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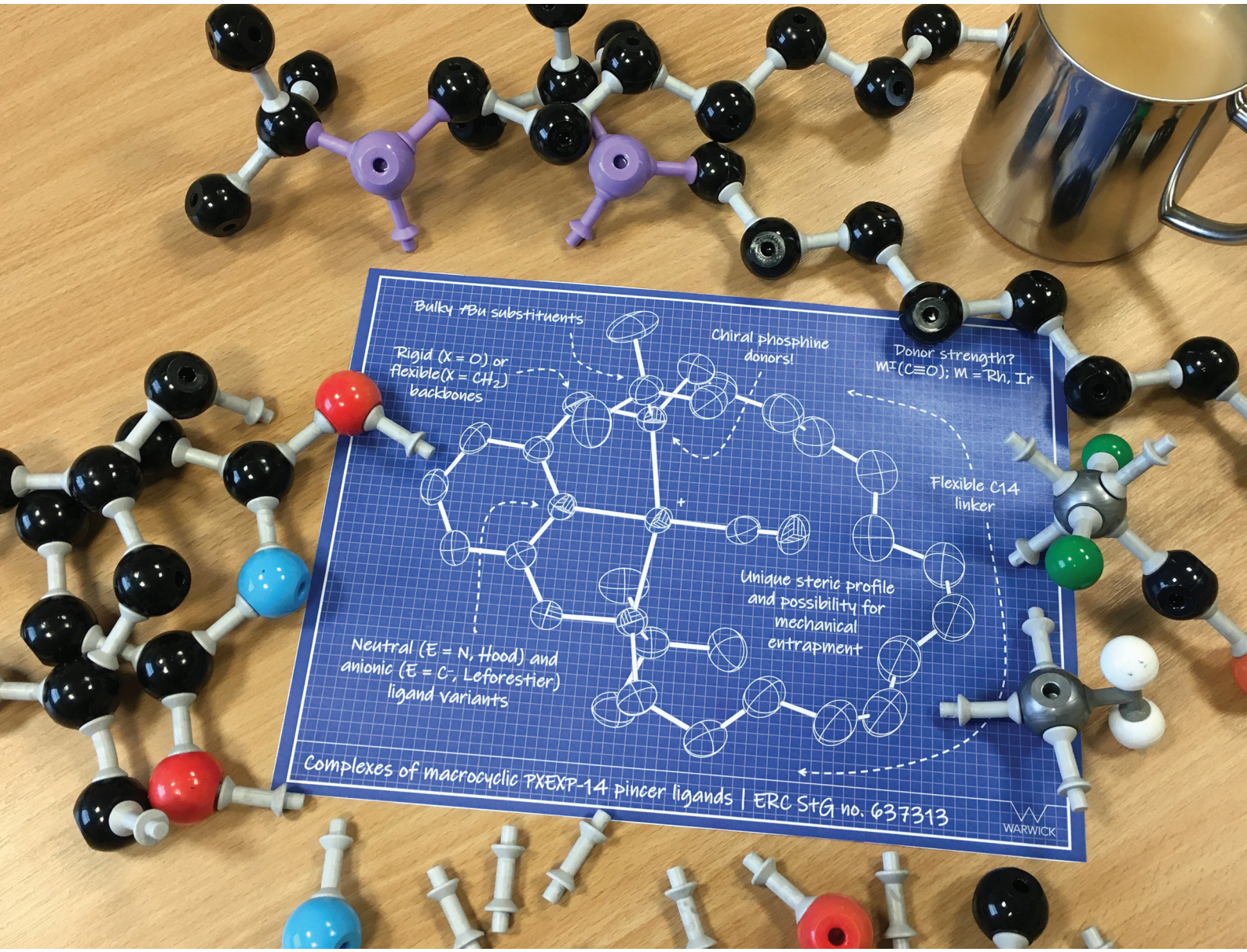

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Synthesis and group 9 complexes of macrocyclic PCP and POCOP pincer ligands

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Synthesis and rhodium complexes of macrocyclic PNP and PONOP pincer ligands†

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The synthesis of macrocyclic variants of commonly employed phosphine-based pincer ligands derived from lutidine (PNP-14) and 2,6-dihydroxypyridine (PONOP-14) is described, where the P-donors are *trans*-substituted with a tetradecamethylene linker. This was accomplished using an eight-step procedure involving borane protection, ring-closing olefin metathesis, chromatographic separation from the *cis*-substituted diastereomers, and borane deprotection. The rhodium coordination chemistry of these ligands has been explored, aided by the facile synthesis of 2,2′-biphenyl (biph) adducts [Rh(PNP-14)(biph)][BAr^F_4] and [Rh(PONOP-14)(biph)][BAr^F_4] (Ar^F = 3,5-$(CF_3)_2C_6H_3$). Subsequent hydrogenolysis enabled generation of dihydrogen, ethylene and carbonyl derivatives; notably the ν(CO) bands of the carbonyl complexes provide a means to compare the donor properties of the new pincer ligands with established acyclic congeners.

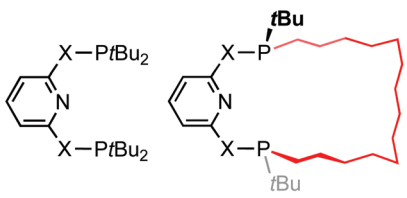
Introduction

Phosphine-based pincers are an important ligand class in organometallic chemistry and catalysis, enabling a diverse variety of metal-based reactivity.[1] Their ability to support reactive metal fragments is often exploited in the literature, with notable examples including a σ-methane complex,[2] alkane dehydrogenation catalysts,[3] and complexes capable of enacting the activation of C(sp^3)–F bonds.[4] Although *mer*-tridentate donor geometries are in principle highly tuneable and adaptable ligand scaffolds, the majority of phosphine-based pincers employed in the literature feature homoleptic aryl and alkyl phosphine donors, exemplified in the case of lutidine- and 2,6-dihydroxypyridine-derived variants by PNP-*t*Bu and PONOP-*t*Bu (Chart 1).[5,6] Motivated by the potential to exploit additional reaction control though their unique steric profile, use in the construction of interlocked assemblies, and as an extension of our related work with NHC-based pincer ligands,[7,8] we became interested in developing the chemistry of macrocyclic phosphine-based pincers. We herein describe the racemic synthesis of the first macrocyclic pincers PNP-14 and PONOP-14, where the chiral P-donors are *trans*-substituted with a tetradecamethylene linker, and some representative complexes with rhodium.[9]

Results and discussion

Preparation of borane protected ligands

PNP-14·2BH_3 (*trans*-**1a**) and PONOP-14·2BH_3 (*trans*-**1b**) were prepared from commercially available *tert*-butyldichlorophosphine using the seven-step synthesis outlined in Scheme 1. Amination of the starting material,[10] enabled selective mono-alkylation (**2**, δ_{31P} 73.3) and following treatment with HCl chloro-*tert*-butyl-octen-7-yl-phosphine **3** (δ_{31P} 128.7) was obtained in 92% yield over three steps. Substitution of **3** by nucleophiles derived from the deprotonation of 2,6-dihydroxypyridine hydrochloride or 2,6-lutidine affords acyclic **4a** (δ_{31P} 33.7) and **4b** (δ_{31P} 144.7) as inseparable mixtures of diastereomers in 55% and 72% yield, respectively, after borane protec-



X = CH_2	PNP-*t*Bu	PNP-14
X = O	PONOP-*t*Bu	PONOP-14

Chart 1

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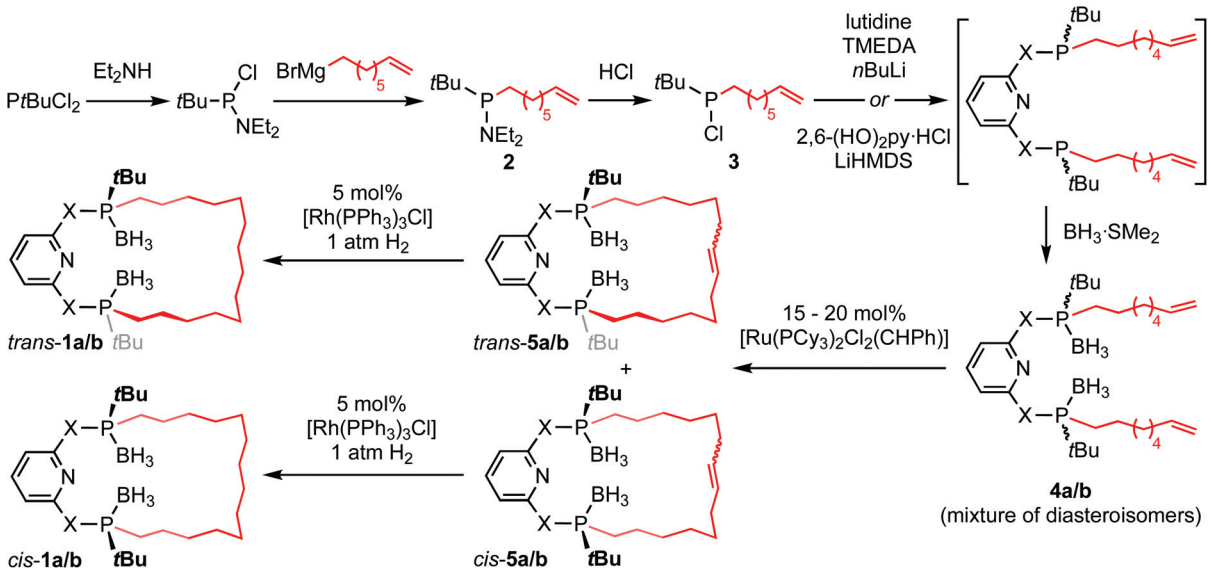
†Electronic supplementary information (ESI) available: NMR, IR and ESI-MS spectra of new compounds, and selected reactions (PDF). Primary NMR data (MNOVA). CCDC 1966918–1966922. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9dt04474d



Scheme 1 Preparation of PNP-14·2BH_3 (*trans*-**1a**) and PONOP-14·2BH_3 (*trans*-**1b**).

tion at −78 °C and purification by chromatography. Thereafter, olefin metathesis of **4a/b** under dilute conditions (<4 mmol L^{-1}) using Grubbs' 1st generation catalyst generated the corresponding macrocycles (*cis*-**5a/b**, δ_{31P} 33.8/144.8; *trans*-**5a/b**, δ_{31P} 34.0/143.4). The component diastereomers of **5a/b** were separated using column chromatography and subsequently hydrogenated using Wilkinson's catalyst to produce the saturated derivatives (*cis*-**1a/b**, δ_{31P} 33.3/145.1; *trans*-**1a/b**, δ_{31P} 33.9/144.1). In this way *trans*-**1a/b** were obtained as analytically pure racemates, in practically useful overall yields of 14/22%, with their configurations confirmed by single crystal X-ray diffraction (Fig. 1).

Deprotection

Deprotection of phosphine–boranes is commonly achieved by reactions with excess amine.[11] Gratifyingly, treatment of *trans*-**1a** with neat Et_2NH at 85 °C resulted in complete conversion to the free-base PNP-14 (δ_{31P} 4.5) within 36 h, which was subsequently isolated in quantitative yield on removal of volatiles. Reactions between *trans*-**1b** and Et_2NH under a range of conditions were, however, characterised by a significant degree of ligand decomposition that we ascribe to rupture of at least one of the P–O bonds.[12] Evaluation of a range of other deprotection methods[13] gave similar outcomes (see ESI†) and consequently we have so far been unable to obtain pure samples of the free-base. Nevertheless, conditions under which PONOP-14 (δ_{31P} 146.5) can be generated *in situ* in 69–83% purity were identified: prolonged stirring of *trans*-**1b** (3.8 mmol L^{-1}) in 1 : 1 THF : Et_2NH at 19 °C.

Rhodium complexes

As convenient {Rh(pincer)}$^+$ synthons, the synthesis of five coordinate derivatives [Rh(pincer)(biph)][$BAr^F{}_4$] (pincer = PNP-14, **6a**; PONOP-14, **6b**; biph = 2,2′-biphenyl; Ar^F = 3,5-$(CF_3)_2C_6H_3$) were targeted (Scheme 2). Exploiting a rhodium(III) precursor first described by Jones,[14] and informed by previous work in our laboratories,[7,15,16] **6a/b** were obtained as analytically pure materials in good isolated yield (79/69%) using a one-pot procedure involving substitution reactions of [Rh(biph)(dtbpm)Cl] (dtbpm = bis(di-*tert*-butylphosphino)methane) with isolated

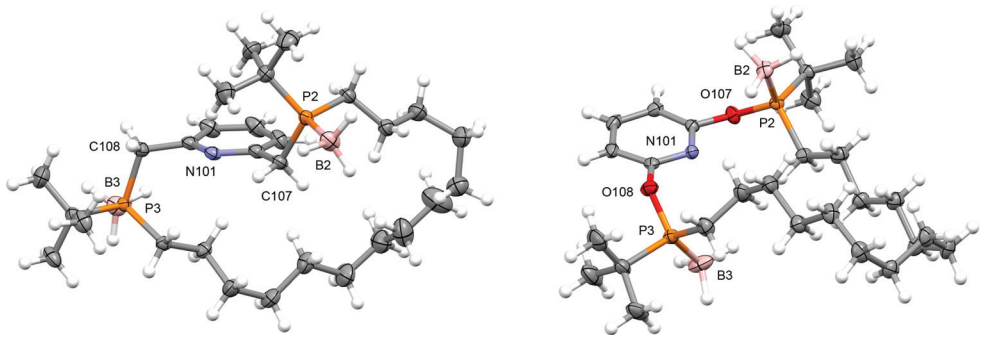
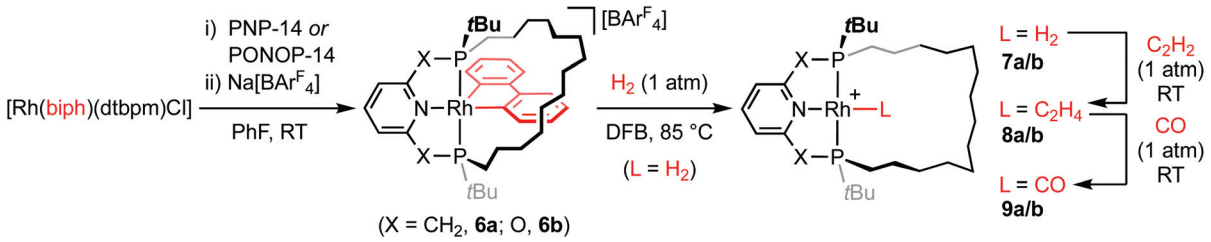


Fig. 1 Solid-state structures of *trans*-**1a** (left) and *trans*-**1b** (right). Thermal ellipsoids drawn at 50% probability; hexane solvent (*trans*-**1b**) omitted for clarity. Selected bond lengths (Å): *trans*-**1a**, P2–B2, 1.918(2), P3–B3, 1.922(2); *trans*-**5b**, P2–B2, 1.903(3), P3–B3, 1.898(3).



Scheme 2 Preparation of rhodium complexes of PNP-14 and PONOP-14.

PNP-14 or *in situ* generated samples of PONOP-14 in the weakly coordinating solvent fluorobenzene[17] and subsequent addition of Na[BAr$^F_4$] as a halide abstracting agent. Complexes **6a** and **6b** are characterised in solution by pairs of ^{31}P resonances centred at δ 43.1 ($^1J_{RhP}$ = 110 Hz)/38.4 ($^1J_{RhP}$ = 113 Hz) and δ 191.1 ($^1J_{RhP}$ = 110 Hz)/182.9 ($^1J_{RhP}$ = 121 Hz), which display diagnostic *trans*-phosphine $^2J_{PP}$ coupling of 339 and 372 Hz, respectively, and indicate adoption of C_1 symmetry. Whilst the acyclic congeners [Rh(pincer)(biph)][BAr$^F_4$] (pincer = PNP-*t*Bu, **6a′**; PONOP-*t*Bu, **6b′**) highlight the propensity for dynamic pseudorotation of the biph ligand on the NMR timescale,[15] the tetradecamethylene linker appears to preclude such fluxionality in **6a/6b**.

The solid-state structures of **6a/6b** demonstrate the adoption of distorted square pyramidal metal geometries, inferred from solution (Fig. 2). The methylene chains of the pincer ligands are skewed to one side of the basal plane, presumably to minimise steric buttressing with the biph ligand, and contorted to enable adoption of a weak γ-agostic interactions (Rh1···H–C129 = 3.184(2) Å **6a**; 2.925(5) Å, **6b**).[18] Agostic interactions of comparable magnitude are observed in **6a′/6b′** and closely related rhodium 2,2′-biphenyl complexes of a NHC-based macrocyclic pincer ligand.[7,15]

Reaction of **6a/b** with dihydrogen (1 atm) in 1,2-difluorobenzene (DFB)[17] resulted in hydrogenolysis of the biph ligand and formation of **7a/b** [δ_{31P} 65.9 ($^1J_{RhP}$ = 120 Hz)/δ_{31P} 211.5 ($^1J_{RhP}$ = 127 Hz)], but elevated temperature and prolonged reactions times were required for complete conversion (t = 2 days/5 days at 85 °C, Scheme 2). In both cases, no organometallic intermediates were observed during this reaction and biphenyl was the sole by-product. The spectroscopic characteristics are consistent with formulation of **7a/b** as C_2 symmetric rhodium(I) dihydrogen complexes, with broad 2H resonances at δ −10.76/−8.51 that exhibit short spin–lattice relaxation (T_1 = 45 ± 11/48 ± 6 ms) at 298 K (600 MHz, Ar) the most diagnostic.[19] Subsequent reaction *in situ* with ethylene (1 atm) confers the corresponding C_2 symmetric π-complexes **8a/8b** [δ_{31P} 53.0 ($^1J_{RhP}$ = 125 Hz)/δ_{31P} 199.1 ($^1J_{RhP}$ = 129 Hz)], with concomitant formation of ethane, in quantitative spectroscopic yield within 5 min at RT. Coordination of ethylene is substantiated by chemically inequivalent 2H signals at δ 3.70/3.52 and 3.95/3.70, and ^{13}C resonances at δ 55.0 ($^1J_{RhC}$ = 12 Hz) and 59.5 ($^1J_{RhC}$ = 11 Hz), which display appreciable coupling to ^{103}Rh, for **8a** and **8b** respectively. Finally, C_2 symmetric carbonyl compounds **9a/b** [δ_{31P} 67.5 ($^1J_{RhP}$ = 122 Hz)/δ_{31P} 210.8 ($^1J_{RhP}$ = 128 Hz)] are obtained by substitution of ethylene on reaction of **8a/b** with carbon monoxide (1 atm <5 min at RT), isolated from solution in 96/72% yield overall from **6a/b** and fully characterised, including in the case of **9b** in the solid state by

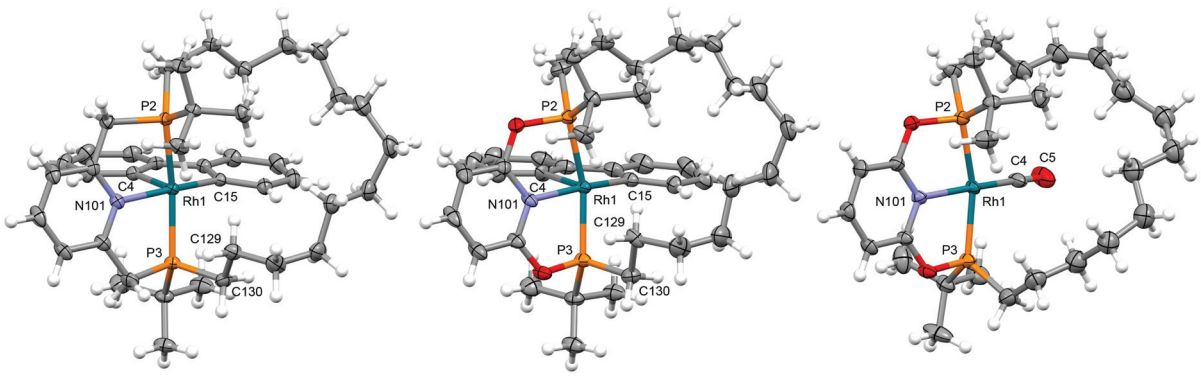


Fig. 2 Solid-state structures of **6a** (left), **6b** (centre) and **9b** (not unique, Z' = 2; right). Thermal ellipsoids drawn at 50%, 30% and 30% probability, respectively; minor disordered component (**9b**, methylene chain) and anions omitted. Selected bond lengths (Å) and bond angles (°): **6a**: Rh1–C4, 2.003(2); Rh1–C15, 2.028(2); Rh1–P2, 2.3340(4), Rh1–P3, 2.2801(4); Rh1–N101, 2.142(1); P2–Rh1–P3, 163.85(2); N101–M1–C15, 172.93(6); Rh1···H–C129, 3.184(2); Rh1–P3–C130, 103.53(6); **6b**: Rh1–C4, 2.065(5); Rh1–C15, 2.034(5); Rh1–P2, 2.330(1), Rh1–P3, 2.243(1); Rh1–N101, 2.091(4); P2–Rh1–P3, 159.89(5); N101–M1–C15, 171.2(2); Rh1···H–C129, 2.925(5); Rh1–P3–C130, 103.0(2); **9b**: Rh1–C4, 1.844(5); C4–O5, 1.141(7); Rh1–P2, 2.291(1); Rh1–P3, 2.256(1); Rh1–N101, 2.051(3); P2–Rh1–P3, 160.67(4); N101–Rh1–C4, 174.0(2); Rh11–C14, 1.846(6); C14–O15, 1.147(8); Rh11–P12, 2.288(2); Rh11–P13, 2.250(2); Rh11–N201, 2.034(4); P12–Rh11–P13, 161.16(7); N201–Rh11–C14, 172.0(3).

Table 1 Carbonyl stretching frequencies (CH_2Cl_2)

Pincer complex	ν(CO)/cm^{-1}
[Rh(PNP-14)(CO)][BAr^F_4] **9a**	1997
[Rh(PNP-*t*Bu)(CO)][BAr^F_4] **9a′** [15]	1990
[Rh(PNP-*i*Pr)(CO)][BAr^F_4] **9a″** [20]	1998
[Rh(PONOP-14)(CO)][BAr^F_4] **9b**	2020
[Rh(PONOP-*t*Bu)(CO)][BAr^F_4] **9b′** [15]	2016

X-ray diffraction (Fig. 2). The ν(CO) bands of rhodium(I) carbonyl derivatives are diagnostic reporter groups for the donor properties of pincer ligands.[20,21] Comparison of the carbonyl bands of **9a/b** with those of acyclic congeners **9a/b′**,[15,22] recorded under the same conditions, suggests PNP-14 and PONOP-14 are marginally weaker net donors than PNP-*t*Bu and PONOP-*t*Bu, respectively (Table 1). By reference to IR data reported for [Rh(PNP-*i*Pr)(CO)][BAr^F_4] (**9a″**; PNP-*i*Pr = 2,6-(iPr$_2$PCH$_2$)$_2$C$_5$H$_3$N) and trends established for monodentate phosphines, these minor differences are in line with changes in the phosphine/phosphinite substituents alone.[20,23]

Conclusions

An eight-step procedure for the synthesis of two macrocyclic phosphine-based pincer ligands, where the P-donors are *trans*-substituted with a tetradecamethylene linker, has been developed. These ligands are derived from lutidine (PNP-14) and 2,6-dihydroxypyridine (PONOP-14), with key steps involving borane protection, ring-closing olefin metathesis, chromatographic separation from the *cis*-substituted diastereomers, and borane deprotection. The final step was accomplished by borane transfer to diethylamine, but a non-trivial amount of decomposition could not be avoided in the case of the phosphinite pincer. The rhodium coordination chemistry of these ligands has been explored, with 2,2′-biphenyl (biph) complexes [Rh(PNP-14)(biph)][BAr^F_4] and [Rh(PONOP-14)(biph)][BAr^F_4] conveniently accessed by substitution reactions of [Rh(biph)(dtbpm)Cl] (dtbpm = bis(di-*tert*-butylphosphino)methane), followed by halide abstraction. These five-coordinate rhodium(III) complexes are well-defined synthons for the generation of rhodium(I) dihydrogen, ethylene and carbonyl derivatives, following hydrogenolysis of the biph ligand that serves as an 'organometallic protecting group'. By comparison with the ν(CO) bands of rhodium(I) carbonyl adducts, determined by IR spectroscopy in CH_2Cl_2, PNP-14 and PONOP-14 can be considered to be marginally weaker net donors than their respective homoleptic *tert*-butyl substituted congeners PNP-*t*Bu and PONOP-*t*Bu, respectively.

Experimental

General methods

All manipulations were performed under an atmosphere of argon using Schlenk and glove box techniques unless otherwise stated. Glassware was oven dried at 150 °C overnight and flame-dried under vacuum prior to use. Molecular sieves were activated by heating at 300 °C *in vacuo* overnight. Dihydrogen and ethylene were dried by passage through a stainless-steel column of activated 3 Å molecular sieves prior to use. Fluorobenzene and 1,2-difluorobenzene (DFB) were pre-dried over Al_2O_3, distilled from calcium hydride and dried twice over 3 Å molecular sieves.[17] CD_2Cl_2 was freeze–pump–thaw degassed and dried over 3 Å molecular sieves. C_6D_6 was distilled from sodium and stored over 3 Å molecular sieves. THF, dioxane, diethyl ether and benzene were distilled from sodium/benzophenone and stored over 3 Å molecular sieves. Et_2NH was distilled from CaH_2. $SiMe_4$ was distilled from liquid Na/K alloy and stored over a potassium mirror. Other anhydrous solvents were purchased from Acros Organics or Sigma-Aldrich, freeze–pump–thaw degassed and stored over 3 Å molecular sieves. LiHMDS was resublimed before use. *n*BuLi was titrated before use.[24] TMEDA was distilled from sodium/benzophenone and stored over 3 Å molecular sieves. Diethylamino-*tert*-butyl-chlorophosphine (yield = 98%),[10] $BrMgC_8H_{15}$,[25] Wilkinson's catalyst,[26] Na[BAr^F_4],[27] and [Rh(biph)(dtbpm)Cl],[14] were synthesised according to published procedures. All other reagents are commercial products and were used as received. NMR spectra were recorded on Bruker spectrometers under argon at 298 K unless otherwise stated. Chemical shifts are quoted in ppm and coupling constants in Hz. NMR spectra in DFB and THF : Et_2NH were recorded using an internal capillary of C_6D_6. ESI-MS were recorded on Bruker Maxis Plus (HR) or Agilent 6130B single Quad (LR) instruments. Infrared spectra were recorded on a Jasco FT-IR-4700 using a KBr transmission cell in CH_2Cl_2. Microanalyses were performed at the London Metropolitan University by Stephen Boyer.

Preparation of PNP-14·2BH$_3$ (*trans*-1a) and PONOP-14·2BH$_3$ (*trans*-1b)

Preparation of diethylamino-*tert*-butyl-octen-7-yl-phosphine 2. A solution of diethylamino-*tert*-butyl-chlorophosphine (3.19 g, 16.3 mmol) in THF (30 mL) was cooled to −78 °C and a solution of $BrMgC_8H_{15}$ (43 mL, 0.38 M) in THF added dropwise over 30 minutes. The suspension was allowed to warm to ambient temperature and stirred for 16 h. The solution was concentrated under vacuum and the product extracted into hexane. Dioxane (10 mL) was added and the resulting suspension filtered, to afford the product on removal of the volatiles *in vacuo*, which was carried forward without further purification. Yield: 4.21 g (95%).

^{1}H NMR (600 MHz, C_6D_6): δ 5.80 (ddt, $^3J_{HH}$ = 16.9, $^3J_{HH}$ = 10.2, $^3J_{HH}$ = 6.7, 1H, C$\underline{H}$=CH$_2$), 5.02–5.08 (m, 1H, CH=C$\underline{H}_2$), 4.98–5.01 (m, 1H, CH=C$\underline{H}_2$), 2.90–2.97 (m, 4H, NCH$_2$), 1.98–2.04 (m, 2H, C$\underline{H}_2$CH=CH$_2$), 1.72–1.78 (m, 1H, CH$_2$), 1.13–1.66 (m, 9H, CH$_2$), 1.06 (d, 9H, $^3J_{PH}$ = 11.8, *t*Bu), 1.00 (t, 6H, $^3J_{HH}$ = 7.1, NCH$_2$C$\underline{H}_3$).

^{13}C{^{1}H} NMR (151 MHz, C_6D_6): δ 139.2 (s, $\underline{C}$H=CH$_2$), 114.6 (s, CH=$\underline{C}$H$_2$), 44.5 (br, NCH$_2$), 34.2 (s, $\underline{C}$H$_2$CH=CH$_2$), 32.5 (d, $^1J_{PC}$ = 20, *t*Bu{C}), 31.7 (d, J_{PC} = 12, CH$_2$), 29.5 (s, CH$_2$), 29.4

(s, CH_2), 27.6 (d, $^2J_{PC}$ = 16, *t*Bu{CH_3}), 26.6 (d, J_{PC} = 18, CH_2), 23.2 (d, $^1J_{PC}$ = 19, CH_2), 15.2 (d, $^4J_{PC}$ = 2, $NCH_2\underline{C}H_3$).

$^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6): δ 73.3 (s).

Preparation of chloro-*tert*-butyl-octen-7-yl-phosphine 3. HCl in diethyl ether (151 mL, 1 M, 151 mmol) was added to a solution of **2** (20.5 g, 75.5 mmol) in hexane (400 mL) at 0 °C. The suspension was allowed to warm to ambient temperature, stirred for 2 h and then allowed to stand for 16 h before being filtered. Analysis of the filtrate by ^{31}P NMR spectroscopy indicated the partial formation of **3**·HCl ($\delta_{^{31}P}$ 46.9), which was subsequently deprotonated by addition a stoichiometric amount of LiHMDS (0.479 g, 2.86 mmol) suspended in hexane (10 mL). The resulting suspension was stirred for 1 h before allowing the precipitate to settle out, filtered and the product obtained on removal of the volatiles removed *in vacuo*, which was carried forward without further purification. Yield: 17.6 g (99%).

^1H NMR (500 MHz, C_6D_6): δ 5.77 (ddt, $^3J_{HH}$ = 16.8, $^3J_{HH}$ = 10.0, $^3J_{HH}$ = 6.5, 1H, $C\underline{H}{=}CH_2$), 5.01–5.06 (m, 1H, $CH{=}C\underline{H}_2$), 4.97–5.01 (m, 1H, $CH{=}C\underline{H}_2$), 1.92–2.00 (m, 2H, $C\underline{H}_2CH{=}CH_2$), 1.15–1.83 (m, 10H, CH_2), 0.99 (d, $^3J_{PH}$ = 12.8, 9H, *t*Bu).

$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ 139.1 (s, $\underline{C}H{=}CH_2$), 114.6 (s, $CH{=}\underline{C}H_2$), 34.1 (s, $\underline{C}H_2CH{=}CH_2$), 32.4 (d, $^1J_{PC}$ = 29, *t*Bu{C}), 31.1 (d, J_{PC} = 11, CH_2), 30.7 (d, $^1J_{PC}$ = 36, CH_2), 29.2 (s, 2 × CH_2), 25.9 (d, J_{PC} = 15, CH_2), 25.5 (d, $^2J_{PC}$ = 17, *t*Bu{CH_3}).

$^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ 128.7 (s).

Preparation of 4a. A solution of 2,6-lutidine (1.22 g, 11.4 mmol) and TMEDA (3.40 mL, 22.7 mmol) in diethyl ether (30 mL) at 0 °C was treated dropwise with *n*BuLi (13.7 mL, 1.66 M, 22.7 mmol). The reaction was warmed to room temperature and stirred for 16 h resulting in a deep red solution, which was cooled to −78 °C and treated with a solution of **3** (5.48 g, 23.3 mmol) in diethyl ether (60 mL), then warmed to room temperature and stirred for 2 days. The suspension was filtered, the filtrate reduced to dryness and the crude product extracted into hexane (50 mL). The resulting solution was washed with degassed water, dried over $MgSO_4$ and the solvent removed *in vacuo* to afford a colourless oil, which was redissolved in THF (150 mL), cooled to −78 °C, treated with $BH_3{\cdot}SMe_2$ (1.10 mL, 11.6 mmol) and an aliquot analysed by ^{31}P NMR spectroscopy. Additional $BH_3{\cdot}SMe_2$ was then added portion-wise (0.40 mL, 4.2 mmol, then 0.60 mL, 6.3 mmol) at −78 °C until no free phosphine remained by ^{31}P NMR spectroscopy. In air, the solution was treated with aqueous ammonium chloride (150 mL), extracted into ethyl acetate (150 mL), dried over $MgSO_4$ and the volatiles removed *in vacuo*. The product was obtained as a colourless oil after repeated purification by column chromatography as a mixture of diastereomers (10% EtOAc in hexane; R_F = 0.19). Yield: 3.30 g (55%).

^1H NMR (500 MHz, $CDCl_3$): δ 7.55 (t, $^3J_{HH}$ = 7.7, 1H, py), 7.19–7.24 (m, 2H, py), 5.72–5.85 (m, 2H, $C\underline{H}{=}CH_2$), 4.95–5.01 (m, 2H, $CH{=}C\underline{H}_2$), 4.91–4.95 (m, 2H, $CH{=}C\underline{H}_2$), 3.09–3.20 (m, 4H, $pyC\underline{H}_2$), 1.97–2.06 (m, 4H, $C\underline{H}_2CH{=}CH_2$), 1.67–1.85 (m, 2H, CH_2), 1.49–1.62 (m, 4H, CH_2), 1.21–1.38 (m, 14H, CH_2), 1.16 (d, $^3J_{PH}$ = 13.3, 7.3H, *t*Bu), 1.12 (d, $^3J_{PH}$ = 13.4, 10.7H, *t*Bu), −0.05–0.77 (m, 6H, BH_3). Some peaks duplicated because of diastereomers.

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 154.4 (dd, $^2J_{PC}$ = 6, $^4J_{PC}$ = 1, py), 154.2 (dd, $^2J_{PC}$ = 5, $^4J_{PC}$ = 2, py), 138.97 (s, $\underline{C}H{=}CH_2$) 138.96 (s, $\underline{C}H{=}CH_2$), 136.8 (t, $^4J_{PC}$ = 2, py), 136.7 (t, $^4J_{PC}$ = 2, py), 123.3 (app t, J_{PC} = 3, py), 123.2 (app t, J_{PC} = 3, py), 114.5 (s, $CH{=}\underline{C}H_2$), 33.8 (s, $\underline{C}H_2CH{=}CH_2$), 31.74 (d, $^2J_{PC}$ = 13, CH_2), 31.70 (d, $^2J_{PC}$ = 13, CH_2), 31.39 (d, $^1J_{PC}$ = 26, $py\underline{C}H_2$), 31.34 (d, $^1J_{PC}$ = 26, $py\underline{C}H_2$), 28.91 (d, $^1J_{PC}$ = 38, *t*Bu{C}), 28.90 (d, $^1J_{PC}$ = 31, *t*Bu{C}), 28.90 (s, CH_2), 28.88 (s, CH_2), 28.8 (br, CH_2), 25.8 (t, $^2J_{PC}$ = 2, *t*Bu{CH_3}), 23.70 (s, CH_2), 23.67 (s, CH_2), 20.0 (d, $^1J_{PC}$ = 30, CH_2). Some peaks duplicated because of diastereomers.

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 33.7 (vbr, fwhm = 150 Hz).

HR ESI-MS (positive ion 4 kV): 554.4366, $[M + Na]^+$ (calcd 554.4368) *m*/*z*.

Preparation of 4b. A suspension of 2,6-dihydroxypyridine hydrochloride (0.890 g, 6.01 mmol) and LiHMDS (3.03 g, 18.1 mmol) in THF (30 mL) was heated at reflux for 16 h. The resulting suspension was treated dropwise with a solution of **3** (2.90 g, 12.4 mmol) in THF (20 mL) and then heated at reflux for 16 h. The solvent was removed *in vacuo* and the crude product extracted into hexane, to afford a colourless oil on removal of the volatiles, which was redissolved in THF (50 mL), cooled to −78 °C, treated $BH_3{\cdot}SMe_2$ (0.85 mL, 12 mmol) and an aliquot analysed by ^{31}P NMR spectroscopy. Additional $BH_3{\cdot}SMe_2$ was then added (0.12 mL, 1.27 mmol) at −78 °C until no free phosphine remained by ^{31}P NMR spectroscopy. In air, the solution was treated with aqueous ammonium chloride (50 mL), extracted into ethyl acetate, dried over $MgSO_4$, filtered and the volatiles removed *in vacuo*. The product was obtained as a colourless oil after repeated purification by column chromatography as a mixture of diastereomers (2% EtOAc in hexane; R_F = 0.22). Yield: 2.31 g (72%).

^1H NMR (500 MHz, $CDCl_3$): δ 7.65 (t, $^3J_{HH}$ = 7.9, 1H, py), 6.81 (d, $^3J_{HH}$ = 7.9, 1.0H, py), 6.80 (d, $^3J_{HH}$ = 7.9, 1.0H, py), 5.80 (ddt, $^3J_{HH}$ = 16.9, $^3J_{HH}$ = 10.3, $^3J_{HH}$ = 6.7, 2H, $C\underline{H}{=}CH_2$), 4.96–5.02 (m, 2H, $CH{=}C\underline{H}_2$), 4.93 (d, $^3J_{HH}$ = 10.1, 2H, $CH{=}C\underline{H}_2$), 2.08–2.24 (m, 2H, CH_2), 2.04 (app q, $^3J_{HH}$ = 7, 4H, $C\underline{H}_2CH{=}CH_2$), 1.79–1.92 (m, 2H, CH_2), 1.67–1.78 (m, 4H, CH_2), 1.33–1.47 (m, 12H, CH_2), 1.29 (d, $^3J_{PH}$ = 14.1, 9.0H, *t*Bu), 1.29 (d, $^3J_{HH}$ = 14.2, 9.0H, *t*Bu), 0.08–0.92 (m, 6H, BH_3). Some peaks duplicated because of diastereomers.

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 158.1 (app t, J_{PC} = 7, py), 142.09 (s, py), 142.05 (s, py), 139.07 (s, $\underline{C}H{=}CH_2$), 139.06 (s, $\underline{C}H{=}CH_2$), 114.5 (s, $CH{=}\underline{C}H_2$), 111.0 (d, $^3J_{PC}$ = 3, py), 110.8 (d, $^3J_{PC}$ = 3, py), 33.84 (s, $\underline{C}H_2CH{=}CH_2$), 33.83 (s, $\underline{C}H_2CH{=}CH_2$), 32.84 (d, $^1J_{PC}$ = 36, *t*Bu{C}), 32.78 (d, $^1J_{PC}$ = 36, *t*Bu{C}), 31.4 (s, CH_2), 31.3 (s, CH_2), 28.90 (s, CH_2), 28.89 (s, CH_2), 28.80 (s, CH_2), 28.78 (s, CH_2), 25.5 (d, $^1J_{PC}$ = 31, CH_2), 25.4 (d, $^1J_{PC}$ = 31, CH_2), 24.94 (d, $^2J_{PC}$ = 3, *t*Bu{CH_3}), 24.92 (d, $^2J_{PC}$ = 3, *t*Bu{CH_3}), 23.01, (s, CH_2), 23.00 (s, CH_2). Some peaks duplicated because of diastereomers.

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 144.7 (vbr, fwhm = 160 Hz).

HR ESI-MS (positive ion 4 kV): 558.3953, $[M + Na]^+$ (calcd 558.3950) *m*/*z*.

Preparation of 5a. A solution of **4a** (3.30 g, 6.21 mmol) in CH_2Cl_2 (1.2 mmol L^{-1}, 5 L) was treated with 15 mol% [$Ru(PCy_3)_2Cl_2(CHPh)$] (0.77 g, 0.94 mmol) in 5 mol% portions in CH_2Cl_2 (5 mL) over 3 days with daily sparging with N_2 for 30 minutes. The solvent was removed *in vacuo* and the *cis*- and *trans*-diastereomers were separated as white solids by repeated purification by column chromatography in air (10% EtOAc in hexane).

cis-**5a** (R_F = 0.22). Yield: 553 mg (18%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (t, $^3J_{HH}$ = 7.7, 1H, py), 7.23 (d, $^3J_{HH}$ = 7.8, 2H, py), 5.27–5.41 (m, 2H, CH=CH), 3.07–3.21 (m, 4H, py$\underline{C}H_2$), 1.94–2.09 (m, 4H, $\underline{C}H_2CH$=CH), 1.80–1.92 (m, 2H, CH_2), 1.47–1.67 (m, 4H, CH_2), 1.23–1.45 (m, 14H, CH_2), 1.12 (d, $^3J_{PH}$ = 13.3, 18H, *t*Bu), 0.02–0.82 (m, 6H, BH_3).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 154.5 (dd, $^2J_{PC}$ = 6, $^4J_{PC}$ = 2, py), 136.9 (t, $^4J_{PC}$ = 1, py), 131.1 (s, CH=CH), 123.3 (app t, J_{PC} = 3, py), 32.1 (s, $\underline{C}H_2CH$=CH), 31.2 (s, CH_2), 31.1 (d, $^1J_{PC}$ = 12, py$\underline{C}H_2$), 28.9 (d, $^1J_{PC}$ = 31, *t*Bu{C}), 28.7 (s, CH_2), 27.5 (s, CH_2), 25.8 (d, $^2J_{PC}$ = 2, *t*Bu{CH_3}), 23.5 (s, CH_2), 19.3 (d, $^1J_{PC}$ = 30, CH_2).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 33.8 (vbr, fwhm = 150 Hz).

HR ESI-MS (positive ion 4 kV): 526.4051, $[M + Na]^+$ (calcd 526.4079) *m*/*z*.

trans-**5a** (R_F = 0.22). Yield: 840 mg (27%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (t, $^3J_{HH}$ = 7.7, 1H, py), 7.17 (d, $^3J_{HH}$ = 7.8, 2H, py), 5.23–5.41 (m, 2H, CH=CH), 3.07–3.20 (m, 4H, py$\underline{C}H_2$), 1.99–2.07 (m, 4H, $\underline{C}H_2CH$=CH), 1.78–1.92 (m, 2H, CH_2), 1.54–1.71 (m, 4H, CH_2), 1.28–1.51 (m, 14H, CH_2), 1.16 (d, $^3J_{PH}$ = 13.2, 18H, *t*Bu), −0.15–0.73 (m, 6H, BH_3).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 154.5 (dd, $^2J_{PC}$ = 5, $^4J_{PC}$ = 2, py), 136.7 (t, $^4J_{PC}$ = 2, py), 131.1 (s, CH=CH), 123.2 (app t, J_{PC} = 3, py), 31.9 (s, $\underline{C}H_2CH$=CH), 31.0 (d, $^2J_{PC}$ = 11, CH_2), 30.8 (d, $^1J_{PC}$ = 26, py$\underline{C}H_2$), 29.0 (d, $^1J_{PC}$ = 31, *t*Bu{C}), 28.6 (s, CH_2), 27.2 (s, CH_2), 25.9 (d, $^2J_{PC}$ = 2, *t*Bu{CH_3}), 23.5 (s, CH_2), 19.8 (d, $^1J_{PC}$ = 30, CH_2).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 34.0 (vbr, fwhm = 150 Hz).

HR ESI-MS (positive ion 4 kV): 526.4054, $[M + Na]^+$ (calcd 526.4079) *m*/*z*.

Preparation of 5b. A solution of **4b** (1.69 g, 3.16 mmol) in CH_2Cl_2 (3.2 mmol L^{-1}, 1 L) was treated with 20 mol% [$Ru(PCy_3)_2Cl_2(CHPh)$] (0.52 g, 0.63 mmol) in 5 mol% portions in CH_2Cl_2 (3 mL) over four days with daily sparging with N_2 for 30 minutes. The solvent was removed *in vacuo* and the *cis*- and *trans*-diastereomers were separated as white solids by repeated purification by column chromatography in air (2% EtOAc in hexane).

cis-**5b** (R_F = 0.21). Yield: 520 mg (33%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (t, $^3J_{HH}$ = 7.9, 1H, py), 6.95 (d, $^3J_{HH}$ = 8.0, 2H, py), 5.29–5.32 (m, 2H, CH=CH), 2.12–2.24 (m, 2H, CH_2), 1.95–2.08 (m, 4H, $\underline{C}H_2CH$=CH), 1.65–1.85 (m, 6H, CH_2), 1.30–1.48 (m, 12H, CH_2), 1.28 (d, $^3J_{PH}$ = 14.1, 18H, *t*Bu), 0.15–0.92 (m, 6H, BH_3). Data for major isomer only.

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 158.2 (d, $^2J_{PC}$ = 5, py), 142.3 (s, py), 131.0 (s, CH=CH), 110.5 (d, $^3J_{PC}$ = 3, py), 32.8 (d, $^1J_{PC}$ = 37, *t*Bu{C}), 32.1 (s, $\underline{C}H_2CH$=CH), 31.1 (d, $^2J_{PC}$ = 14, CH_2), 28.7 (s, CH_2), 27.7 (s, CH_2), 25.5 (d, $^1J_{PC}$ = 31, CH_2), 24.9 (d, $^2J_{CH}$ = 3, *t*Bu{CH_3}), 22.8 (s, CH_2). Data for major isomer only.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 144.8 (vbr, fwhm = 150 Hz).

HR ESI-MS (positive ion 4 kV): 530.3644, $[M + Na]^+$ (calcd 530.3639) *m*/*z*.

trans-**5b** (R_F = 0.22). Yield: 540 mg (34%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (t, $^3J_{HH}$ = 7.8, 1H, py), 6.76 (d, $^3J_{HH}$ = 7.9, 2H, py), 5.29–5.33 (m, 2H, CH=CH), 2.16–2.33 (m, 2H, CH_2), 1.96–2.09 (m, 4H, $\underline{C}H_2CH$=CH), 1.83–1.92 (m, 2H, CH_2), 1.32–1.46 (m, 4H, CH_2), 1.32–1.46 (m, 12H, CH_2), 1.28 (d, $^3J_{PH}$ = 14.0, 18H, *t*Bu), 0.11–0.85 (m, 6H, BH_3). Data for major isomer only.

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 158.2 (d, $^2J_{PC}$ = 6, py), 142.0 (s, py), 131.2 (s, CH=CH), 110.1 (d, $^3J_{PC}$ = 3, py), 32.8 (d, $^1J_{PC}$ = 37, *t*Bu{C}), 31.8 (s, $\underline{C}H_2CH$=CH), 31.2 (d, $^2J_{PC}$ = 14, CH_2), 28.6 (s, CH_2), 27.5 (s, CH_2), 25.5 (d, $^1J_{PC}$ = 30, CH_2), 24.9 (d, $^2J_{PC}$ = 3, *t*Bu{CH_3}), 23.4 (s, CH_2). Data for major isomer only.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 143.4 (vbr, fwhm = 180 Hz).

HR ESI-MS (positive ion 4 kV): 530.3634, $[M + Na]^+$ (calcd 530.3639) *m*/*z*.

General procedure for the hydrogenation of 5. A suspension of **5** and [$Rh(PPh_3)_3Cl$] (5 mol%) in benzene was freeze–pump–thaw degassed and placed under dihydrogen (1 atm). The resulting solution was heated at reflux for 36 h, reduced to dryness *in vacuo*, and the product obtained following purification by column chromatography in air.

cis-**1a** (20% EtOAc in hexane, R_F = 0.20).

Following the general procedure using *cis*-**5a** (80.0 mg, 0.159 mmol) and [$Rh(PPh_3)_3Cl$] (7.4 mg, 8.0 μmol) in benzene (5 mL), the product was isolated as a white solid. Yield: 73.8 mg (92%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55 (t, $^3J_{HH}$ = 7.7, 1H, py), 7.32 (d, $^3J_{HH}$ = 7.8, 2H, py), 3.16 (app d, $^2J_{PH}$ = 12, 4H, py$\underline{C}H_2$), 1.71–1.82 (m, 2H, CH_2), 1.47–1.60 (m, 4H, CH_2), 1.21–1.39 (m, 22H, CH_2), 1.12 (d, $^3J_{PH}$ = 13.3, 18H, *t*Bu), 0.11–0.72 (br, 6H, BH_3).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 153.8 (dd, $^2J_{PC}$ = 4, $^4J_{PC}$ = 2, py), 136.6 (t, $^4J_{PC}$ = 2, py), 123.5 (app t, J_{PC} = 3, py), 31.5 (d, $^1J_{PC}$ = 26, py$\underline{C}H_2$), 30.7 (d, $^2J_{PC}$ = 13, CH_2), 28.9 (d, $^1J_{PC}$ = 31, *t*Bu{C}), 28.0 (s, CH_2), 27.87 (s, CH_2), 27.85 (s, CH_2), 27.8 (s, CH_2), 25.7 (d, $^2J_{PC}$ = 2, *t*Bu{CH_3}), 22.7 (d, $^3J_{PC}$ = 2, CH_2), 20.4 (d, $^1J_{PC}$ = 31, CH_2).

^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ 33.3 (vbr, fwhm = 130 Hz).

HR ESI-MS (positive ion 4 kV): 528.4204, $[M + Na]^+$ (calcd 528.4211) *m*/*z*.

trans-**1a** (20% EtOAc in hexane, R_F = 0.19).

Following the general procedure using *trans*-**5a** (840 mg, 1.67 mmol) and [$Rh(PPh_3)_3Cl$] (77.2 mg, 83.4 μmol) in benzene (50 mL), the product was isolated as a white solid. Yield: 818 mg (97%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (t, $^3J_{HH}$ = 7.7, 1H, py), 7.21 (d, $^3J_{HH}$ = 7.8, 2H, py), 3.13–3.28 (m, 4H, py$\underline{C}H_2$), 1.75–1.86 (m, 2H, CH_2), 1.52–1.68 (m, 4H, CH_2) 1.38–1.50 (m, 4H, CH_2), 1.26–1.35 (m, 18H, CH_2), 1.10 (d, $^3J_{PH}$ = 13.3, 18H, *t*Bu), 0.05–0.77 (m, 6H, BH_3).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 154.7 (dd, $^2J_{PC}$ = 6, $^4J_{PC}$ = 1, py), 136.8 (t, $^4J_{PC}$ = 2, py), 123.0 (app t, J_{PC} = 3, py), 31.5 (d, $^1J_{PC}$ = 26, py$\underline{C}H_2$), 30.8 (d, $^2J_{PC}$ = 13, CH_2), 29.1 (d, $^1J_{PC}$ = 31, *t*Bu{C}), 27.91 (s, CH_2), 27.89 (s, CH_2), 27.74 (s, CH_2), 27.71 (s,

CH_2), 25.9 (d, $^2J_{PC}$ = 2, *t*Bu{CH_3}), 22.9 (d, $^3J_{PC}$ = 1, CH_2), 20.1 (d, $^1J_{PC}$ = 31, CH_2).

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 33.9 (vbr, fwhm = 150 Hz).

HR ESI-MS (positive ion 4 kV): 528.4209, $[M + Na]^+$ (calcd 528.4211) *m*/*z*.

Anal. Calcd for $C_{29}H_{59}B_2NP_2$ (505.37 g mol^{-1}): C, 68.92; H, 11.77; N, 2.77; Found: C, 68.76; H 11.82; N, 2.69.

cis-**1b** (30% CH_2Cl_2 in hexane, R_F = 0.19).

Following the general procedure using *cis*-**5b** (315 mg, 0.620 mmol) and $[Rh(PPh_3)_3Cl]$ (27.2 mg, 29.4 μmol) in benzene (30 mL), the product was isolated as a white solid. Yield: 287 mg (91%).

^1H NMR (500 MHz, $CDCl_3$): δ 7.67 (t, $^3J_{HH}$ = 7.9, 1H, py), 6.98 (d, $^3J_{HH}$ = 7.9, 2H, py), 2.12–2.25 (m, 2H, CH_2), 1.63–1.82 (m, 6H, CH_2), 1.27 (d, $^3J_{PH}$ = 14, 18H, *t*Bu), 1.25–1.49 (m, 20H, CH_2), 0.14–0.88 (m, 6H, BH_3).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 158.2 (d, $^2J_{PC}$ = 5, py), 142.2 (s, py), 110.8 (d, $^3J_{PC}$ = 3, py), 32.9 (d, $^1J_{PC}$ = 36, *t*Bu{C}), 30.6 (d, $^2J_{PC}$ = 13, CH_2), 27.8 (s, 2 × CH_2), 27.5 (s, CH_2), 27.3 (s, CH_2), 25.2 (d, $^1J_{PC}$ = 32, CH_2), 24.9 (d, $^2J_{PC}$ = 3, *t*Bu{CH_3}), 22.1 (s, CH_2).

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 145.1 (vbr, fwhm = 142 Hz).

HR ESI-MS (positive ion 4 kV): 532.3791, $[M + Na]^+$ (calcd 532.3796) *m*/*z*.

trans-**1b** (30% CH_2Cl_2 in hexane, R_F = 0.20).

Following the general procedure using *trans*-**5b** (620 mg, 1.22 mmol) and $[Rh(PPh_3)_3Cl]$ (56.5 mg, 61.1 μmol) in benzene (50 mL), the product was isolated as a white. Yield: 623 mg (95%).

^1H NMR (500 MHz, $CDCl_3$): δ 7.64 (t, $^3J_{HH}$ = 7.8, 1H, py), 6.81 (d, $^3J_{HH}$ = 7.9, 2H, py), 2.13–2.29 (m, 2H, CH_2), 1.85–1.96 (m, 2H, CH_2), 1.69–1.83 (m, 4H, CH_2), 1.38–1.47 (m, 4H, CH_2), 1.28 (d, $^3J_{PH}$ = 13.9, 18H, *t*Bu), 1.23–1.37 (m, 12H, CH_2), 0.11–0.99 (m, 6H, BH_3).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 158.2 (d, $^2J_{PC}$ = 6, py), 142.1 (s, py), 110.2 (d, $^3J_{PC}$ = 3, py), 32.9 (d, $^1J_{PC}$ = 36, *t*Bu{C}), 30.8 (d, $^2J_{PC}$ = 13, CH_2), 27.7 (s, CH_2), 27.52 (s, CH_2), 27.47 (s, CH_2), 26.9 (s, CH_2), 25.5 (d, $^1J_{PC}$ = 31, CH_2), 25.0 (d, $^2J_{PC}$ = 3, *t*Bu{CH_3}), 22.7 (s, CH_2).

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 144.1 (vbr, fwhm = 155 Hz).

HR ESI-MS (positive ion 4 kV): 532.3804, $[M + Na]^+$ (calcd 532.3795) *m*/*z*.

Anal. Calcd for $C_{27}H_{55}B_2NO_2P_2$ (509.31 g mol^{-1}): C, 63.67; H, 10.89; N, 2.75; Found: C, 63.66; H, 11.03; N, 2.74.

Preparation of PNP-14

A solution of *trans*-**1a** in Et_2NH (0.5 mL) was heated at 85 °C for 2 days within a J Young's valve NMR tube. Quantitative conversion was observed by ^1H and ^{31}P NMR spectroscopy. The volatiles were removed *in vacuo* to afford the product as a colourless oil, which was carried forward without further purification.

^1H NMR (500 MHz, C_6D_6): δ 7.08 (t, $^3J_{HH}$ = 7.7, 1H, py), 6.90 (d, $^3J_{HH}$ = 7.7, 2H, py), 3.04 (d, $^2J_{HH}$ = 13.0, 2H, pyC$\underline{H}_2$), 2.87 (dd, $^2J_{HH}$ = 13.0, $^2J_{PH}$ = 2.9, 2H, pyC$\underline{H}_2$), 1.50–1.57 (m, 2H, CH_2), 1.38–1.49 (m, 8H, CH_2), 1.27–1.38 (m, 18H, CH_2), 1.03 (d, $^3J_{PH}$ = 11, 18H, *t*Bu).

$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ 160.4 (d, $^2J_{PC}$ = 8, py), 136.0 (s, py), 120.5 (dd, $^3J_{PC}$ = 6, $^5J_{PC}$ = 2, py), 35.5 (d, $^1J_{PC}$ = 24, py$\underline{C}H_2$), 30.8 (d, $^1J_{PC}$ = 12, *t*Bu{C}), 28.5 (s, CH_2), 28.2 (s, CH_2), 28.1 (s, CH_2), 28.0 (s, CH_2), 27.6 (d, $^2J_{PC}$ = 14, *t*Bu{CH_3}), 27.3 (s, CH_2), 27.1 (s, CH_2), 24.4 (d, $^1J_{PC}$ = 20, CH_2).

$^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): δ 4.5 (s).

LR ESI-MS (positive ion, 4 kV): 532.5, $[M]^+$ (calcd 532.3) *m*/*z*.

Preparation of PONOP-14

A solution of *trans*-**1b** (11.7 mg, 23.0 μmol) in THF (3 mL) was treated with an equal volume of Et_2NH (3 mL) and the resulting solution stirred at 19 °C for 8 days. The volatiles were removed *in vacuo* to afford the product as a yellow oil in 65–84% purity, as determined by ^{31}P NMR spectroscopy, which was carried forward without further purification.

$^{31}P\{^1H\}$ NMR (162 MHz, THF : $HNEt_2$, selected data): δ 146.5 (s).

Preparation of [Rh(PNP-14)(biph)][BAr^F_4] (6a)

A suspension of PNP-14 (16.1 mg, 33.7 μmol) and [Rh(biph)(dtbpm)Cl] (20.0 mg, 33.6 μmol) in PhF (0.50 mL) was stirred at ambient temperature for 16 h. Na[BAr^F_4] (29.8 mg, 33.6 μmol) was added and the suspension stirred for a further 4 h before the volatiles were removed *in vacuo*. The resulting orange oil was washed with pentane (2 × 1 mL), dried *in vacuo* and extracted into CH_2Cl_2 (2 mL). The product was obtained as an orange crystalline solid by slow cooling of CH_2Cl_2 : hexane (1 : 20) solution to −30 °C. Yield: 42.6 mg (79%).

^1H NMR (500 MHz, CD_2Cl_2): δ 7.95 (t, $^3J_{HH}$ = 7.9, 1H, py), 7.70–7.76 (m, 8H, Ar^F), 7.59–7.68 (m, 4H, 2 × py + 2 × biph), 7.56 (br, 4H, Ar^F), 7.48 (d, $^3J_{HH}$ = 7.6, 1H, biph), 7.10–7.26 (m, 2H, biph), 6.98 (t, $^3J_{HH}$ = 7.3, 1H, biph), 6.50 (t, $^3J_{HH}$ = 7.6, 1H, biph), 5.63 (d, $^3J_{HH}$ = 8.2, 1H, biph), 3.85–4.04 (m, 2H, pyC$\underline{H}_2$), 3.51–3.76 (m, 2H, pyC$\underline{H}_2$), 2.66–2.78 (m, 1H, CH_2), 2.05–2.24 (m, 1H, CH_2), 1.74–1.83 (m, 1H, CH_2), 1.40–1.70 (m, 10H, CH_2), 1.18–1.39 (m, 7H, CH_2), 1.16 (d, $^3J_{PH}$ = 13.3, 9H, *t*Bu), 0.96–1.09 (m, 4H, CH_2), 0.66–0.87 (m, 3H, CH_2), 0.51 (d, $^3J_{PH}$ = 15, 9H, *t*Bu), 0.19–0.35 (m, 1H, CH_2).

$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ 162.5 (app t, J_{PC} = 5, py), 162.3 (q, $^1J_{CB}$ = 50, Ar^F), 162.1 (app t, J_{PC} = 3, py), 161.7 (obscured, biph), 152.3 (d app t, $^1J_{RhC}$ = 44, $^2J_{PC}$ = 7, biph), 151.2 (s, biph), 148.9 (s, biph), 140.5 (s, py), 135.4 (s, Ar^F), 133.9 (s, biph), 129.6 (s, biph), 129.4 (qq, $^2J_{FC}$ = 32, $^3J_{CB}$ = 3, Ar^F), 128.5 (s, biph), 126.7 (s, biph), 125.2 (q, $^1J_{FC}$ = 272, Ar^F), 125.1 (s, biph), 124.1 (s, biph), 123.5 (d, $^3J_{PC}$ = 8, py), 123.4 (d, $^3J_{PC}$ = 10, py), 122.4 (s, biph), 121.9 (s, biph), 118.0 (sept, $^3J_{FC}$ = 4, Ar^F), 40.1 (d, $^1J_{PC}$ = 23, py$\underline{C}H_2$), 38.7 (d, $^1J_{PC}$ = 19, py$\underline{C}H_2$), 34.4 (dd, $^1J_{PC}$ = 16, $^3J_{PC}$ = 5, *t*Bu{C}), 33.0 (ddd, $^1J_{PC}$ = 20, $^3J_{PC}$ = 5, $^2J_{RhC}$ = 2, *t*Bu{C}), 32.0 (d, $^2J_{PC}$ = 14, CH_2), 30.3 (s, CH_2), 29.7 (s, CH_2), 29.54 (s, CH_2), 29.51 (s, CH_2), 29.43 (d, $^2J_{PC}$ = 4, *t*Bu{CH_3}), 29.37 (s, CH_2), 29.3 (s, CH_2), 28.0 (s, CH_2), 27.3 (s, CH_2), 26.2 (d, $^1J_{PC}$ = 21, PCH_2), 25.7 (s, *t*Bu{CH_3}), 25.6

(obscured, CH_2), 24.9 (s, CH_2), 24.6 (s, CH_2), 21.0 (d app t, $^1J_{PC}$ = 16, J = 2, PCH_2).

$^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 43.1 (dd, $^2J_{PP}$ = 339, $^1J_{RhP}$ = 110, 1P), 38.4 (dd, $^2J_{PP}$ = 339, $^1J_{RhP}$ = 113, 1P).

HR ESI-MS (positive ion, 4 kV): 732.3329, $[M]^+$ (calcd 732.3329) *m*/*z*.

Anal. Calcd for $C_{73}H_{73}BF_{24}NP_2Rh$ (1596.02 g mol^{-1}): C, 54.94; H, 4.61; N, 0.88; Found: C, 54.89; H, 4.80; N, 0.86.

Preparation of [Rh(PONOP-14)(biph)][BAr$^F_4$] (6b)

A suspension of PONOP-14 (17.8 μmol, generated *in situ* as described above) and [Rh(biph)(dtbpm)Cl] (10.6 mg, 17.8 μmol) in PhF (0.5 mL) was stirred at ambient temperature for 16 h. Na[BAr$^F_4$] (15.8 mg, 17.8 μmol) was added and the suspension stirred for a further 4 h before the volatiles were removed *in vacuo*. The resulting orange oil was washed with pentane (2 × 1 mL), dried *in vacuo* and extracted into CH_2Cl_2 (2 mL). The product was recrystallised by slow diffusion of hexane into a CH_2Cl_2 solution (1 : 20). Yield: 19.6 mg (69%).

^1H NMR (500 MHz, CD_2Cl_2): δ 8.11 (t, $^3J_{HH}$ = 8.2, 1H, py), 7.70–7.76 (m, 8H, Ar^F), 7.65 (d, $^3J_{HH}$ = 7.3, 1H, biph), 7.56 (br, 4H, Ar^F), 7.54 (obscured, 1H, biph), 7.47 (d, $^3J_{HH}$ = 7.2, 1H, biph), 7.16–7.21 (m, 2H, biph), 7.15 (d, $^3J_{HH}$ = 8.2, 1H, py), 7.10 (d, $^3J_{HH}$ = 8.2, 1H, py), 7.06 (t, $^3J_{HH}$ = 7.4, 1H, biph), 6.56 (t, $^3J_{HH}$ = 7.7, 1H, biph), 5.32 (d, $^3J_{HH}$ = 8.8, 1H, biph), 2.64–2.86 (m, 2H, CH_2), 1.85–2.08 (m, 3H, CH_2), 1.60–1.78 (m, 4H, CH_2), 1.29 (d, $^3J_{PH}$ = 14.6, 9H, *t*Bu), 1.00–1.58 (m, 13H, CH_2), 0.84–0.96 (m, 1H, CH_2), 0.65–0.83 (m, 3H, CH_2), 0.62 (d, $^3J_{PH}$ = 17.4, 9H, *t*Bu), 0.37–0.48 (m, 2H, CH_2).

$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ 162.7 (dd, $^2J_{PC}$ = 6, $^4J_{PC}$ = 2, py), 162.3 (q, $^1J_{CB}$ = 50, Ar^F), 161.5 (dd, $^2J_{PC}$ = 6, $^4J_{PC}$ = 2, py), 159.1 (ddd, $^1J_{RhC}$ = 32, $^2J_{PC}$ = 11, $^2J_{PC}$ = 5, biph), 151.9 (ddd, $^1J_{RhC}$ = 43, $^2J_{PC}$ = 9, $^2J_{PC}$ = 7, biph), 151.2 (s, biph), 149.1 (br, biph), 147.2 (s, py), 135.4 (s, Ar^F), 133.9 (s, biph), 129.4 (qq, $^2J_{FC}$ = 32, $^3J_{CB}$ = 3, Ar^F), 129.35 (s, biph), 128.3 (s, biph), 127.6 (biph), 126.2 (s, biph), 125.2 (q, $^1J_{FC}$ = 272, Ar^F), 125.0 (s, biph), 123.3 (s, biph), 122.5 (s, biph), 118.0 (sept, $^3J_{FC}$ = 4, Ar^F), 106.1 (d, $^3J_{PC}$ = 4, py), 105.7 (d, $^3J_{PC}$ = 5, py), 41.6 (dd, $^1J_{PC}$ = 9, $^2J_{RhC}$ = 7, *t*Bu{C}), 38.1 (ddd, $^1J_{PC}$ = 17.8, $^3J_{PC}$ = 7, $^2J_{PC}$ = 3, *t*Bu{C}), 35.8 (d, J_{PC} = 11, CH_2), 31.3 (s, CH_2), 30.9 (dd, $^1J_{PC}$ = 15, $^3J_{PC}$ = 3, PCH_2), 30.7 (s, CH_2), 30.5 (s, CH_2), 30.3 (s, CH_2), 30.0 (s, CH_2), 29.2 (s, CH_2), 28.6 (s, CH_2), 28.2 (s, CH_2), 28.0 (d, J_{PC} = 7, CH_2), 27.5 (d, $^2J_{PC}$ = 5, *t*Bu{CH_3}), 25.0 (d app t, $^1J_{PC}$ = 14, J = 3, PCH_2), 24.4 (d, $^2J_{PC}$ = 4, *t*Bu{CH_3}), 24.2 (d, J_{PC} = 4, CH_2), 23.7 (s, CH_2).

$^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 191.1 (dd, $^2J_{PP}$ = 373, $^1J_{RhP}$ = 110, 1P), 182.9 (dd, $^2J_{PP}$ = 373, $^1J_{RhP}$ = 121, 1P).

HR ESI-MS (positive ion, 4 kV): 736.2909, $[M]^+$ (calcd 736.2914) *m*/*z*.

Anal. Calcd for $C_{71}H_{69}BF_{24}NO_2P_2Rh$ (1599.96 g mol^{-1}): C, 53.30; H, 4.35; N, 0.88; Found: C, 53.12; H, 4.48; N, 0.86.

General procedure for *in situ* synthesis of dihydrogen complexes 7

A solution of **6** in DFB (0.5 mL) was freeze–pump–thaw degassed and placed under dihydrogen (1 atm) within a J Young's valve NMR tube and heated at 85 °C to afford the corresponding dihydrogen complex, which was characterised *in situ* under dihydrogen, and biphenyl.

[Rh(PNP-14)(H$_2$)][BAr$^F_4$] (7a). Following the general procedure using **6a** (16.0 mg, 10.0 μmol) and heating for 2 days at 85 °C gave quantitative conversion to **7a** by ^1H and ^{31}P NMR spectroscopy.

^1H NMR (500 MHz, DFB, H_2): δ 8.09–8.15 (m, 8H, Ar^F), 7.54 (t, $^3J_{HH}$ = 7.8, 1H, py), 7.49 (br, 4H, Ar^F), 7.22 (obscured 2H, py), 3.46 (dvt, $^2J_{HH}$ = 17.7, J_{PH} = 4, 2H, pyC$\underline{H}_2$), 3.23 (dvt, $^2J_{HH}$ = 17.7, J_{PH} = 4, 2H, pyC$\underline{H}_2$), 1.51–1.71 (m, 10H, CH_2), 1.14–1.41 (m, 18H, CH_2), 0.94 (vt, J_{PH} = 8, 18H, *t*Bu), −10.43 (vbr, fwhm ~800 Hz, 2H, RhH).

$^{13}C\{^1H\}$ NMR (126 MHz, DFB, H_2): δ 164.1 (vt, J_{PC} = 5, py), 162.3 (q, $^1J_{CB}$ = 50, Ar^F), 140.1 (s, py), 135.4 (s, Ar^F), 129.6 (qq, $^2J_{FC}$ = 32, $^3J_{CB}$ = 3, Ar^F), 125.2 (q, $^1J_{FC}$ = 272, Ar^F), 121.1 (vt, J_{PC} = 5, py), 117.6 (sept, $^3J_{FC}$ = 4, Ar^F), 37.9 (vt, J_{PC} = 9, py$\underline{C}H_2$), 32.0 (vt, J_{PC} = 12, *t*Bu{C}), 28.7 (vt, J_{PC} = 4, CH_2), 28.5 (s, CH_2), 28.4 (s, CH_2), 28.0 (s, CH_2), 27.0 (s, CH_2), 26.4 (vt, J_{PC} = 3, *t*Bu{CH_3}), 24.7 (vt, J_{PC} = 3, CH_2), 20.8 (vtd, J_{PC} = 12, $^2J_{RhC}$ = 2, PCH_2).

$^{31}P\{^1H\}$ NMR (162 MHz, DFB, H_2): δ 65.9 (d, $^1J_{RhP}$ = 120).

^1H NMR (600 MHz, DFB, selected data under argon): δ −10.76 (vbr, fwhm = 60 Hz, T_1 = 45 ± 11 ms, 2H, RhH).

[Rh(PONOP-14)(H$_2$)][BAr$^F_4$] (7b). Following the general procedure using **6b** (12.0 mg, 7.50 μmol) and heating for 5 days at 85 °C gave quantitative conversion to **7b** by ^1H and ^{31}P NMR spectroscopy.

^1H NMR (500 MHz, DFB, H_2): δ 8.09–8.15 (m, 8H, Ar^F), 7.63 (t, $^3J_{HH}$ = 8.2, 1H, py), 7.49 (br, 4H, Ar^F), 6.63 (obscured 2H, py), 2.03–2.18 (m, 4H, CH_2), 1.53–1.78 (m, 6H, CH_2), 1.15–1.41 (m, 18H, CH_2), 1.11 (vt, J_{PH} = 8, 18H, *t*Bu), −8.65 (vbr, fwhm = 100 Hz, 2H, RhH).

$^{13}C\{^1H\}$ NMR (126 MHz, DFB, H_2): δ 163.5 (br, py), 162.3 (q, $^1J_{CB}$ = 50, Ar^F), 145.9 (s, py), 135.4 (s, Ar^F), 129.6 (qq, $^2J_{FC}$ = 32, $^3J_{CB}$ = 3, Ar^F), 125.2 (q, $^1J_{FC}$ = 272, Ar^F), 117.6 (sept, $^3J_{FC}$ = 4, Ar^F), 103.3 (vt, J_{PC} = 3, py), 37.6 (vt, J_{PC} = 12, *t*Bu{C}), 29.0 (br, CH_2), 28.5 (s, CH_2), 28.1 (s, CH_2), 28.0 (s, CH_2), 27.5 (vt, J_{PC} = 9, PCH_2), 27.3 (s, CH_2), 24.7 (vt, J_{PC} = 4, *t*Bu{CH_3}), 23.9 (vt, J_{PC} = 3, CH_2).

$^{31}P\{^1H\}$ NMR (162 MHz, DFB, H_2): δ 211.5 (d, $^1J_{RhP}$ = 127).

^1H NMR (600 MHz, DFB, selected data under argon): δ −8.51 (vbr d, fwhm = 60 Hz, $^1J_{RhH}$ = 21, T_1 = 48 ± 6 ms, 2H, RhH).

General procedure for *in situ* synthesis of ethylene complexes 8

A solution of **7** in DFB (0.5 mL) was freeze–pump–thaw degassed and placed under ethylene (1 atm) within a J Young's valve NMR tube to afford the corresponding ethylene complex, which was characterised *in situ* under ethylene. All spectra contained ethane ($\delta_{^1H}$ 0.70).

[Rh(PNP-14)(C$_2$H$_4$)][BAr$^F_4$] (8a). Following the general procedure using **7a** (10 μmol, generated *in situ* as described above) gave quantitative conversion to **8a** by ^1H and ^{31}P NMR spectroscopy within 5 minutes at room temperature.

^1H NMR (500 MHz, DFB, C_2H_4): δ 8.09–8.15 (m, 8H, Ar^F), 7.51 (t, $^3J_{HH}$ = 8.0, 1H, py), 7.49 (br, 4H, Ar^F), 7.15 (obscured, 2H, py), 3.70 (br, 2H, C_2H_4), 3.52 (br, 2H, C_2H_4), 3.31 (dvt, $^2J_{HH}$ = 17.3, J_{PH} = 4, 2H, pyC$\underline{H}_2$), 3.22 (dvt, $^2J_{HH}$ = 17.4, J_{PH} = 4,

2H, pyC$\underline{H}_2$), 1.72–1.93 (m, 4H, CH_2), 1.55–1.67 (m, 2H, CH_2), 1.39–1.50 (m, 2H, CH_2), 1.07–1.37 (m, 20H, CH_2), 0.83 (vt, J_{PH} = 7, 18H, *t*Bu).

$^{13}C\{^1H\}$ NMR (126 MHz, DFB, C_2H_4): δ 162.9 (vt, J_{PH} = 5, py), 162.3 (q, $^1J_{CB}$ = 50, Ar^F), 140.1 (s, py), 135.1 (s, Ar^F), 129.6 (qq, $^2J_{FC}$ = 32, $^3J_{CB}$ = 3, Ar^F), 125.2 (q, $^1J_{FC}$ = 272, Ar^F), 120.7 (vt, J_{PC} = 5, py), 117.6 (sept, $^3J_{FC}$ = 4, Ar^F), 55.0 (d, $^1J_{RhC}$ = 12, C_2H_4), 37.5 (vt, J_{PC} = 8, py$\underline{C}H_2$), 32.8 (vt, J_{PC} = 10, *t*Bu{C}), 29.5 (vt, J_{PC} = 4, CH_2), 29.3 (s, CH_2), 28.7 (s, CH_2), 28.2 (s, CH_2), 27.9 (s, CH_2), 26.6 (vt, J_{PC} = 3, *t*Bu{CH_3}), 24.1 (s, CH_2), 21.9 (vt, J_{PC} = 10, PCH_2).

$^{31}P\{^1H\}$ NMR (162 MHz, DFB, C_2H_4): δ 53.0 (d, $^1J_{RhP}$ = 125).

[Rh(PONOP-14)(C_2H_4)][BAr^F_4] (8b). Following the general procedure using **7b** (7.5 μmol, generated *in situ* as described above) gave quantitative conversion to **8a** by ^1H and ^{31}P NMR spectroscopy within 5 minutes at room temperature.

^1H NMR (500 MHz, DFB, C_2H_4): δ 8.09–8.15 (m, 8H, Ar^F), 7.61 (t, $^3J_{HH}$ = 8.1, 1H, py), 7.49 (br, 4H, Ar^F), 6.59 (obscured 2H, py), 3.95 (br, 2H, C_2H_4), 3.70 (br, 2H, C_2H_4), 2.19–2.29 (m, 2H, CH_2), 2.05–2.16 (m, 2H, CH_2), 1.74–1.86 (m, 2H, CH_2), 1.46–1.60 (m, 4H, CH_2), 1.02–1.45 (m, 18H, CH_2), 0.96 (vt, J_{PH} = 8, 18H, *t*Bu).

$^{13}C\{^1H\}$ NMR (126 MHz, DFB, C_2H_4): δ 162.8 (vt, J_{PC} = 3, py), 162.3 (q, $^1J_{CB}$ = 50, Ar^F), 145.3 (s, py), 135.1 (s, Ar^F), 129.6 (qq, $^2J_{FC}$ = 32, $^3J_{CB}$ = 3, Ar^F), 125.2 (q, $^1J_{FC}$ = 272, Ar^F), 117.6 (sept, $^3J_{FC}$ = 4, Ar^F), 103.2 (vt, J_{PC} = 3, py), 59.5 (d, $^1J_{RhC}$ = 11, C_2H_4), 39.1 (vt, J_{PC} = 10, *t*Bu{C}), 30.0 (vt, J_{PC} = 2, CH_2), 28.7 (s, CH_2), 28.6 (s, CH_2), 28.5 (s, CH_2), 28.4 (s, CH_2), 27.3 (vtd, J_{PC} = 8, $^2J_{RhC}$ = 2, PCH_2), 24.9 (vt, J_{PC} = 3, *t*Bu{CH_3}), 23.7 (s, CH_2).

$^{31}P\{^1H\}$ NMR (162 MHz, DFB, C_2H_4): δ 199.1 (d, $^1J_{RhP}$ = 129).

General procedure for the preparation of carbonyl complexes 9

A solution of **8** in DFB (0.5 mL) was freeze–pump–thaw degassed and placed under carbon monoxide (1 atm) within a J Young's valve NMR tube, resulting in an immediate colour change. The volatiles were removed *in vacuo*, and the resulting yellow solid washed and dried *in vacuo*.

Preparation of [Rh(PNP-14)(CO)][BAr^F_4] (9a). Following the general procedure using **8a** (10 μmol, generated *in situ* as described above), washing with hexane afforded the pure product as a yellow solid. Yield: 14.1 mg (96%).

^1H NMR (500 MHz, CD_2Cl_2): δ 7.79 (t, $^3J_{HH}$ = 7.8, 1H, py), 7.70–7.76 (m, 8H, Ar^F), 7.56 (br, 4H, Ar^F), 7.42 (d, $^3J_{HH}$ = 7.9, 2H, py), 3.70 (dvt, $^2J_{HH}$ = 17.5, J_{PH} = 4, 2H, pyC$\underline{H}_2$), 3.56 (dvt, $^2J_{HH}$ = 17.5, J_{PH} = 4, 2H, pyC$\underline{H}_2$), 2.02–2.09 (m, 4H, CH_2), 1.78–1.98 (m, 4H, CH_2), 1.63–1.75 (m, 2H, CH_2), 1.49–1.63 (m, 2H, CH_2), 1.21–1.49 (m, 16H, CH_2), 1.13 (vt, J_{PH} = 8, 18H, *t*Bu).

$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ 194.7 (dt, $^1J_{RhC}$ = 70, $^2J_{PC}$ = 13, CO), 163.8 (vtd, J_{PC} = 5, $^2J_{RhC}$ = 1, py), 162.3 (q, $^1J_{CB}$ = 50, Ar^F), 141.6 (s, py), 135.4 (s, Ar^F), 129.4 (qq, $^2J_{FC}$ = 32, $^3J_{CB}$ = 3, Ar^F), 125.2 (q, $^1J_{FC}$ = 272, Ar^F), 122.1 (vt, J_{PC} = 5, py), 118.0 (sept, $^3J_{FC}$ = 4, Ar^F), 38.7 (vt, J_{PC} = 9, py$\underline{C}H_2$), 33.9 (vt, J_{PC} = 12, *t*Bu{C}), 30.3 (vt, J_{PC} = 4, CH_2), 29.3 (s, CH_2), 28.94 (s, CH_2), 28.88 (s, CH_2) 28.4 (s, CH_2), 27.8 (vt, J_{PC} = 3, *t*Bu{CH_3}), 26.2 (s, CH_2), 23.2 (vtd, J_{PC} = 12, $^2J_{RhC}$ = 3, PCH_2).

$^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 67.5 (d, $^1J_{RhP}$ = 122).

IR (CH_2Cl_2): ν(CO) 1997 cm^{-1}.

HR ESI-MS (positive ion, 4 kV): 608.2653, $[M]^+$ (calcd 608.2652) *m*/*z*.

Anal. Calcd for $C_{62}H_{65}BF_{24}NOP_2Rh$ (1471.83 g mol^{-1}): C, 50.60; H, 4.45; N, 0.95 Found: C, 50.53; H, 4.47; N, 1.08.

[Rh(PONOP-14)(CO)][BAr^F_4] (9b). Following the general procedure using **8b** (7.5 μmol, generated *in situ* as described above), washing with hexane afforded the pure product as a yellow solid. Crystals suitable for X-ray crystallography were grown by the slow diffusion of $SiMe_4$ into CH_2Cl_2 at −30 °C. Yield: 8.0 mg (72%).

^1H NMR (500 MHz, CD_2Cl_2): δ 7.91 (t, $^3J_{HH}$ = 8.2, 1H, py), 7.70–7.76 (m, 8H, Ar^F), 7.56 (br, 4H, Ar^F), 6.86 (d, $^3J_{HH}$ = 8.2, 2H, py), 2.40–2.60 (m, 4H, CH_2), 1.76–1.98 (m, 6H, CH_2), 1.52–1.65 (m, 3H, CH_2), 1.11–1.48 (m, 15H, CH_2), 1.29 (vt, J_{PH} = 8, 18H, *t*Bu).

$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ 193.2 (dt, $^1J_{RhC}$ = 71, $^2J_{PC}$ = 13, CO), 163.1 (vt, J_{PC} = 3, py), 162.3 (q, $^1J_{CB}$ = 50, Ar^F), 147.7 (s, py), 135.4 (s, Ar^F), 129.5 (qq, $^2J_{FC}$ = 32, $^3J_{CB}$ = 3, Ar^F), 125.2 (q, $^1J_{FC}$ = 272, Ar^F), 118.0 (sept, $^3J_{FC}$ = 4, Ar^F), 104.5 (vt, J_{PC} = 3, py), 39.9 (vtd, J_{PC} = 11, $^2J_{RhC}$ = 2, *t*Bu{C}), 30.9 (vt, J_{PC} = 2, CH_2), 29.5 (vtd, J_{PC} = 9, $^2J_{RhC}$ = 3, PCH_2), 29.3 (s, CH_2), 29.1 (s, 2 × CH_2), 28.8 (s, CH_2), 26.1 (vt, J_{PC} = 4, *t*Bu{CH_3}), 25.1 (vt, J_{PC} = 2, CH_2).

$^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 210.8 (d, $^1J_{RhP}$ = 128).

IR (CH_2Cl_2): ν(CO) 2020 cm^{-1}.

HR ESI-MS (positive ion, 4 kV): 612.2228, $[M]^+$ (calcd 612.2237) *m*/*z*.

Anal. Calcd for $C_{60}H_{61}BF_{24}NO_3P_2Rh$ (1475.78 g mol^{-1}): C, 48.83; H, 4.17; N, 0.95 Found: C, 48.91; H, 4.26; N, 1.02.

Conflicts of interest

There are no conflicts to declare.

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