Haddow, M. F., Jaltai, J., Hanton, M., Pringle, P. G., Rush, L. E., Sparkes, H. A., & Woodall, C. H. (2016). Aminophobanes: hydrolytic stability, tautomerism and application in Cr-catalysed ethene oligomerisation. *Dalton Transactions*, 45(5), 2294-307. https://doi.org/10.1039/c5dt04394h
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. Woodala

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 Cy2PNMe with Cy2PCl readily gave Cy2PNMePCy2. By contrast, treatment of PhobPCl with PhobPNMe in the presence of Et3N does not afford PhobPNMePPhob but instead the salt [PhobP(==NMeH)PPhob]Cl is formed which, upon addition of [PtCl3(NCMe)2] gives the zwitterionic complex [PtCl3(PhobP(==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 diphos 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 R2PNHR (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 R2PNHR2 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 $R_2PCl$ or $R'NH_2$ are bulky, a complication is the formation of the phosphinimine PPN compounds (Scheme 1); Maumela et al. have shown that when $R = Ph$ and $R' = tBu$, 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 $La–Ld$ 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 $Cy_2P$ 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 and the approximately 90° $C–P–C$ bridgehead angle in PhobP has the effect of lowering the HOMO and LUMO energies. Ligands $L_1–L_4$ (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 $L_a$ and $L_b$ were readily prepared by aminolysis of PhobPCI. The relative lability of $L_a$ and $L_b$ to hydrolysis (eqn (1)) was gauged by treatment of $L_a$, $L_b$, $L_1$ and $L_2$ with aqueous solutions under the same conditions and monitoring the formation of $R_2P(=O)H$ by $^31P$ 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 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(L2)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)2] 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

Table 2 Comparison of some properties of aminophobanes and acyclic analogues

|                  | % Hydrolysis at 16 h | νCO /cm⁻¹ |
|------------------|---------------------|-----------|
| PhobPNHMe (La)   | 5                   | 1957      |
| Cy2PNHMe (L1)   | 100                 | 1955      |
| PhobPNHiPr (Lb) | 1                   | 1954      |
| Cy2PNHiPr (L2)  | 64                  | 1951      |

Table 2

"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 31P NMR spectrum. The IR spectrum in the 2050–1850 cm⁻¹ region was measured in CH2Cl2 for the trans-[RhCl(CO)(L)2] complexes generated in situ by combining [Rh2Cl2(CO)4] with 4 equiv. of L.

L1 was 50% hydrolysed after 0.5 h.

Fig. 1 Crystal structure of trans-[PtCl2(PhobPNHPr)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(PhobPNHPr)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).
groups are gauche to each other, a conformation not previously observed in PhobPZ complexes.

Bidentate aminophobanes

The previously reported16 diphosphinoamine \( \text{L}_4 \) is readily prepared from MeNH\(_2\) and Cy\(_2\)PCL in the presence of Et\(_3\)N (Scheme 3). The intermediate in this reaction is presumably Cy\(_2\)PNHMe (\( \text{L}_1 \)) and indeed treatment of the isolated \( \text{L}_1 \) with Cy\(_2\)PCL in the presence of Et\(_3\)N in CH\(_2\)Cl\(_2\) gave \( \text{L}_4 \) 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 \( \text{L}'_4 \) is assigned. The PPN species \( \text{L}'_3 \) smoothly converted over 30 min to PNP ligand \( \text{L}_3 \) whose structure was confirmed by its conversion to the chelate complex 4 (Scheme 3), the crystal structure of which has been determined (Fig. 4).

The asymmetric unit consists of three independent molecules of 4 along with six chloroform molecules. Although the PP\(_2\)Cl\(_2\) fragment is approximately planar (rms deviation \( \sim 0.03 \text{ Å} \)), 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 \( \sim 0.03 \text{ Å} \).

In contrast to the ready reaction of \( \text{L}_4 \) with Cy\(_2\)PCL to give PNP ligand \( \text{L}_3 \) (Scheme 3), the reaction of PhobPNHMe (\( \text{L}_4 \)) with PhobPCL in the presence of NEt\(_3\) or \( \text{N}\)-methylpyrrolidine did not give 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 \( ^1\)H NMR spectrum (which showed a multiplet at 7.01 ppm integrating for 1H) and mass spectrum \((M^+ \text{ at } [L'_c + 1])\) led to its assignment as the HCl adduct \( \text{L}'_c\text{-HCl} \) (Scheme 4). This was supported by its reaction with [PtCl\(_2\)(NC\(_5\)Bu\(_2\))] which yielded crystals of the insoluble, zwitterionic complex [PtCl\(_3\)(\( \text{L}'_c\text{-H} \))] \( ^5 \) whose X-ray crystal structure is shown in Fig. 5. The conditions under which \( \text{L}'_c\text{-HCl} \) was formed (Scheme 4) indicate that the imino-phosphine \( \text{L}'_c \) is more basic than either NEt\(_3\) or \( \text{N}\)-methylpyrrolidine.

The crystal structure of 4 has a square planar Pt with an rms deviation of the atoms from the square plane of \( \sim 0.03 \text{ Å} \). The PPN ligand is rotated away from the PtCl\(_3\) plane with torsion angles Cl1–Pt1–P1–P2 of \(-102.4(1)^\circ \) and Cl3–Pt3–P3–P4 of 75.6(1)^\circ \).

Treatment of PhobPNMeH with \(^6\)BuLi at \(-78 \text{ °C} \) followed by PhobPCL gave a PPN species with a \( J_{PP} = 327 \text{ Hz} \) (significantly smaller than the \( J_{PP} \) of 407 Hz for \( \text{L}'_c\text{-HCl} \)) that is assigned to the neutral \( \text{L}'_4 \) which has been isolated. No reaction occurred upon addition of PhobPCL to \( \text{L}'_c \) in CH\(_2\)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 [MCl\(_2\)(cod)] \( (M = \text{Pd or Pt})^{17} \) or [NiBr\(_2\)(dme)]\(^{18} \) to give PNP chelate complexes. Reaction

---

**Fig. 3** Crystal structure of trans-[PtCl\(_2\)(Cy\(_2\)P)NHMe\(_2\)] (3). All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pt(1)–P(1) 2.3187(7), Pt(1)–Cl(1) 2.3193(7), Pt(1)–N(1) 1.681(3), Pt(1)–P(1)–N(1) 113.91(10).

**Scheme 3**

\[
\text{Cy}_2\text{PNHMe} \xrightarrow{\text{Cy}_2\text{PCLI}} \text{NEt}_3 \xrightarrow{\text{[PtCl}_2\text{(cod)]}} \text{Cy}_2\text{P} \xrightarrow{\text{NMe}_2} \text{Cy}_2\text{P} = \text{P}(\text{NMe}_2)
\]

---

**Fig. 4** Crystal structure of complex [PtCl\(_2\)(\( \text{L}_4 \))] (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), Pt(1)–N(1) 1.745(17), Pt(2)–N(1) 1.668(18), Pt(2)–P(2)–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 [PdCl₂(cod)] with L₁ c gave the chelate [PdCl₂(L₁ c)] (6) whose crystal structure has been determined and is shown in Fig. 6. The asymmetric unit contains one molecule of 6, with the PdP₂Cl₂ 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 L₄ and L₅ with RXCl (see Schemes 3 and 4), it appears that the PhobP group differs from Cy₂P and Ar₂P groups in promoting PPN over PNP formation; this raised the question of what would happen when the syntheses of the heterodiphos PNP ligands PhobPNMePR₂ where R = Cy (L₆), Ph (L₇) or o-Tol (L₈) were attempted?

The reaction between PhobPNHMe and Cy₂PCl was followed by ³¹P NMR spectroscopy and it was unambiguously shown that a PPN product was formed which, on the basis of its Jₚₚ of 358 Hz, was tentatively assigned to the protonated species L₁ e·HCl (Scheme 5); addition of Et₃N led to multiple P-containing species but there was no evidence for the formation of the neutral PPN (L₁ e) or PNP (L₁ e) species. The reaction between PhobPCl and Cy₂PNHMe was also monitored and in this case, ³¹P NMR spectroscopy revealed that a PPN product was formed (Jₚₚ = 403 Hz) which was assigned to the cationic species L₂ e·HCl (Scheme 5), an isomer of L₁ e·HCl. It therefore appears that the PPN-promoting effect of the PhobP group dominates over the PNP-preference of the Cy₂P group.

The unsymmetrical PNP ligands L₄ and L₅ (Jₚₚ = 80 Hz in both) featuring PhobP groups were successfully prepared upon treatment of PhobPNHMe with Ar₂PCl (Ar = Ph or o-Tol) in the presence of Et₃N (eqn (2)). It therefore appears that the PPN formation promoted by the PhobP group is superseded by the PNP preference of the Ar₂P groups.
The reaction of PhobPNHMe with Tol₂PCl was monitored by $^{31}$P NMR spectroscopy. A PPN species ($J_{PP} = 331$ Hz), tentatively assigned to $L'_g\cdot HCl$ (Scheme 6) was formed rapidly which, upon treatment with NEt₃, was transformed to $L_g$ ($J_{PP} = 80$ Hz).

Treatment of the bulky $R_2PN^HPr$ ($L_b$ or $L_2$) with $R_2PCl$ ($R_2P = Cy_2P$ or PhobP) under the conditions that converted $R_2PNHMe$ to the corresponding $L_3$ (Scheme 3) or $L'_c\cdot HCl/L'_c$ (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 $L_f$ and $L_g$ (eqn (2)), $L_b$ reacted with Ar₂PCl to give PPN species whose structures were assigned to the protonated $L'_h\cdot HCl$ and $L'_i\cdot HCl$ (eqn (3)) on the basis of the large $J_{PP}$ values of 338 and 359 Hz respectively. Crystals of $L'_h\cdot HCl$ 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 that the PPN can be converted to the PNP tautomer using a $R_2PbCl$ 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. An additional element observed in this work is the formation of a protonated $A'\cdot HCl$ 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 $A'\cdot HCl$ (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 Cy₂PNMePCy₂ 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 Lf and Lg 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 Lf or Lg 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).

\begin{align*}
\text{Me-N} & \quad \text{PhobP} \quad \text{Me-N} \\
\text{PAr₂} & \quad \text{PhobP} \quad \text{PAr₂}
\end{align*}

In combination with chromium, the ligands Lf and Lg 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 Lg) 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(Lf)] (7). 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 1Pr) have been readily prepared and are more resistant to hydrolysis than their Cy₂PNHR analogues consistent with the PhobP group having a greater effective steric bulk than Cy₂P. 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 [PdCl₂(cod)] to give the desired PNP–Pd chelate. The readily prepared mixed diphos ligands PhobPNMePAr₂ (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 N₂-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 N₂ saturation. The starting materials PhobPCl, [Cr(CO)₄(η⁵-norbordiane)], [PtCl₂(NC₄Bu₂)] and [PdCl₂(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 under a dry nitrogen atmosphere.
Preparation of PhobPNHiPr (Lb)

A solution of PhobPCl (0.88 g, 5.0 mmol) was dissolved in a solution of PhobPNHiPr (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 colourless oil (0.57 g, 63%). 31P{1H} NMR (121 MHz; CDCl3) δ 1.47. 1H NMR (270 MHz; CDCl3) δ 1.48 (14H, m, phobane), 2.20 (14H, m, phobane), 1.14 (6H, d, J = 6.1 Hz, CH3), 2.66 (1H, m, HN), 2.15 (14H, m, phobane), 1.14 (6H, d, J = 6.1 Hz, CH3), 2.66 (1H, m, HN), 2.15 (14H, m, phobane). 13C{1H} NMR (75 MHz; CDCl3) δ 15.5. MS (ESI): Found (Calc. for C9H18NP 199.1496 (199.1490).

Preparation of PhobPNHMe (La)

PhobPCI (0.88 g, 5.0 mmol) was dissolved in a solution of PhobPNHMe (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 (1.42 g, 75%). 31P{1H} NMR (121 MHz; CDCl3) δ 26.8. 1H NMR (270 MHz; CDCl3) δ 1.48-2.20 (14H, m, phobane), 2.67 (3H, d, J = 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, CH2), 23.7 (d, JCP = 3.1 Hz, CH2), 28.1 (d, JCP = 10.9 Hz, CH2N), 31.2 (d, JCP = 14.0 Hz, CH2), 33.0 (d, JCP = 26.9 Hz, CH). Elemental analysis: Found (Calc. for C8H16NP) C, 63.5 (63.1); N, 8.1 (8.1); H, 10.4 (10.6) %. MS (ESI; m/z 171 (M+)).

Preparation of [PhobP(=NHMe)PPhob]Cl (L′c·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 g, 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, d, JHP = 12.3 Hz, JHP = 5.68 Hz, CH3N), 7.01 (1H, m, HCP). 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 (d, 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

Table 3 Ethene oligomerisation results

| L | Rxn time/min | TON/kg per g Cr | TOF/kg per g Cr per h | Liquid product/wt% | Solid product (PE)/wt% | C4/wt% | C5/wt% (% 1-C4) | C6/wt% (% 1-C6) | C7/wt% | 1-C4 | 1-C6 | C10-14/wt% | C15+/wt% |
|---|-------------|----------------|----------------------|-------------------|-----------------------|-------|----------------|----------------|-------|------|-----|-------------|---------|
| L4 | 24.8 | 393 | 951 | 89.5 | 10.5 | 1.7 | 16.1 (20.7) | 26.7 (93.0) | 7.5 | 22.4 | 33.0 |
| L6 | 16.7 | 31 | 110 | 56.6 | 43.4 | 1.8 | 163 (70.2) | 61.1 (99.4) | 5.3 | 7.2 | 13.6 |

*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 PhobPNMePPh2 (L2)
Aminophosphate L4 (0.280 g, 1.64 mmol) and NET3 (0.220 g, 2.17 mmol) were dissolved in MeCN (1 mL). To this stirred mixture, Ph2PCl (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 recrystallized from hot MeCN to afford white needles (0.17 g, 38%).

Elemental analysis: Found (Calc. for C21H27NP2) C, 71.8 (70.9); N, 3.8 (3.6); H, 8.1 (8.1) %. HRMS (EI): Found (Calc. for C21H27N3P2) 383.1931 (383.1932).

Preparation of PhobPNMeP(o-Tol)2Cl (L5)
Aminophosphate L4 (0.200 g, 1.16 mmol) and NET3 (0.240 g, 2.32 mmol) were dissolved in MeCN (1 mL). To this stirred mixture, Ph2P(o-Tol)Cl (0.380 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%).

Elemental analysis: Found (Calc. for C23H31NP2) C, 72.2 (72.0); N, 3.8 (3.6); H, 8.1 (8.1) %. HRMS (EI): Found (Calc. for C23H31NP2) 383.1931 (383.1932).

Preparation of PhobPNMePPh2Cl (L3)
Ph2PPh2Cl (0.620 g, 2.51 mmol) in MeCN (5.0 mL) was added in portions to PhobPNMePPh2 (L4) (0.530 g, 2.67 mmol) and N-methylpyrrolidinone (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 recrystallized from hot MeCN to yield white crystals (0.71 g, 62%).

1H NMR (400 MHz; CDCl3) δ 0.89 (6H, d, JHF = 6.2 Hz, CH3), 1.35 (1H, d, JHF = 6.4 Hz, CH), 1.74–2.94 (14H, m, phobane), 7.46–7.54 (10H, m, Ph). HRMS (EI): Found (Calc. for C21H20N3P2) 353.1122 (353.1123).
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}N_{2}P_{2}H) C, 70.4 (70.9); N, 2.8 (3.3); H, 11.4 (11.2) %. HRMS (CI): Found (Calc. for C_{25}H_{47}N_{2}P_{2}H) 424.3262 (424.3262).

Preparation of trans-[PdCl_{2}(PhobPNMePPhob)] (6)

A mixture of L\textsubscript{3}HCl (0.025 g, 0.070 mmol) and [PtCl\textsubscript{2}(NC\textsubscript{Bu})\textsubscript{2}] (0.034 g, 0.070 mmol) was dissolved in CH\textsubscript{2}Cl\textsubscript{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 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\textsubscript{2}(PhobPNMePPhob)] (5)

To a suspension of L\textsubscript{3} (0.031 g, 0.099 mmol) in toluene (3 mL), [PdCl\textsubscript{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\textsubscript{3} although satisfactory elemental analysis was not obtained. 3\textsuperscript{1}P\textsuperscript{1}H NMR (121 MHz; CDCl\textsubscript{3}) δ 37.1 (J_{PP} = 3111 Hz). 1\textsuperscript{H} NMR (300 MHz; CDCl\textsubscript{3}) δ 1.20−1.97 (44H, m, CH and CH\textsubscript{2}), 2.72 (3H, t, J_{HH} = 9.4 Hz, CH\textsubscript{2}N). 13C\textsuperscript{1}H NMR (75 MHz; CDCl\textsubscript{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\textsubscript{25}H\textsubscript{47}Cl\textsubscript{2}N\textsubscript{2}P\textsubscript{2}Pt) C, 34.3 (43.5); N, 2.3 (2.0); H, 6.8 (6.9) %. HRMS (EI): Found (Calc. for C\textsubscript{25}H\textsubscript{47}Cl\textsubscript{2}N\textsubscript{2}P\textsubscript{2}Pt) 652.3259 (652.3250).

Preparation of [Cr(CO)\textsubscript{4}(PhobPNMePPhob)] (7)

To a solution of L\textsubscript{4} (0.030 g, 0.070 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (2 mL), [Cr(CO)\textsubscript{4}(n\textsuperscript{-norbomadiene})] (0.018 g, 0.070 mmol) in CH\textsubscript{2}Cl\textsubscript{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%). 3\textsuperscript{1}P\textsuperscript{1}H NMR (121 MHz, CDCl\textsubscript{3}) δ 105.7 (d, J_{PP} = 62 Hz), 108.1 (d, J_{PP} = 62 Hz). 1\textsuperscript{H} NMR (300 MHz, CDCl\textsubscript{3}) δ 1.50−2.65 (14H, m, phobane), 2.97 (3H, t, J_{HH} = 6.9 Hz, CH\textsubscript{2}N), 7.33−7.59 (10H, m, HAhr). 13C\textsuperscript{1}H NMR (125 MHz; CDCl\textsubscript{3}) 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_jr305 | 4_jj228 | 5_jj200 |
|---------------------|---------|---------|---------|---------|---------|
| **Empirical formula** | C_{22}H_{41}NCl_{2}P_{2}Pt | C_{26}H_{55}CrN_{2}O_{2}P_{2} | C_{30}H_{63}CrN_{2}P_{3}Pt | C_{27}H_{59}NP_{2}Cl_{2}Pt | C_{18}H_{31}Cl_{2}NP_{2}Pt |
| **Formula weight** | 664.52 | 562.57 | 776.72 | 928.30 | 755.23 |
| **Temperature/K** | 99.99 | 173(2) | 100.00 | 99.99 | 100.00 |
| **Space group** | P2_1/n | P1 | Triclinic | Triclinic | Orthorhombic |
| **α/°** | 9.9057(7) | 9.5179(2) | 9.488(4) | 9.493(5) | 10.497(4) |
| **β/°** | 7.2983(5) | 12.2783(2) | 10.788(5) | 10.788(5) | 17.7763(8) |
| **Volume/Å³** | 1281.86(16) | 1376.68(4) | 860.5(7) | 863.4(7) | 5418.99(14) |
| **ρ_{calc}/g cm^{-3}** | 1.722 | 1.357 | 1.499 | 1.436 | 1.585 |
| **F(000)** | 600.00 | 600.00 | 396.00 | 396.00 | 5544.00 |
| **Crystal size/mm³** | 0.6×0.25×0.1 | 0.6×0.15×0.08 | 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) | MoKα (λ = 0.71073) |
| **Index ranges** | 1 ≤ h ≤ 15, −11 ≤ k ≤ 10, −27 ≤ l ≤ 26 | 1 ≤ h ≤ 15, −11 ≤ k ≤ 10, −27 ≤ l ≤ 26 | 1 ≤ h ≤ 15, −11 ≤ k ≤ 17, −14 ≤ l ≤ 16 | 1 ≤ h ≤ 15, −11 ≤ k ≤ 14, −14 ≤ l ≤ 16 | 1 ≤ h ≤ 15, −11 ≤ k ≤ 14, −14 ≤ l ≤ 16 |
| **Reflections collected** | 4442 | 5652 | 8447 | 6208 | 30075 |
| **Independent reflections** | 4710 | 5685 | 8497[R_{int} = 0.0365, R_{sigma} = 0.02035] | 6208[R_{int} = 0.0186, R_{sigma} = 0.0126] | 24919 | |
| **Data/restraints/parameters** | 4710/139 | 8497/328 | 6208/0.0186 | 6208/0.0186 | 9590/1290 |
| **Goodness-of-fit on F²** | 1.078 | 1.055 | 1.075 | 1.085 | 1.155 |
| **Final R indexes [1 ≤ h ≤ 26]** | R₁ = 0.0334, wR₂ = 0.0717 | R₁ = 0.0282, wR₂ = 0.0745 | R₁ = 0.0167, wR₂ = 0.0426 | R₁ = 0.0561, wR₂ = 0.1363 | R₁ = 0.0278, wR₂ = 0.0668 |
| **Final R indexes [all data]** | R₁ = 0.0357, wR₂ = 0.0745 | R₁ = 0.0332, wR₂ = 0.0777 | R₁ = 0.0167, wR₂ = 0.0426 | R₁ = 0.0846, wR₂ = 0.1581 | R₁ = 0.0367, wR₂ = 0.0909 |
| **Largest diff. peak/ hole Å⁻³** | 4.08/-1.91 | 0.45/-0.55 | 1.34/-1.00 | 4.17/-2.14 | 1.38/-1.76 |
| **Flack parameter** | — | — | — | — | — |

| Identification code | 6_jj380 | 1b_HCl_jj353 | 7_jj68 | 8_jj82 |
|---------------------|---------|---------|---------|---------|
| **Empirical formula** | C_{21}H_{13}ClNP_{2}Pd | C_{23}H_{31}ClNP_{2}Pd | C_{26}H_{2}CrNO_{2}P_{2} | C_{27}H_{31}ClNP_{2}Pd |
| **Formula weight** | 488.67 | 419.89 | 519.41 | 547.47 |
| **Temperature/K** | 100(2) | 100(2) | 120(2) | 120.0 |
| **Space group** | P2_{1}/c | P2_{1}/c | Monoclinic | Monoclinic |
| **α/°** | 11.9640(3) | 16.8271(8) | 11.5207(3) | 10.0549(10) |
| **β/°** | 15.7623(5) | 16.7912(6) | 16.7912(6) | 10.8831(2) |
| **c/Å** | 90.00 | 90.00 | 90.00 | 90.00 |
| **Volume/Å³** | 1928.63(10) | 2206.98(19) | 2447.85(14) | 2591.96(7) |
| **ρ_{calc}/g cm⁻³** | 1.683 | 1.264 | 1.409 | 1.403 |
Identification code 6·HCl

\[\text{(000) 1000.0 896.0 1080.0 1144.0}\]

\[\alpha \text{Radiation MoK}_\alpha (\lambda = 0.71073) \text{MoK}_\alpha \]

\[\text{R} = 0.0231, \quad \text{sigma} = 0.0169\]

\[\text{R} = 0.1046, \quad \text{sigma} = 0.1035\]

\[\text{R} = 0.0548, \quad \text{sigma} = 0.0494\]

\[\text{HRMS (EI): Found (Calc. for C}_{27}\text{H}_{31}\text{CrNO}_4\text{P}_2) 547.1130 (547.1133). IR (in CH}_2\text{Cl}_2): \nu \text{CH}_2\text{Cl}_2): 2971, 2948, 2920, 2851, 2825, 1712, 1684, 1490, 1462, 1447, 1436, 1401, 1375, 1352, 1281, 1260, 1163, 1079, 1017, 938, 870, 719 cm}^{-1}.\]

Preparation of \([\text{Cr(CO)}_4(\text{PhobPNMeP(o-Tol)})_2] (8)\)

To a solution of \([\text{L}_\text{obs} [0.030 \text{ g}, 0.060 \text{ mmol}]) \text{ in CH}_2\text{Cl}_2 [2 \text{ mL}], [\text{Cr(CO)}_4(\eta^1\text{-norbornadiene})] (0.017 \text{ g}, 0.060 \text{ mmol}) \text{ in CH}_2\text{Cl}_2 [2 \text{ mL}] \text{ was added. The resulting yellow solution was stirred for}\)

\[\text{24 h. The solvent was then removed under reduced pressure to}\]

yield a yellow solid, which was washed with hexane (5 mL) \[\text{(0.021 \text{ g}, 30\%)].}^{31}\text{P}{^1\text{H} \text{NMR (121 MHz, CDCl}_3):} 81.24 (6 \text{H, s, CH}_3), 104.6 (d,}\]

\[\text{J}_{\text{PP}} = 2003, 1910, 1885, 1873 \text{ cm}^{-1}.\]

\[\text{Oligomerisation catalysis}\]

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 \text{via syringe. The auto-}

\[\text{clave was pressurised with ethylene to 10 bar and vented. On a Schlenk line, a pre-activated catalyst solution was prepared by stirring the Cr source, ligand and modified methylaluminoxane (MMAO) together for 24 h. The solvent was then removed under reduced pressure to}\]

yield a yellow solid, which was washed with hexane (5 mL) \[\text{(0.021 g, 30\%)].}^{31}\text{P}{^1\text{H} \text{NMR (121 MHz, CDCl}_3):} 81.24 (6 \text{H, s, CH}_3), 104.6 (d,}\]

\[\text{J}_{\text{PP}} = 2003, 1910, 1885, 1873 \text{ cm}^{-1}.\]

\[\text{HRMS (EI): Found (Calc. for C}_{27}\text{H}_{31}\text{CrNO}_4\text{P}_2) 547.1130 (547.1133). IR (in CH}_2\text{Cl}_2): \nu (\text{CO}) 2003, 1908, 1885, 1869 \text{ cm}^{-1}.\]

**Crystal structure determinations**

X-ray diffraction experiments for \(1b, 3, 4, 5, 6\) \text{ and L}_4\text{HCl were carried out at 100 K and for 2b at 173 K on a Bruker APEX II diffractometer using Mo-K}_\alpha \text{ radiation (λ = 0.71073 Å).} 7 \text{ was collected at 120 K on a Bruker Nonius FR591 Rotating Anode using Mo-K}_\alpha \text{ radiation (λ = 0.71073 Å)\text{ and }8 \text{ was collected on EH1 of Station I19 of Diamond Light Source (λ = 0.71073 Å) at 120 K.}}^{26} \text{ Data collections were performed using a CCD area detector from a single crystal mounted on a glass fibre. Inten-}
ities were integrated using SAINT with a multi-scan absorption correction performed using SADABS. All structures were solved using SHELXS and refined against all F2 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

We thank Sasol for a Ph.D. studentship ([J]). We thank the Bristol Chemical Synthesis Centre for Doctoral Training, funded by EPSRC (EP/G036764/1), and the University of Bristol, for a Ph.D. studentship ([LR]).

References

1 (a) M. F. Haddow, A. J. Middleton, A. G. Orpen, P. G. Pringle and R. Papp, Dalton Trans., 2009, 202–209 and references therein; (b) J. A. Gillespie, D. L. Dodds and P. C. J. Kamer, Dalton Trans., 2010, 39, 2751–2764; (c) F. Matthey, in Phosphorus-Carbon Heterocyclic Chemistry, Elsevier, 2001.

2 L. Kollár and G. Keglevich, Chem. Rev., 2010, 110, 4257–4302.

3 D. L. Dodds, J. Floure, M. Garland, M. F. Haddow, T. R. Leonard, C. L. McMullin, A. G. Orpen and P. G. Pringle, Dalton Trans., 2011, 40, 7137–7146 and references therein.

4 For recent examples see: (a) C. Schotten, D. Plaza, S. Manzini, S. P. Nolan, S. V. Ley, D. L. Browne and A. Lapkin, ACS Sustainable Chem. Eng., 2015, 3, 1453–1459; (b) D. Schweitzer and K. D. Snell, Org. Process Res. Dev., 2015, 19, 715–720; (c) S. Manzini, A. Poater, D. J. Nelson, L. Cavallo, A. M. Z. Slawin and S. P. Nolan, Angew. Chem., Int. Ed., 2014, 53, 8995–8999; (d) S. Manzini, D. J. Nelson, T. Lebl, A. Poater, L. Cavallo, A. M. Z. Slawin and S. P. Nolan, Chem. Commun., 2014, 50, 2205–2207; (e) J. A. Bailey, M. F. Haddow and P. G. Pringle, Chem. Commun., 2014, 50, 1432–1434; (f) S. RaoufMohgaddam, E. Drent and E. Bouwman, Adv. Synth. Catal., 2013, 355, 717–733; (g) M. Czapiewski, O. Kreye, H. Mutlu and M. A. R. Meier, Eur. J. Lipid Sci. Technol., 2013, 115, 76–85; (h) A. Behr, S. Krema and A. Kämper, RSC Adv., 2012, 2, 12775–12781; (j) M. Yoshida, T. Nemoto, Z. Zhao, Y. Ishige and Y. Hamada, Tetrahedron: Asymmetry, 2012, 23, 859–866; (j) D. M. Ohlmann, N. Tschauder, J.-P. Stockis, K. Gooßen, M. Dierker and L. Gooßen, J. Am. Chem. Soc., 2012, 134, 13716–13729.

5 (a) J. P. Mulders, Neth. Patent, 660409 to Shell, 1966; (b) J. L. V. Winkle and R. F. Mason, U. S. Patent, 3400163 to Shell, 1968; (c) J. L. V. Winkle, R. C. Morris and R. F. Mason, Ger. Patent, 1909620 to Shell, 1969; (d) P. N. Bungu and S. Otto, Dalton Trans., 2007, 2876; (e) J. M. Birbeck, A. Haynes, H. Adams, L. Damoensense and S. Otto, ACS Catal., 2012, 2, 2512–2523; M. de Boer-Wildschut, M. Charrenskus, C. A. Krom and P. G. Pringle, World Patent, WO2012072594, 2012.

6 N. Fey, M. Garland, J. P. Hopewell, C. L. McMullin, S. Mastroianni, A. G. Orpen and P. G. Pringle, Angew. Chem., Int. Ed., 2012, 51, 118–122.

7 K. Blann, A. Bollmann, H. de Bod, J. T. Dixon, E. Killian, P. Nongodlwana, M. C. Maumela, H. Maumela, A. E. McConnell, D. H. Morgan, M. J. Overett, M. Prétorius, S. Kuhlmann and P. Waterscheid, J. Catal., 2007, 249, 244–249.

8 A. Bollmann, K. Blann, J. T. Dixon, F. M. Hess, E. Killian, H. Maumela, D. S. McGuinness, D. H. Morgan, A. Neveling, S. Otto, M. Overett, A. M. Z. Slawin, P. Waterscheid and S. Kuhlmann, J. Am. Chem. Soc., 2004, 126, 14712–14713.

9 (a) D. F. Wass, Dalton Trans., 2007, 816–819; (b) P. W. N. M. van Leeuwen, N. D. Clement and M. J.-L. Tschan, Coord. Chem. Rev., 2011, 255, 1499–1517; (c) D. S. McGuinness, Chem. Rev., 2011, 111, 2321; (d) T. Agapie, Coord. Chem. Rev., 2011, 255, 861; (e) G. P. Below, Pet. Chem., 2012, 52, 139–154; (f) G. J. P. Britovsek, R. Malinowski, D. S. McGuinness, J. D. Nobbs, A. K. Tomov, A. W. Wadley and C. T. Young, ACS Catal., 2015, 5, 6922–6923.

10 (a) S. Raouf-Moghaddam, E. Drent and E. Bouwman, Adv. Synth. Catal., 2013, 355, 717–733; (g) M. Czapiewski, O. Kreye, H. Mutlu and M. A. R. Meier, Eur. J. Lipid Sci. Technol., 2013, 115, 76–85; (h) A. Behr, S. Krema and A. Kämper, RSC Adv., 2012, 2, 12775–12781; (j) M. Yoshida, T. Nemoto, Z. Zhao, Y. Ishige and Y. Hamada, Tetrahedron: Asymmetry, 2012, 23, 859–866; (j) D. M. Ohlmann, N. Tschauder, J.-P. Stockis, K. Gooßen, M. Dierker and L. Gooßen, J. Am. Chem. Soc., 2012, 134, 13716–13729.

11 L. E. Bowen, M. Charrenskus, T. W. Hey, C. L. McMullin, A. G. Orpen and D. F. Wass, Dalton Trans., 2010, 39, 560–567.

12 J. M. Lister, M. Carreira, M. F. Haddow, A. Hamilton, C. L. McMullin, A. G. Orpen, P. G. Pringle and T. E. Stennett, Organometallics, 2014, 33, 702–714.

13 M. Carreira, M. Charrenskus, M. Eberhard, N. Fey, R. van Ginkel, A. Hamilton, W. P. Mul, A. G. Orpen, H. Phetum and P. G. Pringle, J. Am. Chem. Soc., 2009, 131, 3078–3092.

14 (a) A. Roodt, S. Otto and G. Steyl, Coord. Chem. Rev., 2003, 245, 121–137; (b) M. L. Clarke, D. J. Cole-Hamilton, A. M. Z. Slawin and J. D. Woollins, Chem. Commun., 2000, 2065–2066.

15 M. R. Eberhard, E. Carrington-Smith, E. E. Drent, P. S. Marsh, A. G. Orpen, H. Phetum and P. G. Pringle, Adv. Synth. Catal., 2005, 347, 1345–1348.

16 I. Pernik, J. F. Hooper, A. B. Chaplin, A. S. Weller and M. C. Willis, ACS Catal., 2012, 2, 2779–2786.

17 Z. Fei, R. Scoppelliti and P. J. Dyson, Eur. J. Inorg. Chem., 2004, 530–534.
18 P. Boulens, M. Lutz, E. Jeanneau, H. Olivier-Bourbigou, J. N. H. Reek and P.-A. R. Breuil, *Eur. J. Inorg. Chem.*, 2014, 3754–3762.

19 V. L. Foss, Y. A. Veits, T. E. Chernykh and I. F. Lutsenko, *Zh. Obshch. Khim.*, 1984, 54, 2670–2684.

20 (a) Z. Fei, R. Scopelliti and P. J. Dyson, *Dalton Trans.*, 2003, 2272–2279; (b) Z. Fei, N. Biricik, D. Zhao, R. Scopelliti and P. J. Dyson, *Inorg. Chem.*, 2004, 43, 2228–2230.

21 A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, 1996, 15, 1518.

22 M. A. Bennett, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 1961, 2037.

23 D. Fraccarollo, R. Bertani, M. Mozzon, U. Belluco and R. A. Michelin, *Inorg. Chim. Acta*, 1992, 201, 15–22.

24 D. Drew and J. R. Doyle, *Inorg. Synth.*, 1991, 28, 346–349.

25 S. J. Coles and P. A. Gale, *Chem. Sci.*, 2012, 3, 683–689.

26 H. Nowell, S. A. Barnett, K. E. Christensen, S. J. Teat and D. R. Allan, *J. Synchrotron Radiat.*, 2012, 19, 435–441.

27 Bruker-Nonius, SAINT version 7.32A, 2006, Bruker-AXS, Madison, Wisconsin, USA; G. M. Sheldrick, SADABS V2008/1, University of Göttingen, Germany.

28 (a) G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2008, 64, 112–122; (b) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Ghoshmann, *J. Appl. Crystallogr.*, 2009, 42, 339–341.