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Synthesis and rhodium complexes of macrocyclic PNP and PONOP pincer ligands
Synthesis and group 9 complexes of macrocyclic PCP and POCOP pincer ligands
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)][BArF₄] and [Rh(PONOP-14)(biph)][BArF₄] (ArF = 3,5-(CF₃)₂C₆H₃). 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(sp³)–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-ᵗBu and PONOP-ᵗBu (Chart 1).⁵,⁶ Motivated by the potential to exploit additional reaction control through 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-14·2BH₃ (trans-1a) and PONOP-14·2BH₃ (trans-1b) were prepared from commercially available tert-butyldichlorophosphate using the seven-step synthesis outlined in Scheme 1. Amination of the starting material,¹⁰ enabled selective mono-alkylation (2, δ₃¹P 73.3) and following treatment with HCl chloroterti-butylocten-7-yl-phosphine 3 (δ₃¹P 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 (δ₃¹P 33.7) and 4b (δ₃¹P 144.7) as inseparable mixtures of diastereomers in 55% and 72% yield, respectively, after borane protec-
ation 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, δ₃¹P 33.8/144.8; trans-5a/b, δ₃¹P 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, δ₃¹P 33.3/145.1; trans-1a/b, δ₃¹P 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. Gratifyingly, treatment of trans-1a with neat Et₂NH at 85 °C resulted in complete conversion to the free-base PNP-14 (δ₃¹P 4.5) within 36 h, which was subsequently isolated in quantitative yield on removal of volatiles. Reactions between trans-1b and Et₂NH 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. Evaluation of a range of other deprotection methods 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 (δ₃¹P 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 : Et₂NH at 19 °C.

**Rhodium complexes**

As convenient {Rh(pincer)}⁺ synthons, the synthesis of five coordinate derivatives [Rh(pincer)(biph)][BF₄] (pincer = PNP-14, 6a; PONOP-14, 6b; biph = 2,2'-biphenyl; ArF = 3,5-(CF₃)₂C₆H₃) were targeted (Scheme 2). Exploiting a rhodium(III) precursor first described by Jones, and informed by previous work in our laboratories, Rhodium complexes 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).
PNP-14 or in situ generated samples of PONOP-14 in the weakly coordinating solvent fluorobenzene and subsequent addition of Na[BF$_4$] as a halide abstracting agent. Complexes 6a and 6b are characterised in solution by pairs of $^{31}$P resonances centred at $\delta$ 43.1 ($^{31}$P$_{RbP} = 110$ Hz)/38.4 ($^{31}$P$_{RbP} = 113$ Hz) and $\delta$ 191.1 ($^{31}$P$_{RbP} = 110$ Hz)/182.9 ($^{31}$P$_{RbP} = 121$ Hz), which display diagnostic trans-phosphine $^{3}$P coupling of 339 and 372 Hz, respectively, and indicate adoption of C$_{3v}$ symmetry. Whilst the acyclic congeners [Rh(pincer)$(biph)_{2}$] (pincer = PNP-bBu, 6a; PONOP-bBu, 6b) highlight the propensity for dynamic pseudorotation of the biph ligand on the NMR timescale, 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 butressing with the biph ligand, and, with formulation of 7a/b as C$_{2}$ symmetric rhodium(1) dihydrogen complexes, with broad 2H resonances at $\delta$ –7.76/11.26 ± 11/48 ± 6 ms) at 298 K (600 MHz, Ar) the most diagnostic. Subsequent reaction in situ with ethylene (1 atm) confers the corresponding C$_{2}$ symmetric π-complexes 8a/8b [δ$_{Iv}$ 53.0 ($^{31}$P$_{RbP} = 125$ Hz)/δ$_{Iv}$, 199.1 ($^{31}$P$_{RbP} = 129$ 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 $\delta$ 3.70/3.52 and 3.95/3.70, and $^{13}$C resonances at $\delta$ 55.0 ($^{31}$P$_{RbC} = 12$ Hz) and 59.5 ($^{31}$P$_{RbC} = 11$ Hz), which display appreciable coupling to $^{103}$Rh, for 8a and 8b respectively. Finally, C$_{2}$ symmetric carbonyl compounds 9a/b [δ$_{Iv}$ 67.5 ($^{31}$P$_{RbP} = 122$ Hz)/δ$_{Iv}$, 210.8 ($^{31}$P$_{RbP} = 128$ 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

![Figure 2](image-url)

**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, 2.334(4); Rh1–P3, 2.280(4); Rh1–N101, 2.142(1); P2–Rh1–P3, 163.85(2); N101–M1–C15, 172.93(6); Rh1–H–C129, 1.84(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, 2.093(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); Rh1–C14, 1.846(6); C14–O15, 1.147(8); Rh1–P12, 2.288(2); Rh11–P13, 2.250(2); Rh11–N201, 2.034(4); P12–Rh11–P13, 161.167(7); N201–Rh11–C14, 172.0(3).
Table 1 Carboxyl stretching frequencies (CH$_2$Cl$_2$)

| Pincer complex | $\nu$(CO)/cm$^{-1}$ |
|----------------|---------------------|
| [Rh(PNP-14)(CO)][BArF$_4^-$] | 9a 1997 |
| [Rh(PNP-Bu)(CO)][BArF$_4^-$] | 9a 1990 |
| [Rh(PNP-Pr)(CO)][BArF$_4^-$] | 9a 1998 |
| [Rh(PONOP-14)(CO)][BArF$_4^-$] | 9b 2020 |
| [Rh(PONOP-Bu)(CO)][BArF$_4^-$] | 9b 15 2016 |

X-ray diffraction (Fig. 2). The $\nu$(CO) bands of rhodium(i) carboxyl derivatives are diagnostic reporter groups for the donor properties of pincer ligands. Comparison of the carboxyl bands of 9a/b with those of acyclic congeners 9a/b, recorded under the same conditions, suggests PNP-14 and PONOP-14 are marginally weaker net donors than PNP-Bu and PONOP-Bu, respectively (Table 1). By reference to IR data reported for [Rh(PNP-Pr)(CO)][BArF$_4^-$] (9a$^\dagger$); PNP-Pr = 2,6-(iPr,PhCH$_2$)$_2$C$_5$H$_3$N and trends established for monodentate phosphines, these minor differences are in line with changes in the phospine/phosphinite substituents alone.

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-dihydropyridine (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)][BArF$_4^-$] and [Rh(PONOP-14)(biph)][BArF$_4^-$] conveniently accessed by substitution reactions of [Rh(biph)(dbtbpm)Cl] (dbtbpm = 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 $\nu$(CO) bands of rhodium(i) carbynyl adducts, determined by IR spectroscopy in CH$_2$Cl$_2$, PNP-14 and PONOP-14 can be considered to be marginally weaker net donors than their respective homoleptic tert-butyl substituted congeners PNP-tBu and PONOP-tBu, 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$_2$O$_3$, distilled from calcium hydride and dried twice over 3 Å molecular sieves. CD$_2$Cl$_2$ was freeze-pump-thaw degassed and dried over 3 Å molecular sieves. Cs$_2$D$_8$ 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$_4$NH 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. nBuLi was titrated before use. TMEDA was distilled from sodium/benzophenone and stored over 3 Å molecular sieves. Diethylamino-tert-butyl-chlorophosphine (yield = 98%),$^{10}$ BrMgC$_6$H$_{15},^{25}$ Wilkinson’s catalyst,$^{26}$ Na[BArF$_4$]$^{27}$ and [Rh(biph)(dbtbpm)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 were recorded 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 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$_2$Cl$_2$. Microanalyses were performed at the London Metropolitan University by Stephen Boyer.

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

Preparation of diethylamino-tert-butyl-octen-7-yl-phosphine (3.19 g, 16.3 mmol) in THF (30 mL) was cooled to −78 °C and a solution of BrMgC$_6$H$_{15}$ (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, CD$_2$D$_8$): δ 5.80 (ddt, $^3$J$_{HH}$ = 16.9, $^3$J$_{HH}$ = 10.2, $^3$J$_{HH}$ = 6.7, 1H, CH=CH$_2$), 5.02–5.08 (m, 1H, CH=CH$_2$), 4.98–5.01 (m, 1H, CH=CH$_2$), 2.90–2.97 (m, 4H, NCH$_2$), 1.98–2.04 (m, 2H, CH$_2$CH=CH$_2$), 1.72–1.78 (m, 1H, CH$_2$), 1.13–1.66 (m, 9H, CH$_3$), 1.06 (d, 9H, $^3$J$_{PH}$ = 11.8, tBu), 1.00 (t, 6H, $^3$J$_{HH}$ = 7.1, NCH$_2$CH$_3$).

$^{13}$C($^1$H) NMR (151 MHz, CD$_2$D$_8$): δ 139.2 (s, CH$_2$), 114.6 (s, CH$_2$), 44.5 (br, NCH$_3$), 34.2 (s, CH$_2$CH=CH$_2$), 32.5 (d, $^1$J$_{FC}$ = 20, tBu(C)), 31.7 (d, $^1$J$_{FC}$ = 12, CH$_3$), 29.5 (s, CH$_2$), 29.4
Preparation of chloro-t-butyl-octen-7-yl-phosphine. HCl in diethyl ether (151 mL) 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 31P NMR spectroscopy indicated the partial formation of 3-HCl (δ = 46.9), which was subsequently deprotonated by addition of a stoichiometric amount of LiHMDS (0.479 g, 2.86 mmol) suspended in hexane (20 mL) at 0 °C. The LiHMDS suspension was treated dropwise with a solution of BH3·SMe2 (0.12 mL, 1.27 mmol) at −78 °C and treated with a solution of HCl (0.890 g, 6.01 mmol) and LiHMDS (3.03 g, 22.7 mmol). The reaction was warmed to room temperature and stirred for 2 days. The suspension was allowed to warm to ambient temperature, filtered to remove the LiHMDS, washed with degassed water, dried over MgSO4 and the solvent removed in vacuo. The resulting suspension was stirred for 1 h before the precipitate to settle out, filtered and the product obtained on removal of the volatiles in vacuo, which was carried forward without further purification. Yield: 17.6 g (99%).

1H NMR (500 MHz, CDCl3): δ 5.77 (ddt, 3JHH = 16.8, 3JHH = 10.0, 3JHH = 6.5, 1H, CH=CH2), 5.01–5.06 (m, 1H, CH = CH2), 4.97–5.01 (m, 1H, CH2 = CH2), 1.92–2.00 (m, 2H, CH2CH=CH2), 1.15–1.83 (m, 10H, CH2), 0.99 (d, 3JHH = 12.8, 9H, tBu).

13C{1H} NMR (126 MHz, CDCl3): δ 139.1 (s, CH = CH2), 114.6 (s, CH = CH2), 34.1 (s, CH2CH=CH2), 32.4 (d, 3JPC = 29, tBu{C}), 31.1 (d, JPC = 11, CH2), 30.7 (d, 3JPC = 36, CH2), 29.2 (s, 2 × CH2), 25.9 (d, JPC = 15, CH2), 25.5 (d, 3JPC = 17, tBu{CH3}).

31P{1H} NMR (162 MHz, CDCl3): 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 nBuLi (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 obtained as a colourless oil after repeated purification by column chromatography as a mixture of diastereomers (10% EtOAc in hexane; Rf = 0.22). Yield: 2.31 g (72%).

1H NMR (500 MHz, CDCl3): δ 7.65 (t, 3JHH = 7.9, 1H, py), 6.81 (d, 3JHH = 7.9, 1.0H, py), 6.80 (d, 3JHH = 7.9, 1.0H, py), 5.80 (ddt, 3JHH = 16.9, 3JHH = 10.3, 3JHH = 6.7, 2H, CH = CH2), 4.96–5.02 (m, 2H, CH = CH2), 4.93 (d, 3JHH = 10.1, 2.1H, CH2), 2.80–2.24 (m, 2H, CH2), 2.04 (app q, 4JPH = 7, 4H, CH2CH = CH2), 1.79–1.92 (m, 2H, CH2), 1.67–1.78 (m, 4H, CH2), 1.33–1.47 (m, 12H, CH2), 1.29 (d, 3JHH = 14.1, 9.0H, tBu), 1.29 (d, 3JHH = 14.2, 9.0H, tBu), 0.80–0.92 (m, 6H, BHM). Some peaks duplicated because of diastereomers.

13C{1H} NMR (126 MHz, CDCl3): δ 158.1 (app t, 3JPC = 7, py), 142.09 (s, py), 142.05 (s, py), 139.07 (s, CH = CH2), 139.06 (s, CH = CH2), 131.0 (s, CH = CH2), 111.0 (d, 3JPC = 3, py), 110.8 (d, 3JPC = 3, py), 33.84 (s, CH2CH = CH2), 33.83 (s, CH2CH = CH2), 32.84 (d, 3JPC = 36, tBu{C}), 32.78 (d, 3JPC = 36, tBu{C}), 31.4 (s, CH3), 31.3 (s, CH3), 28.90 (s, CH3), 28.89 (s, CH3), 28.80 (s, CH3), 28.78 (s, CH3), 25.5 (d, 3JPC = 31, CH3), 25.4 (d, 3JPC = 31, CH3), 24.94 (d, 3JPC = 3, tBu{CH3}), 24.92 (d, 3JPC = 3, tBu{CH3}), 23.01 (s, CH3), 23.00 (s, CH3). Some peaks duplicated because of diastereomers.

31P{1H} NMR (162 MHz, CDCl3): δ 144.7 (vbr, fwhm = 140 Hz).

HR ESI-MS (positive ion 4 kV): 554.3466, [M + Na]+ (calcd 554.3468) m/z.
Preparation of 5a. A solution of 4a (3.30 g, 6.21 mmol) in CH2Cl2 (1.2 mmol L⁻¹, 5 L) was treated with 15 mol% [Ru(PCy3)3Cl2(CHA)][PF6] (0.577 g, 0.94 mmol) in 5 mol% portions in CH2Cl2 (5 mL) over 3 days with daily sparging with N2 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 (Rf = 0.22). Yield: 553 mg (18%).

 1H NMR (500 MHz, CDCl3): δ 7.75 (t, 3JHH = 7.7, 1H, py), 7.23 (d, 3JHH = 7.8, 2H, py), 5.27−5.41 (m, 2H, CH=CH=CH), 3.07−3.21 (m, 4H, pyCH2), 1.94−2.09 (m, 4H, CH2CH=CH=CH), 1.80−1.92 (m, 2H, CH2), 1.47−1.67 (m, 4H, CH2), 1.23−1.45 (m, 14H, CH2), 1.12 (d, 3JHH = 13.3, 18H, tBu), 0.02−0.82 (m, 6H, BH3).

 cis-5a (Rf = 0.22). Yield: 840 mg (27%).

 1H NMR (500 MHz, CDCl3): δ 7.54 (t, 3JHH = 7.7, 1H, py), 7.17 (d, 3JHH = 7.8, 2H, py), 5.23−5.41 (m, 2H, CH=CH=CH), 3.07−3.20 (m, 4H, pyCH2), 1.99−2.07 (m, 4H, CH2CH=CH=CH), 1.78−1.92 (m, 2H, CH2), 1.54−1.71 (m, 4H, CH2), 1.28−1.51 (m, 14H, CH2), 1.16 (d, 3JHH = 13.2, 18H, tBu), −0.15−0.73 (m, 6H, BH3).

 13C{1H} NMR (126 MHz, CDCl3): δ 154.5 (dd, 3JPC = 4, 3JPC = 2, py), 136.9 (t, 3JPC = 1, py), 131.1 (s, CH=CH=CH), 123.3 (app t, 3JPC = 3, py), 32.1 (s, CH2CH=CH=CH), 31.2 (s, CH2), 31.1 (d, 3JPC = 12, pyCH2), 28.9 (d, 3JPC = 31, tBu[C]), 28.7 (s, CH2), 27.5 (s, CH2), 25.8 (d, 3JPC = 2, tBu[CH2]), 23.5 (s, CH2), 19.3 (d, 3JPC = 30, CH2).

 13P{1H} NMR (162 MHz, CDCl3): δ 6.38 (vbr, fwhm = 150 Hz).

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

 trans-5a (Rf = 0.22). Yield: 540 mg (34%).

 1H NMR (500 MHz, CDCl3): δ 7.63 (t, 3JHH = 7.8, 1H, py), 6.76 (d, 3JHH = 7.9, 2H, py), 5.29−5.33 (m, 2H, CH=CH=CH), 2.16−2.33 (m, 2H, CH2), 1.96−2.09 (m, 4H, CH2CH=CH=CH), 1.83−1.92 (m, 2H, CH2), 1.32−1.46 (m, 4H, CH2), 1.32−1.46 (m, 12H, CH2), 1.28 (d, 3JHH = 14.0, 18H, tBu), 0.11−0.85 (m, 6H, BH3).

 cis-5a (20% EtOAc in hexane, Rf = 0.20).

 Following the general procedure using cis-5a (80.0 mg, 0.159 mmol) an[d [R(PPh3)3]Cl (7.4 mg, 8.0 μmol) in benzene (5 mL), the product was isolated as a white solid. Yield: 73.8 mg (92%).

 1H NMR (600 MHz, CDCl3): δ 7.55 (t, 3JHH = 7.7, 1H, py), 7.32 (d, 3JHH = 7.8, 2H, py), 3.16 (app t, 3JPC = 12, 4H, pyCH2), 1.71−1.82 (m, 2H, CH2), 1.47−1.60 (m, 4H, CH2), 1.21−1.39 (m, 22H, CH2), 1.12 (d, 3JHH = 13.3, 18H, tBu), 0.11−0.72 (br, 6H, BH3).

 13C{1H} NMR (151 MHz, CDCl3): δ 153.8 (dd, 3JPC = 4, 3JPC = 2, py), 136.6 (t, 3JPC = 2, py), 123.5 (app t, 3JPC = 3, py), 31.5 (d, 3JPC = 26, pyCH2), 30.7 (d, 3JPC = 13, CH2), 28.9 (d, 3JPC = 31, tBu[C]), 28.0 (s, CH2), 27.87 (s, CH2), 27.85 (s, CH2), 27.8 (s, CH2), 25.7 (d, 3JPC = 2, tBu[CH2]), 22.7 (d, 3JPC = 2, CH2), 20.4 (d, 3JPC = 31, CH2).

 13P{1H} NMR (243 MHz, CDCl3): δ 33.3 (vbr, fwhm = 130 Hz).

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

 General procedure for the hydrogenation of 5. A suspension of 5 and [Rh(PPh3)3]Cl (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, Rf = 0.20).

 Following the general procedure using cis-5a (840 mg, 1.67 mmol) and [R(PPh3)3]Cl (77.2 mg, 83.4 μmol) in benzene (50 mL), the product was isolated as a white solid. Yield: 818 mg (97%).

 1H NMR (500 MHz, CDCl3): δ 7.55 (t, 3JHH = 7.7, 1H, py), 7.21 (d, 3JHH = 7.8, 2H, py), 3.13−3.28 (m, 4H, pyCH2), 1.75−1.86 (m, 2H, CH2), 1.52−1.68 (m, 4H, CH2), 1.38−1.50 (m, 4H, CH2), 1.26−1.35 (m, 18H, CH2), 1.10 (d, 3JHH = 13.3, 18H, tBu), 0.05−0.77 (m, 6H, BH3).

 13C{1H} NMR (126 MHz, CDCl3): δ 154.7 (dd, 3JPC = 6, 3JPC = 1, py), 136.8 (t, 3JPC = 2, py), 123.0 (app t, 3JPC = 3, py), 31.5 (d, 3JPC = 26, pyCH2), 30.8 (d, 3JPC = 13, CH2), 29.1 (d, 3JPC = 31, tBu[C]), 27.91 (s, CH2), 27.89 (s, CH2), 27.74 (s, CH2), 27.71 (s,
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 NH (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 31P NMR spectroscopy, which was carried forward without further purification.

Preparation of [Rh(PNP-14)(biph)][BARF]₄ (6a)

A suspension of PNP-14 (16.1 mg, 33.6 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[BARF]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 CH₂Cl₂ (2 mL). The product was obtained as an orange crystalline solid by slow cooling of CH₂Cl₂: hexane (1:20) solution to −30 °C. Yield: 42.6 mg (79%).

Preparation of PNP-14

A solution of trans-1a in Et NH (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 31P NMR spectroscopy. The volatiles were removed in vacuo to afford the product as a colourless oil, which was carried forward without further purification.

A solution of trans-1a in Et NH (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 31P NMR spectroscopy. The volatiles were removed in vacuo to afford the product as a colourless oil, which was carried forward without further purification.
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 bifrophene.

**[Rh(PNP-14)(H)]_2[BF_4]^2- (7a).** Following the general procedure using 6a (16.0 mg, 10.0 μmol) and heating for 10 days at 85 °C gave quantitative conversion to 7a by 1H and 31P NMR spectroscopy.

**[Rh(PNP-14)(H)]_2[BF_4]^2- (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 31P NMR spectroscopy.

**[Rh(PNP-14)(H)]_2[BF_4]^2- (7c).** Following the general procedure using 7a (16.0 mg, 10.0 μmol) and heating for 10 days at 85 °C gave quantitative conversion to 7c by 1H and 31P NMR spectroscopy within 5 minutes at room temperature.

**[Rh(PNP-14)(C,H)]_2[BF_4]^2- (8a).** Following the general procedure using 7a (10 μmol, generated in situ as described above) gave quantitative conversion to 8a by 1H and 31P NMR spectroscopy within 5 minutes at room temperature.
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2H, pyCH2)], 1.72–1.93 (m, 4H, CH2), 1.55–1.67 (m, 2H, CH2), 1.39–1.50 (m, 2H, CH2), 1.07–1.37 (m, 20H, CH2), 0.83 (vt, JPH = 7, 18H, tBu).

13C{1H} NMR (126 MHz, DFB, C2H4): δ 162.9 (vt, JPC = 5, py), 162.3 (q, JCB = 50, ArF), 140.1 (s, py), 135.1 (s, ArF), 126.9 (qq, JPC = 32, 3JCF = 3, ArF), 125.2 (q, JFC = 272, ArF), 120.7 (vt, JPC = 5, py), 117.6 (sept, JFB = 4, ArF), 35.0 (d, JFB = 12, C2H4), 37.5 (vt, JFC = 8, pyCH2), 32.8 (vt, JFC = 10, tBu(C)), 29.5 (vt, JFC = 4, CH2), 29.3 (s, CH3), 28.7 (s, CH2), 28.2 (s, CH2), 27.9 (s, CH2), 26.6 (vt, JPC = 3, tBuCH), 24.1 (s, CH3), 21.9 (vt, JPC = 10, PCH2).

13P{1H} NMR (162 MHz, DFB, C2H4): δ 5.30 (d, JFB = 125).

[Rh(PONOP-14)(C2H4)][BarF4] (9b). Following the general procedure using 7b (7.5 µmol, generated in situ as described above) gave quantitative conversion to 8a by 1H and 31P NMR spectroscopy within 5 minutes at room temperature.

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)][BarF4] (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, CD2Cl2): δ 7.99 (t, JFFT = 7.8, 1H, py), 7.70–7.76 (m, 8H, ArF), 7.56 (br, 4H, ArF), 7.42 (d, JFFT = 7.9, 2H, py), 3.70 (dvt, JFFT = 17.5, JFFT = 4, 2H, pyCH2), 3.56 (dvt, JFFT = 17.5, JFFT = 4, 2H, pyCH2), 2.02–2.09 (m, 4H, CH2), 1.78–1.98 (m, 4H, CH2), 1.63–1.75 (m, 2H, CH2), 1.49–1.63 (m, 2H, CH2), 1.21–1.49 (m, 16H, CH2), 1.13 (vt, JPH = 8, 18H, tBu).

13C{1H} NMR (126 MHz, CD2Cl2): δ 194.7 (dt, JFB = 70, JCF = 13, CO), 163.8 (vt, JPC = 5, JFB = 1, py), 162.3 (q, JCB = 50, ArF), 141.6 (s, py), 135.4 (s, ArF), 129.4 (qq, JFC = 32, JCB = 3, ArF), 125.2 (q, JFC = 272, ArF), 122.1 (vt, JPC = 5, py), 118.0 (sept, JFB = 4, ArF), 38.7 (vt, JFC = 9, pyCH2), 33.9 (vt, JFC = 12, tBu(C)), 30.3 (vt, JFC = 4, CH2), 29.3 (s, CH3), 28.9 (s, CH2), 28.88 (s, CH2), 28.4 (s, CH2), 27.8 (vt, JFC = 3, tBu(CH3)), 26.2 (s, CH2), 23.2 (vt, JFC = 12, JFB = 3, PCH2).

13P{1H} NMR (162 MHz, CD2Cl2): δ 67.5 (d, JFB = 122).

IR (CH2Cl2): ν(CO) 1997 cm−1.

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

Anal. Calcd for C69H32BF24N3OP2Rh: 1471.83 g mol−1: C, 50.60; H, 4.45; N, 0.95 Found: C, 50.53; H, 4.47; N, 1.08.

References

1 (a) Pincer Compounds: Chemistry and Applications, ed. D. Morales-Morales, Elsevier, 2018, vol. 1; (b) E. Peris and R. H. Crabtree, Chem. Soc. Rev., 2018, 47, 1959–1968; (c) R. E. Andrew, L. González-Sebastián and A. B. Chaplin, Dalton Trans., 2016, 45, 1299–1305; (d) The Privileged Pincer-Metal Platform: Coordination Chemistry & Applications, ed.
G. van Koten and R. A. Gossage, Topics in Organometallic Chemistry, Springer, 2016, vol. 45; (e) Pincer and Pincer-Type Complexes: Applications in Organic Synthesis and Catalysis, ed. K. J. Szabó and O. F. Wendt, Wiley-VCH, 2014; (f) Organometallic Pincer Chemistry, ed. G. van Koten and D. Milstein; Topics in Organometallic Chemistry, Springer, 2013, vol. 40; (g) M. E. van der Boom and D. Milstein, Chem. Rev., 2003, 103, 1759–1792; (h) M. Albrecht and G. van Koten, Angew. Chem., Int. Ed., 2001, 40, 3750–3781.

2 W. H. Bernskoetter, C. K. Schauer, K. I. Goldberg and M. Brookhart, Science, 2009, 326, 553–556.

3 A. Kumar, T. M. Bhatti and A. S. Goldman, Chem. Rev., 2017, 117, 12357–12384.

4 J. Choi, D. Y. Wang, S. Kundu, Y. Choliy, T. J. Emge, K. Krogh-Jespersen and A. S. Goldman, Science, 2011, 332, 1545–1548.

5 (a) E. M. Pelczar, T. J. Emge, K. Krogh-Jespersen and A. S. Goldman, Organometallics, 2008, 27, 5759–5767; (b) D. Hermann, M. Gandelman, H. Rooney, L. J. W. Shimon and D. Milstein, Organometallics, 2002, 21, 812–818.

6 W. H. Bernskoetter, S. K. Hanson, S. K. Buzak, Z. Davis, P. S. White, R. Swartz, K. I. Goldberg and M. Brookhart, J. Am. Chem. Soc., 2009, 131, 8603–8613.

7 M. R. Gyton, B. Leforestier and A. B. Chaplin, Organometallics, 2018, 37, 3963–3971.

8 (a) C. M. Storey, M. R. Gyton, R. E. Andrew and A. B. Chaplin, Angew. Chem., Int. Ed., 2018, 57, 12003–12006; (b) S. L. Apps, R. E. Allafat, B. Leforestier, C. M. Storey and A. B. Chaplin, Polyhedron, 2018, 143, 57–61; (c) R. E. Andrew, C. M. Storey and A. B. Chaplin, Dalton Trans., 2016, 45, 8937–8944; (d) R. E. Andrew, D. W. Ferdani, C. A. Ohlin and A. B. Chaplin, Organometallics, 2015, 34, 913–917; (e) R. E. Andrew and A. B. Chaplin, Inorg. Chem., 2015, 54, 312–322; (f) R. E. Andrew and A. B. Chaplin, Dalton Trans., 2014, 43, 1413–1423.

9 The synthesis and coordination chemistry of analogous ortho-xylene- and resorcinol-derived macrocyclic pincer ligands will be described in a following contribution.

10 D. Dakternieks and R. Di Giacomo, Phosphorus Sulfur Relat. Elem., 1985, 24, 217–224.

11 (a) T. Imamoto, T. Kusumoto, N. Suzuki and K. Sato, J. Am. Chem. Soc., 1985, 107, 5301–5303; (b) G. C. Lloyd-Jones and N. P. Taylor, Chem. – Eur. J., 2015, 21, 5423–5428.

12 A. P. T. Athanasiopoulos, PhD Thesis, University of Waterloo, 2009.

13 (a) M. Van Overschelde, E. Verbecken, S. G. Modha, S. Cogen, E. Van der Eycken and J. Van der Eycken, Tetrahedron, 2009, 65, 6410–6415; (b) K. Jouvin, R. Veillard, C. Theunissen, C. Alayrac, A-C. Gaumont and G. Evano, Org. Lett., 2013, 15, 4592–4595.

14 C. N. Iverson and W. D. Jones, Organometallics, 2001, 20, 5745–5750.

15 T. M. Hood, B. Leforestier, M. R. Gyton and A. B. Chaplin, Inorg. Chem., 2019, 58, 7593–7601.

16 (a) J. Emerson-King, I. Prokes and A. B. Chaplin, Chem. – Eur. J., 2019, 25, 6317–6319; (b) R. C. Knighton, J. Emerson-King, J. P. Rourke, C. A. Ohlin and A. B. Chaplin, Chem. – Eur. J., 2018, 24, 4927–4938.

17 S. D. Pike, M. R. Crimin and A. B. Chaplin, Chem. Commun., 2017, 53, 3615–3633.

18 M. Brookhart, M. L. H. Green and G. Parkin, Proc. Natl. Acad. Sci. U. S. A., 2007, 104, 6908–6914.

19 (a) G. J. Kubas, Metal Dihydrogen and o-Bond Complexes, Kluwer Academic/Plenum Publishers, New York, 2001; (b) R. H. Crabtree, Chem. Rev., 2016, 116, 8750–8769.

20 G. L. Parker, S. Lau, B. Leforestier and A. B. Chaplin, Eur. J. Inorg. Chem., 2019, 3791–3798.

21 J. J. Davidson, J. C. DeMott, C. Douvris, C. M. Fafard, N. Bhuvanes, C.-H. Chen, D. E. Herbert, C.-I. Lee, B. J. McCulloch, B. M. Foxman and O. V. Ozerov, Inorg. Chem., 2015, 54, 2916–2935.

22 M. R. Gyton, T. M. Hood and A. B. Chaplin, Dalton Trans., 2019, 48, 2877–2880.

23 C. A. Tolman, Chem. Rev., 1977, 77, 313–348.

24 T. R. Hoyer, B. M. Eklov and M. Voloshin, Org. Lett., 2004, 6, 2567–2570.

25 Y. Chen, T. P. Clark, B. A. Jadzdzewski, S. B. Klamo and T. T. Wenzel, Polyhedron, 2014, 84, 32–36.

26 J. A. Osborn, G. Wilkinson and J. J. Mrowca, Inorg. Synth., 1990, 28, 77–79.

27 (a) A. J. Martinez-Martinez and A. S. Weller, Dalton Trans., 2019, 48, 3551–3554; (b) W. E. Buschmann, J. S. Miller, K. Bowman-James and C. N. Miller, Inorg. Synth., 2002, 33, 83–91.