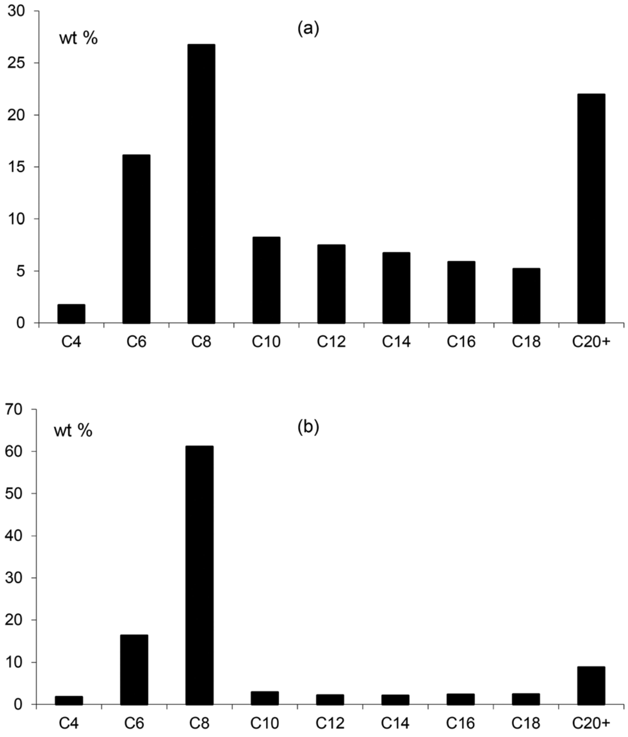


Fig. 10 The distribution of products in the liquid fraction formed in the ethene oligomerisation catalysed by Cr catalysts of (a) $\mathbf{L_f}$ and (b) $\mathbf{L_g}$ showing the preferential formation of C_6 and C_8 alkenes.

out on a Perkin Elmer 1600 Series FTIR. Mass spectra were recorded on a MD800 by the Mass Spectrometry Service, University of Bristol. Elemental analyses were carried out by the Microanalytical Laboratory of the School of Chemistry, University of Bristol.

Preparation of PhobPNHMe (L_a)

PhobPCl (2.00 g, 11.3 mmol) was dissolved in a 2 M THF solution of $MeNH_2$ (22.9 mL, 45.3 mmol). The resulting suspension was stirred at room temperature for 16 h. The solvent was removed under reduced pressure to give a white residue which was extracted with diethyl ether (35 mL). The ethereal solution was filtered to remove the methylammonium chloride and then the solvent was evaporated to dryness to give a white solid (1.42 g, 75%). $^{31}P\{^1H\}$ NMR (121 MHz; $CDCl_3$) δ 26.8. ^1H NMR (270 MHz; $CDCl_3$) δ 1.48–2.20 (14H, m, phobane), 2.67 (3H, d, J_{HP} = 15.0 Hz, CH_3N). $^{13}C\{^1H\}$ NMR (67 MHz; $CDCl_3$) δ 21.5 (d, J_{CP} = 2.0 Hz, CH_2), 22.9 (d, J_{CP} = 4.6 Hz, CH_2), 23.7 (d, J_{CP} = 3.1 Hz, CH_2), 28.1 (d, J_{CP} = 10.9 Hz, CH_3N), 31.2 (d, J_{CP} = 14.0 Hz, CH_2), 33.0 (d, J_{CP} = 26.9 Hz, CH). Elemental analysis: Found (Calc. for $C_9H_{18}NP$) C, 63.5 (63.1); N, 8.1 (8.1); H, 10.4 (10.6) %. MS (ESI: m/z 171 (M^+).

Preparation of PhobPNH^{i}Pr (L_b)

PhobPCl (0.88 g, 5.0 mmol) was dissolved in a solution of $^iPrNH_2$ (1.54 mL, 20.1 mmol) in THF (9.0 mL). The resulting suspension was stirred at room temperature for 16 h and the filtered to remove the isopropylammonium chloride. The solvent was removed under reduced pressure to give an oily residue which was dissolved in toluene (10 mL) to precipitate any remaining isopropylammonium chloride. This toluene solution was filtered to remove the methylammonium chloride and then the solvent was evaporated to dryness to give a colourless oil (0.57 g, 63%). $^{31}P\{^1H\}$ NMR (121 MHz; $CDCl_3$) δ 15.5. ^1H NMR (270 MHz; $CDCl_3$) δ 1.47–2.15 (14H, m, phobane), 1.14 (6H, d, J_{HP} = 6.2 Hz, CH_3N), 3.1–3.3 (1H, m, CH). $^{13}C\{^1H\}$ NMR (75 MHz; $CDCl_3$) δ 21.6 (s, CH_2), 22.9 (s, CH_2), 24.0 (d, J_{CP} = 3.1 Hz, CH_3), 26.7 (d, J_{CP} = 6.9 Hz, CH_2), 29.5 (d, J_{CP} = 9.2 Hz, CH), 31.4 (d, J_{CP} = 13.8 Hz, CH_2), 48.6 (d, J_{CP} = 24.3 Hz, CH). Elemental analysis: Found (Calc. for $C_{11}H_{22}NP$) C, 66.7 (66.3); N, 6.9 (7.0); H, 11.3 (11.1) %. HRMS (EI): Found (Calc. for $C_{11}H_{22}NP$ 199.1496 (199.1490).

Preparation of [PhobP(═NHMe)PPhob]Cl ($L'_c\cdot$HCl)

A solution of PhobPCl (0.530 g, 3.03 mmol) in CH_2Cl_2 (2.0 mL) was added in portions to a solution of $\mathbf{L_a}$ (0.510 g, 3.00 mmol)) and N-methylpyrrolidine (2.40 g, 28.2 mmol) in CH_2Cl_2 (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%). $^{31}P\ \{^1H\}$ NMR (121 MHz; $CDCl_3$) δ 46.5 (d, J_{PP} = 407 Hz), −24.2 (d, J_{PP} = 407 Hz). ^1H NMR (400 MHz; $CDCl_3$) δ 1.60–2.54 (28H, m, phobane), 2.66 (3H, dd, J_{HP} = 12.3 Hz, J_{HP} = 5.68 Hz, CH_3N), 7.01 (1H, m, HCl). $^{13}C\ \{^1H\}$ NMR (100 MHz; $CDCl_3$) δ 20.4 (d, J_{CP} = 6.9 Hz), 20.7 (d, J_{CP} = 6.9 Hz), 20.8 (d, J_{CP} = 6.9 Hz), 21.2 (d, J_{CP} = 1.5 Hz), 21.9 (d, J_{CP} = 6.9 Hz), 24.9 (d, J_{CP} = 6.1 Hz), 25.1 (d, J_{CP} = 6.1 Hz), 26.2 (d, J_{CP} = 6.1 Hz), 26.9 (d, J_{CP} = 6.1 Hz), 27.3 (d, J_{CP} = 6.1 Hz), 27.5 (dd, J_{CP} = 9.2 Hz, J_{CP} = 1.5 Hz) 27.7 (d, J_{CP} = 3.8 Hz), 28.9 (t, J_{CP} = 3.84 Hz), 32.7 (d, J_{CP} = 14.6 Hz), 32.9 (d, J_{CP} = 15.3 Hz). Elemental analysis: Found (Calc. for $C_{17}H_{32}ClNP_2$) C, 59.1

(58.7); N, 3.8 (4.0); H, 9.4 (9.3) %. HRMS (EI): Found (Calc. for $C_{17}H_{32}NP_2$) 312.2004 (312.2011).

Preparation of PhobP(=NMe)PPhob ($\mathbf{L'_c}$)

To the solution of $\mathbf{L_a}$ (0.45 g, 2.6 mmol) in THF (3.0 mL), a 1.6 M solution of ^{n}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. PhobPCl (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%) $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6) δ 30.7 (d, J_{PP} = 320 Hz), −32.3 (d, J_{PP} = 320 Hz). ^1H NMR (300 MHz, C_6D_6) δ 1.25–2.52 (14H, m, phobane), 2.62 (3H, dd, J_{HP} = 14.5 Hz, J_{HP} = 5.7 Hz, CH_3N).

Preparation of PhobPNMePPh$_2$ ($\mathbf{L_f}$)

Aminophobane $\mathbf{L_a}$ (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, Ph_2PCl (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%). $^{31}P\ \{^1H\}$ NMR (121 MHz; CD_2Cl_2) NMR δ 57.6 (d, J_{PP} = 80 Hz), 51.1 (d, J_{PP} = 80 Hz). ^1H NMR (270 MHz; CD_2Cl_2) δ 1.21–2.24 (14H, m, phobane), 2.32 (3H, dd, J_{HP} = 4.3 Hz, J_{HP} = 8.5 Hz CH_3N), 7.05–7.22, 7.55–7.69 (10H, 2 m, *Ar*H). $^{13}C\ \{^1H\}$ NMR (67 MHz; CD_2Cl_2) δ 21.8 (d, J_{CP} = 1.5 Hz, CH_2), 23.2 (d, J_{CP} = 2.6 Hz, CH_2), 28.7 (dd, J_{CP} = 20.7 Hz, J_{CP} = 11.9 Hz, CH_3N), 30.2 (d, J_{CP} = 17.1 Hz, CH_2), 33.0 (dd, J_{CP} = 16.6 Hz, J_{CP} = 7.2 Hz, CH), 24.1 (t, J_{CP} = 3.1 Hz, CH_2), 128.2 (d, J_{CP} = 5.7 Hz, CH), 128.4 (s, CH) 132.2 (d, J_{CP} = 19.2 Hz, CH), 138.4 (dd, J_{CP} = 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 (EI): Found (Calc. for $C_{21}H_{27}NP_2$) 355.1613 (355.1619).

Preparation of PhobPNMeP(*o*-Tol)$_2$ ($\mathbf{L_g}$)

Aminophobane $\mathbf{L_a}$ (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, (*o*-Tol)$_2$PCl (0.580 g, 1.52 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 recrystallized from hot MeCN to afford white needles (0.17 g, 38%). $^{31}P\ \{^1H\}$ NMR (121 MHz; CD_2Cl_2) δ 60.2, (d, J_{PP} = 80 Hz), 36.8 (d, J_{PP} = 80 Hz). ^1H NMR (300 MHz; CD_2Cl_2) δ 1.44–2.59 (14H, m, phobane), 2.34 (3H, dd, J_{HP} = 3.9 Hz, J_{HP} = 8.9 Hz, CH_3N), 2.35 (6H, s, CH_3), 7.07–7.42 (8H, m, H*Ar*). $^{13}C\ \{^1H\}$ (100 MHz; CD_2Cl_2) 21.0 (d, J_{CP} = 5.3 Hz, CH_3), 21.2 (d, J_{CP} = 5.3 Hz, CH_3), 21.7 (d, J_{CP} = 1.5 Hz, CH_2), 23.1 (d, J_{CP} = 3.0 Hz, CH_2), 24.3 (t, J_{CP} = 2.8 Hz, CH_2), 28.7 (dd, J_{CP} = 20.7 Hz, J_{CP} = 11.5 Hz, CH_3N), 30.5 (dd, J_{CP} = 16.9 Hz, J_{CP} = 1.1 Hz CH_2), 33.9 (dd, J_{CP} = 16.1 Hz, J_{CP} = 6.1 Hz, CH), 128.5 (s, CH) 125.5 (s, CH), 130.3 (d, J_{CP} = 3.8 Hz, CH), 131.6 (d, J_{CP} = 2.3 Hz, CH), 136.7 (dd, J_{CP} = 17.6 Hz, J_{CP} = 1.5 Hz, C), 141.7 (d, J_{CP} = 26.9 Hz, C). Elemental analysis: Found (Calc. for $C_{23}H_{31}NP_2$) C, 72.2 (72.0); N, 3.8 (3.6); H, 8.1 (8.1) %. HRMS (EI): Found (Calc. for $C_{23}H_{31}NP_2$) 383.1931 (383.1932).

Preparation of [PhobP(=NH^{i}Pr)PPh$_2$]Cl ($\mathbf{L'_h}$·HCl)

Ph_2PCl (0.90 g, 5.0 mmol) was added dropwise to a solution of $\mathbf{L_b}$ (0.83 g, 4.2 mmol) and *N*-methylpyrrolidine (0.39 g, 4.2 mmol) in CH_2Cl_2 (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, 44%) suitable for X-ray crystallography. $^{31}P\{^1H\}$ NMR (121 MHz; $CDCl_3$) δ 50.0 (d, J_{PP} = 338 Hz), 39.1 (d, J_{PP} = 338 Hz). ^1H NMR (400 MHz; $CDCl_3$) δ 0.94 (6H, d, J_{HH} = 6.2 Hz, CH_3), 1.35 (1H, d, J_{HH} = 6.4 Hz, CH), 1.74–2.94 (14H, m, phobane), 7.46–7.54, 7.64–7.77 (10H, 2 m, H*Ar*). $^{13}C\{^1H\}$ NMR (100 MHz; CD_2Cl_2) 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 (EI): Found (Calc. for $C_{23}H_{32}NP_2$) 384.2004 (384.1999).

Preparation of [PhobP(=NH^{i}Pr)P(*o*-Tol)$_2$]Cl ($\mathbf{L'_i}$·HCl)

A solution of (*o*-Tol)$_2$PCl (0.620 g, 2.51 mmol) in MeCN (5.0 mL) was added in portions to PhobPNH(^{i}Pr) ($\mathbf{L_b}$) (0.530 g, 2.67 mmol) and *N*-methylpyrrolidine (3.20 g, 37.5 mmol) in MeCN (5 mL). The reaction mixture was stirred for 1 h and then the solvent was removed under reduced pressure. The remaining white solid was recrystallised from hot MeCN to yield white crystals (0.71 g, 62%). $^{31}P\ \{^1H\}$ NMR (161 MHz; $CDCl_3$) δ 49.3 (d, J_{PP} = 359 Hz), −39.8 (d, J_{PP} = 359 Hz). ^1H (400 MHz; $CDCl_3$) δ 0.89 (6H, d, J_{HH} = 6.36 Hz, $CH_3{}^i$*Pr*), 1.65–2.40 (14H, m, phobane), 2.53 (6H, s, CH_3), 7.20–7.40 (8H, m, H*Ar*). $^{13}C\{^1H\}$ NMR (100 MHz; $CDCl_3$) δ 19.5 (dd, J_{CP} = 14.1 Hz, J_{CP} = 5.4 Hz), 21.1 (d, J_{CP} = 24.1 Hz), 23.8 (d, J_{CP} = 4.6 Hz), 25.8 (d, J_{CP} = 6.2 Hz), 26.8 (d, J_{CP} = 10.9 Hz), 28.5 (d, J_{CP} = 3.8 Hz), 28.9 (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), 135.9 (d, J_{CP} = 7.0 Hz), 142.3 (dd, J_{CP} = 31.9 Hz, J_{CP} = 7.0 Hz). Elemental analysis: Found (Calc. for $C_{25}H_{36}ClNP_2$) C, 67.0 (67.0); N, 3.5 (3.1); H, 8.5 (8.1)%.

Preparation of Cy$_2$PNMePCy$_2$ ($\mathbf{L_3}$)

Cy_2PCl (2.79 g, 11.9 mmol) was dissolved in CH_2Cl_2 (6.0 mL). To this, a 2 M THF solution of $MeNH_2$ (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 redissolved in toluene (30 mL). The [Et_3NH]Cl salt was filtered off to give a clear solution. The solvent was removed under reduced pressure to give the crude product, which was recrystallized from hot acetonitrile (0.77 g, 32%). $^{31}P\{^1H\}$ NMR (121 MHz; $CDCl_3$) δ 86.8. ^1H NMR (300 MHz; $CDCl_3$) δ 1.10–1.60 (44H, m, CH and CH_2), 2.64 (s, CH_2), 27.2 (s, CH_2), 29.5 (t, J_{CP} = 9.2 Hz, CH_3N). $^{13}C\{^1H\}$ NMR (300 MHz; $CDCl_3$)

δ 26.7 (d, J_{CP} 36.9 Hz, CH_3), 26.8 (s, CH_2), 24.9 (s, CH_2), 32.2 (t, J_{CP} 8.6 Hz, CH), 45.7 (s, CH_3). Elemental analysis: Found (Calc. for $C_{25}H_{47}NP_2$) C, 70.4 (70.9); N, 2.8 (3.3); H, 11.4 (11.2) %. HRMS (CI): Found (Calc. for $[C_{25}H_{47}NP_2H]$) 424.3262 (424.3262).

Preparation of *trans*-[PtCl$_2$(PhobPNHMe)$_2$] (1a)

PhobPNHMe (0.069 g, 0.45 mmol) was dissolved in CH_2Cl_2 (2.0 mL). $[PtCl_2(NC^tBu)_2]$ (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%). $^{31}P\{^1H\}$ NMR (121 MHz; $CDCl_3$) δ 46.3 (J_{PtP} = 2638 Hz). ^1H NMR (300 MHz; $CDCl_3$) δ 1.52–2.16 (28H, m, phobane), 2.98 (6H, t, J_{HP} = 6.6 Hz, CH_3N). $^{13}C\{^1H\}$ NMR (75 MHz; $CDCl_3$) δ 21.3 (s), 22.1 (s), 24.2 (t, J_{CP} = 6.6 Hz), 25.8 (s), 29.2 (s), 30.8 (s). Elemental analysis: Found (Calc. for $C_{18}H_{36}Cl_2N_2P_2Pt$) C, 35.4 (35.5); H, 5.5 (6.0); N, 4.6 (5.0) %. HRMS (EI): Found (Calc. for $[C_{18}H_{36}Cl_2N_2P_2Pt]H$) 608.1451 (608.1438).

Preparation of *trans*-[PtCl$_2$(PhobPNH^{i}Pr)$_2$] (1b)

PhobPNH^{i}Pr (0.18 g, 0.90 mmol) was dissolved in CH_2Cl_2 (2.0 mL). $[PtCl_2(NC^tBu)_2]$ (0.20 g, 0.46 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 (0.26 g, 85%). $^{31}P\{^1H\}$ NMR (121 MHz; $CDCl_3$) δ 40.4 (J_{PtP} = 2646 Hz). ^1H NMR (300 MHz; $CDCl_3$) δ 1.56–2.15, 2.55–2.76 (28H, m, phobane), 1.31 (12H, d, J_{HH} = 6.6 Hz, $CH_3{}^iPr$), 4.14–4.26 (2H, m, CH). $^{13}C\{^1H\}$ NMR (75 MHz; $CDCl_3$) δ 21.4 (t, J_{CP} = 2.3 Hz), 22.0 (t, J_{CP} = 2.3 Hz), 25.4 (t, J_{CP} = 24.3 Hz). Elemental analysis: Found (Calc. for $C_{22}H_{44}Cl_2N_2P_2Pt$) C, 39.7 (39.7); N, 3.9 (4.2); H, 6.6 (6.6)%. MS (ESI): *m/z* 665.21 $(M + 2H)^+$.

Preparation of *trans*-[Cr(CO)$_4$(PhobPNHMe)$_2$] (2a)

PhobPNHMe (0.048 g, 0.29 mmol) was dissolved in CH_2Cl_2 (4.0 mL). $[Cr(CO)_4(\eta^4\text{-norbornadiene})]$ (0.048 g, 0.15 mmol) was added and the resulting yellow solution was stirred for 24 h. The solvent was removed under reduced pressure and the resulting yellow solid product was washed with hexane (0.023 g, 26%). $^{31}P\{^1H\}$ NMR (121 MHz; $CDCl_3$) δ 102.5. ^1H NMR (300 MHz; $CDCl_3$) δ 1.53–2.57 (28H, m, phobane), 2.70 (6H, d, J_{HH} = 8.4 Hz, CH_3N). $^{13}C\{^1H\}$ NMR (75 MHz; $CDCl_3$) δ 21.5 (d, J_{CP} = 52.2 Hz, CH_3), 26.4 (s, CH_2), 28.3 (s, CH_2), 29.9 (t, J_{CP} = 8.6 Hz, CH). HRMS (ES): Found (Calc. for $C_{22}H_{36}CrN_2O_2P_2$) 506.1552 (506.1555). IR (CH_2Cl_2): ν(CO) 1869, 1858 cm^{-1}.

Preparation of *trans*-[Cr(CO)$_4$(PhobPNH^{i}Pr)$_2$] (2b)

PhobPNH^{i}Pr (0.078 g, 0.39 mmol) was dissolved in CH_2Cl_2 (4.0 mL). $[Cr(CO)_4(\eta^4\text{-norbornadiene})]$ (0.050 g, 0.19 mmol) was added and the resulting yellow solution was stirred for 24 h. The solvent was removed under reduced pressure and the resulting yellow solid product was washed with hexane (0.042 g, 36%). $^{31}P\{^1H\}$ NMR (121 MHz; $CDCl_3$) δ 94.9. ^1H NMR (300 MHz; $CDCl_3$) d 1.24 (12H, d, J_{HH} = 6.4 Hz, $CH_3{}^iPr$), 1.49–2.65 (12H, m, phobane). $^{13}C\{^1H\}$ NMR (75 MHz; $CDCl_3$) δ 21.3 (d, J_{CP} = 36.9 Hz, CH_3), 26.8 (s, CH_2), 24.9 (s, CH_2), 32.2 (t, J_{CP} = 8.6 Hz, CH), 45.7 (s, CH_3). IR (CH_2Cl_2): ν(CO) 1863 cm^{-1}.

Preparation of [PtCl$_2$(Cy$_2$PNMePCy$_2$)] (4)

To a solution of $\mathbf{L_3}$ (0.032 g, 0.070 mmol) in CH_2Cl_2 (2 mL), $[PtCl_2(NC^tBu)_2]$ (0.034 g, 0.070 mmol) in CH_2Cl_2 (2 mL) was added and the mixture was stirred for 2 h. The solvent was then reduced to *ca.* 2 mL, hexane was added (4 mL) and a yellow solid was obtained (0.023 g, 47%). $^{31}P\{^1H\}$ NMR (121 MHz; $CDCl_3$) δ 37.1 (J_{PtP} = 3211 Hz). ^1H NMR (300 MHz; $CDCl_3$) δ 1.20–1.97 (44H, m, CH and CH_2), 2.72 (3H, t, J_{HP} = 9.4 Hz, CH_3N). ^{13}C $\{^1H\}$ NMR (75 MHz; $CDCl_3$) δ 25.7 (s), 26.9 (m) 28.7 (s), 27.9 (s), 38.0 (t, J_{CP} = 15.2 Hz). Elemental analysis: Found (Calc. for $C_{25}H_{47}Cl_2NP_2Pt$) C, 43.3 (43.5); N, 2.3 (2.0); H, 6.8 (6.9) %. HRMS (EI): Found (Calc. for $C_{25}H_{47}ClNP_2Pt$) 653.2529 (653.2520).

Preparation of [PtCl$_3$(PhobP(=NHMe)PPhob)] (5)

A mixture of $\mathbf{L'_c}$·HCl (0.025 g, 0.070 mmol) and $[PtCl_2(NC^tBu)_2]$ (0.034 g, 0.070 mmol) were dissolved in CH_2Cl_2 (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 **5** 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 [PdCl$_2$(PhobPNMePPhob)] (6)

To a suspension of $\mathbf{L'_c}$ (0.031 g, 0.099 mmol) in toluene (3 mL), $[PdCl_2(cod)]$ (0.031 g, 0.12 mmol) was added. The suspension was stirred at 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 $CDCl_3$ although satisfactory elemental analysis was not obtained. $^{31}P\{^1H\}$ NMR (121 MHz; $CDCl_3$) δ 37.0. ^1H NMR (300 MHz; $CDCl_3$) δ 1.65–2.40 (28H, m, phobane), 2.58 (d, J_{HP} = 8.3 Hz). HRMS (EI): Found (Calc. for $[C_{17}H_{31}NP_2ClPd]^+$) 452.0672 (452.0649).

Preparation of [Cr(CO)$_4$(PhobPNMePPh$_2$)] (7)

To a solution of $\mathbf{L_f}$ (0.030 g, 0.070 mmol) in CH_2Cl_2 (2 mL), $[Cr(CO)_4(\eta^4\text{-norbornadiene})]$ (0.018 g, 0.070 mmol) in CH_2Cl_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) (0.014 g, 27%). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$) δ 105.7 (d, J_{PP} = 42 Hz), 108.1 (d, J_{PP} = 42 Hz). ^1H NMR (300 MHz, $CDCl_3$) δ 1.50–2.65 (14H, m, phobane), 2.97 (3H, t, J_{HP} = 6.9 Hz, CH_3N), 7.33–7.59 (10H, m, H*Ar*). ^{13}C $\{^1H\}$NMR (125 MHz; CD_2Cl_2) δ 20.3 (d, J_{CP} = 7.8 Hz), 21.2 (d, J_{CP} = 6.3 Hz), 23.4 (d, J_{CP} = 4.4 Hz), 23.6 (d, J_{CP} = 8.3 Hz), 29.6 (m), 34.7 (m), 126.1 (d, J_{CP} = 10.7 Hz), 126.7 (d, J_{CP} = 12.2 Hz) 132.7 (m). HRMS (EI):

Table 4 Crystal data and structure refinement for all structures in the paper

Identification code	**1b**_LR302	**2b**_jj142	**3**_lr305	**4**_jj228	**5**_jj200
Empirical formula	$C_{22}H_{44}Cl_2N_2P_2Pt$	$C_{26}H_{44}CrN_2O_4P_2$	$C_{30}H_{60}Cl_2N_2P_2Pt$	$C_{27}H_{49}NP_2Cl_8Pt$	$C_{19.5}H_{37}Cl_6NP_2Pt$
Formula weight	664.52	562.57	776.72	928.30	755.23
Temperature/K	99.99	173(2)	100.0	99.99	100.0
Crystal system	Monoclinic	Triclinic	Triclinic	Orthorhombic	Hexagonal
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$Pna2_1$	$P6_5$
a/Å	9.9057(7)	9.5739(2)	9.448(4)	21.9631(6)	16.7268(3)
b/Å	7.2983(5)	12.2783(2)	9.493(5)	27.7581(8)	16.7268(3)
c/Å	17.7434(13)	13.2759(2)	10.788(5)	17.7763(5)	17.0407(4)
α/°	90	69.2670(10)	109.190(10)	90	90.00
β/°	92.139(2)	89.1370(10)	107.174(9)	90	90.00
γ/°	90	71.601 (10)	93.167(15)	90	120.00
Volume/Å^3	1281.86(16)	1376.68(4)	860.5(7)	10 837.4(5)	4128.99(14)
Z	2	2	1	12	6
ρ_{calc}/g cm^{-3}	1.722	1.357	1.499	1.707	1.822
μ/mm^{-1}	5.819	0.566	4.346	4.585	5.806
F(000)	664.0	600.0	396.0	5544.0	2226.0
Crystal size/mm^3	0.6 × 0.25 × 0.1	0.16 × 0.15 × 0.08	0.4 × 0.25 × 0.2	0.1 × 0.21 × 0.27	0.3 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	Mo Kα (λ = 0.71074)
2Θ range for data collection/°	4.594 to 66.432	6.328 to 61.144	4.238 to 66.332	2.72 to 55.062	3.7 to 68.3
Index ranges	$-15 \le h \le 15$, $-11 \le k \le 10$, $-27 \le l \le 26$	$-13 \le h \le 13$, $-17 \le k \le 17$, $-18 \le l \le 18$	$-14 \le h \le 14$, $-14 \le k \le 14$, $-16 \le l \le 16$	$-28 \le h \le 28$, $-36 \le k \le 36$, $-23 \le l \le 23$	$-26 \le h \le 26$, $-26 \le k \le 26$, $-17 \le l \le 26$
Reflections collected	46 419	56 825	36 290	300 715	137 345
Independent reflections	4710 [R_{int} = 0.0365, R_{sigma} = 0.0203]	8447 [R_{int} = 0.0291, R_{sigma} = 0.0188]	6208 [R_{int} = 0.0186, R_{sigma} = 0.0126]	24 919 [R_{int} = 0.0572, R_{sigma} = 0.0279]	9590 [R_{int} = 0.0716, R_{sigma} = 0.0407]
Data/restraints/ parameters	4710/0/139	8447/0/328	6208/0/175	24 919/955/1060	9590/1/290
Goodness-of-fit on F^2	1.078	1.055	1.075	1.085	1.155
Final R indexes [$I \ge = 2\sigma(I)$]	R_1 = 0.0304, wR_2 = 0.0717	R_1 = 0.0282, wR_2 = 0.0745	R_1 = 0.0167, wR_2 = 0.0426	R_1 = 0.0561, wR_2 = 0.1363	R_1 = 0.0278, wR_2 = 0.0668
Final R indexes [all data]	R_1 = 0.0357, wR_2 = 0.0745	R_1 = 0.0332, wR_2 = 0.0777	R_1 = 0.0167, wR_2 = 0.0426	R_1 = 0.0846, wR_2 = 0.1581	R_1 = 0.0367, wR_2 = 0.0909
Largest diff. peak/ hole/e Å^{-3}	4.08/−1.91	0.45/−0.55	1.34/−1.00	4.17/−2.14	1.38/−1.76
Flack parameter	—	—	—	—	−0.021(6)

Identification code	**6**_jj380	$\mathbf{L_h}$·HCl _jj353	**7**_jj68	**8**_jj82
Empirical formula	$C_{17}H_{31}Cl_2NP_2Pd$	$C_{23}H_{32}ClNP_2$	$C_{25}H_{27}CrNO_4P_2$	$C_{27}H_{31}CrNO_4P_2$
Formula weight	488.67	419.89	519.41	547.47
Temperature/K	100(2)	100(2)	120(2)	120.0
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_12_12_1$
a/Å	11.9640(3)	16.8271(8)	11.5207(3)	10.05490(10)
b/Å	12.5989(4)	8.5130(4)	13.1975(5)	10.8831(2)
c/Å	13.8207(4)	15.6725(8)	16.7912(6)	23.6863(4)
α/°	90.00	90.00	90	90
β/°	112.2130(10)	100.569(2)	106.502(2)	90
γ/°	90.00	90.00	90	90
Volume/Å^3	1928.63(10)	2206.98(19)	2447.85(14)	2591.96(7)
Z	4	4	4	4
ρ_{calc}/g cm^{-3}	1.683	1.264	1.409	1.403

Table 4 (*Contd.*)

Identification code	**6**_jj380	L_h·HCl _jj353	**7**_jj68	**8**_jj82
μ/mm^{-1}	1.404	0.327	0.630	0.599
F(000)	1000.0	896.0	1080.0	1144.0
Crystal size/mm^3	0.26 × 0.11 × 0.08	0.35 × 0.28 × 0.28	0.1 × 0.06 × 0.02	0.24 × 0.2 × 0.15
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.68 to 55.08	2.46 to 55.08	5.902 to 55.066	6.376 to 55.032
Index ranges	$-13 \le h \le 15$, $-12 \le k \le 16$, $-17 \le l \le 17$	$-21 \le h \le 21$, $-8 \le k \le 11$, $-19 \le l \le 20$	$-13 \le h \le 14$, $-16 \le k \le 17$, $-21 \le l \le 21$	$-12 \le h \le 13$, $-14 \le k \le 14$, $-30 \le l \le 30$
Reflections collected	19 685	19 574	25 383	30 546
Independent reflections	4437 [R_{int} = 0.0231, R_{sigma} = 0.0191]	5066 [R_{int} = 0.0194, R_{sigma} = 0.0169]	5589 [R_{int} = 0.1046, R_{sigma} = 0.1035]	5929 [R_{int} = 0.0548, R_{sigma} = 0.0494]
Data/restraints/parameters	4437/0/220	5066/1/249	5589/0/299	5929/0/319
Goodness-of-fit on F^2	1.040	1.034	1.082	1.041
Final R indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0178, wR_2 = 0.0446	R_1 = 0.0277, wR_2 = 0.0707	R_1 = 0.0979, wR_2 = 0.1670	R_1 = 0.0328, wR_2 = 0.0712
Final R indexes [all data]	R_1 = 0.0198, wR_2 = 0.0458	R_1 = 0.0300, wR_2 = 0.0724	R_1 = 0.1546, wR_2 = 0.1940	R_1 = 0.0404, wR_2 = 0.0742
Largest diff. peak/hole/e Å^{-3}	0.90/−0.30	0.43/−0.23	0.55/−0.58	0.27/−0.36
Flack parameter	—	—	—	0.020(10)

Found (Calc. for $C_{25}H_{27}CrNO_4P_2$) 519.0812 (519.0820). IR (in CH_2Cl_2): ν(CO) 2003, 1910, 1885, 1873 cm^{-1}.

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

To a solution of $\mathbf{L_g}$ (0.030 g, 0.060 mmol) in CH_2Cl_2 (2 mL), [Cr(CO)$_4$(η^4-norbornadiene)] (0.017 g, 0.060 mmol) in CH_2Cl_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%). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$) δ 104.1 (d, J_{PP} = 27 Hz), 104.6 (d, J_{PP} = 27 Hz). ^1H NMR (300 MHz, $CDCl_3$) δ 1.24 (6H, s, CH_3), 1.52–2.65 (14H, m, phobane), 2.97 (3H, dd, J_{HP} = 7.4 Hz, J_{HP} = 8.1 Hz, CH_3N), 7.11–7.56 (8H, m, H*Ar*). HRMS (EI): Found (Calc. for $C_{27}H_{31}CrNO_4P_2$) 547.1130 (547.1133). IR (in CH_2Cl_2): ν(CO) 2003, 1908, 1885, 1869 cm^{-1}.

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 methylaluminoxane (MMAO) together for 60 s, then transferred to the autoclave *via* syringe. The autoclave was pressurised and the pressure kept constant throughout the reaction by the continuous addition of ethylene, which was monitored *via* flow-meter. Once ethylene uptake had ceased or the autoclave was filled, the gas supply was closed and the reactor cooled to 5 °C. The reactor was carefully vented. The reactor contents were treated with 1000 μL of nonane (GC internal standard) and 10% HCl (aq). A sample of the organic phase was taken for GC-FID analysis. Any solid formed was collected, washed repeatedly with EtOH, then acetone and dried overnight and weighed.

GC-FID analysis was performed on an Agilent Technologies 6890N GC system equipped with PONA (50 m × 0.20 mm × 0.50 μm) and MDN-12 (60 m × 0.25 mm × 0.25 μm) columns. Catalysis was performed in a stainless steel 300 mL volume AE autoclave with Viton-ETP seals, equipped with a customised gas-entraining mechanical stirrer, internal cooling coil (tap water) and fluidised jacket (connected to an external thermostatic bath). Ethylene was passed through moisture and oxygen scrubbing columns prior to use and the flow measured using a Siemens Sitrans F C Massflo system (Mass 6000-Mass 2100) and the data logged.

Crystal structure determinations

X-ray diffraction experiments for **1b**, **3**, **4**, **5**, **6** and $\mathbf{L_h}$·HCl were carried out at 100 K and for **2b** at 173 K on a Bruker APEX II diffractometer using Mo-K$_\alpha$ radiation (λ = 0.71073 Å). **7** was collected at 120 K on a Bruker Nonius FR591 Rotating Anode using Mo-K$_\alpha$ radiation (λ = 0.71073 Å)[25] and **8** was collected on EH1 of Station I19 of Diamond Light Source (λ = 0.71073 Å) at 120 K.[26] Data collections were performed using a CCD area detector from a single crystal mounted on a glass fibre. Intensities were integrated using SAINT with a multi-scan absorption correction preformed using SADABS.[27] All structures were solved using SHELXS and refined against all F_o^2 using SHELXL and OLEX2.[28] 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.

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