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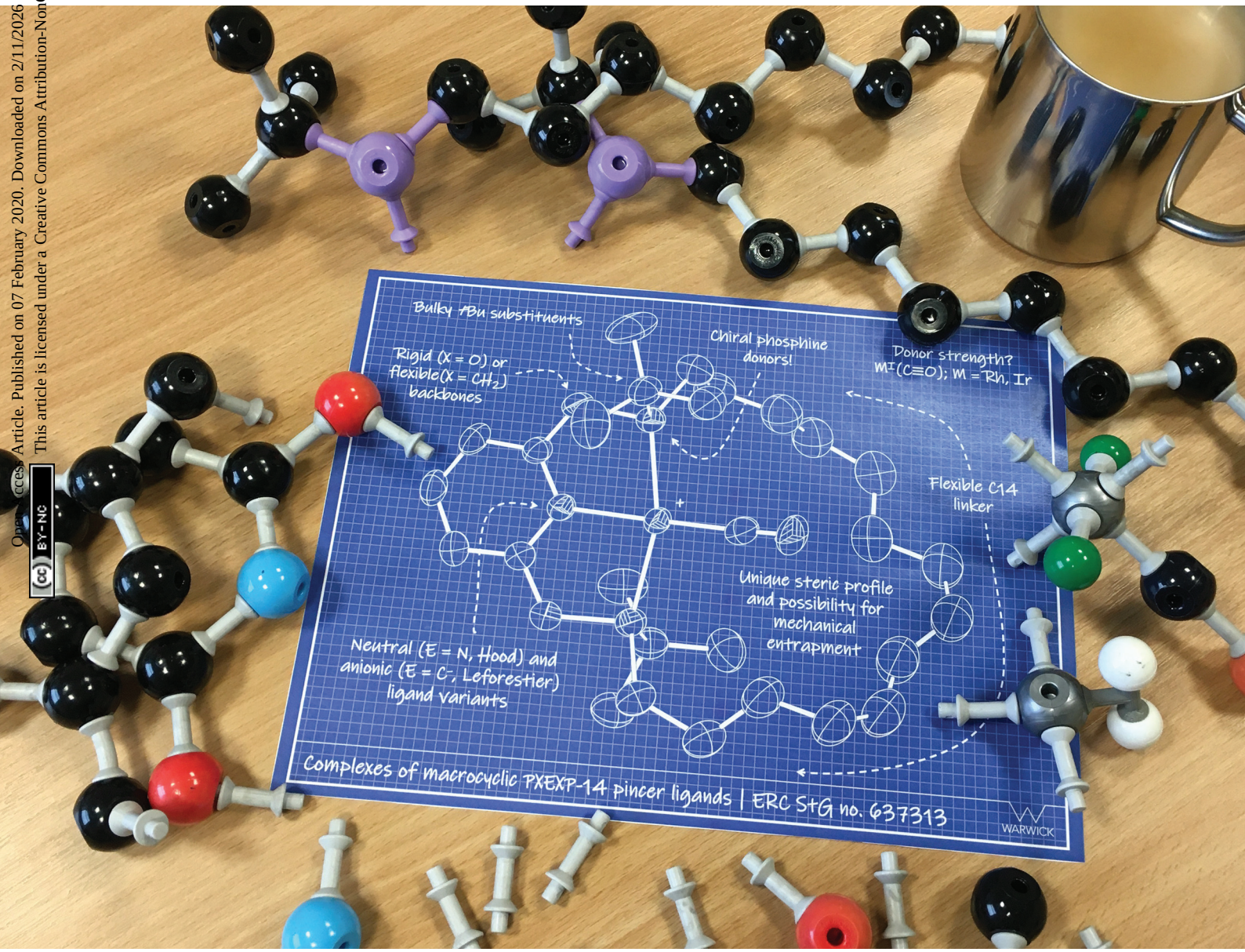

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BACK-TO-BACK PAPERS by Chaplin *et al.*
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Synthesis and group 9 complexes of macrocyclic PCP and POCOP pincer ligands†

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The synthesis of macrocyclic variants of commonly employed phosphine-based pincer (pro)ligands derived from *meta*-xylene (PCP-14) and resorcinol (POCOP-14) is described, where the P-donors are *trans*-substituted with a tetradecamethylene linker. The former was accomplished using a seven-step asymmetric procedure involving (–)-*cis*-1-amino-2-indanol as a chiral auxiliary and ring-closing olefin metathesis. A related, but non-diastereoselective route was employed for the latter, which consequently necessitated chromatographic separation from the *cis*-substituted by-product. The proligands are readily metalated and homologous series of $M^{I}(CO)$ and $M^{III}Cl_2(CO)$ derivatives (M = Rh, Ir) have been isolated and fully characterised in solution and the solid state. Metal hydride complexes are generated during the synthesis of the former and have been characterised *in situ* using NMR spectroscopy.

Introduction

Conferring thermal stability whilst permitting a broad range of metal-based reactivity, the application of *mer*-tridentate "pincer" ligands in organometallic chemistry and homogeneous catalysis has had a profound impact.[1] Phosphine-based examples bearing a central aryl donor were first reported by Shaw in the late 1970s,[2] but these archetypical PCP ligands continue to attract contemporary interest, with iridium derivatives noteworthy for their ability to catalyse the dehydrogenation of alkanes.[3] The predictable and modular composition of pincer ligands enables the steric and electronic properties of metal derivatives to be tuned through changes to the constituent donor groups, their substituents or the backbone configuration itself, and these adaptions have been extensively explored over the intervening four decades.[4] Motivated by the potential to exploit additional reaction control though their unique steric profile and their use in the construction of interlocked assemblies, we have become interested in exploring the chemistry of macrocyclic pincer ligands, with our initial efforts devoted to NHC-based CNC ligands.[5] We herein describe the synthesis and coordination chemistry of *meta*-xylene- and resorcinol-derived macrocyclic (pro)ligands PCP-14 and POCOP-14, where the chiral P-donors are *trans*-substituted with a tetradecamethylene linker (Chart 1). The preparation of analogous lutidine- and 2,6-dihydroxypyridine-derived PNP-14 and PONOP-14 ligands was described in a preceding contribution.[6]

Results and discussion

Proligand synthesis

Circumventing problems associated with the generation of the unwanted *cis*-substituted diastereoisomer, the proligand PCP-14′ was prepared using an adapted asymmetric procedure developed by Riera and Verdaguer that employs (–)-*cis*-1-amino-2-indanol as a chiral auxiliary and ring-closing olefin metathesis (Scheme 1).[7] The known oxazaphospholidine borane **1** (δ_{31P} 167.9) was first stereoselectively ring-opened by treatment with octen-7-yl-magnesium bromide, affording **2** (δ_{31P} 76.5). The auxiliary was then removed by acidolysis using an excess of H_2SO_4 in 3 : 1 MeOH–water to generate phosphinous acid borane **3** (δ_{31P} 125.6), which was subsequently converted into phosphine borane **4** (δ_{31P} 22.2, $^{1}J_{PH}$ = 352 Hz) by

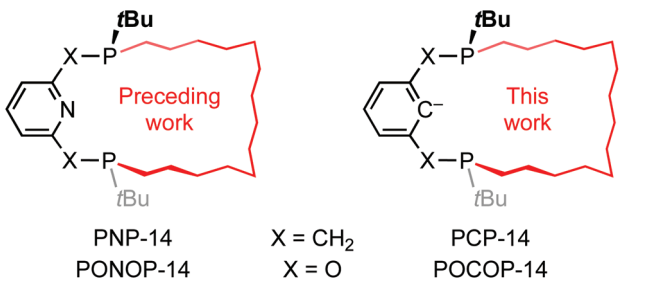

Chart 1

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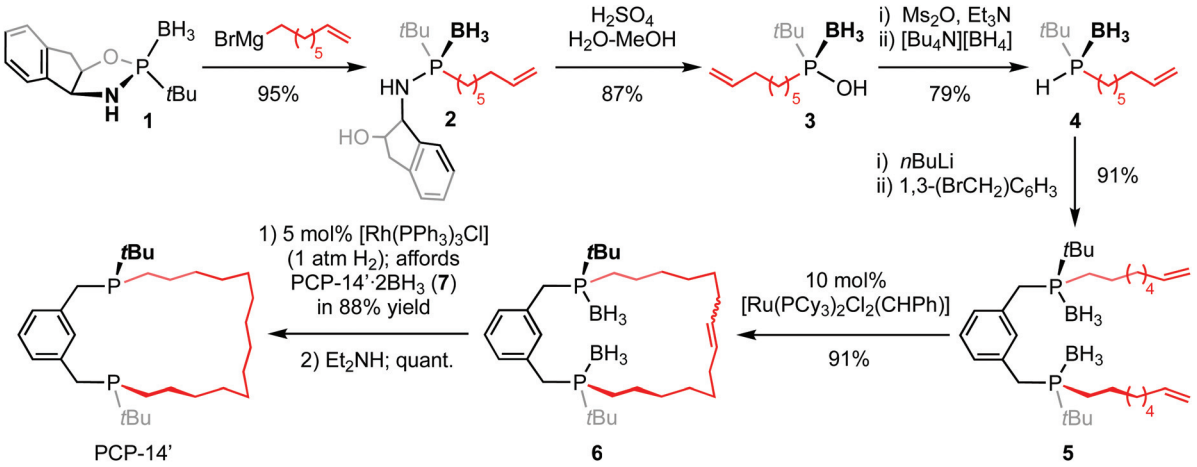
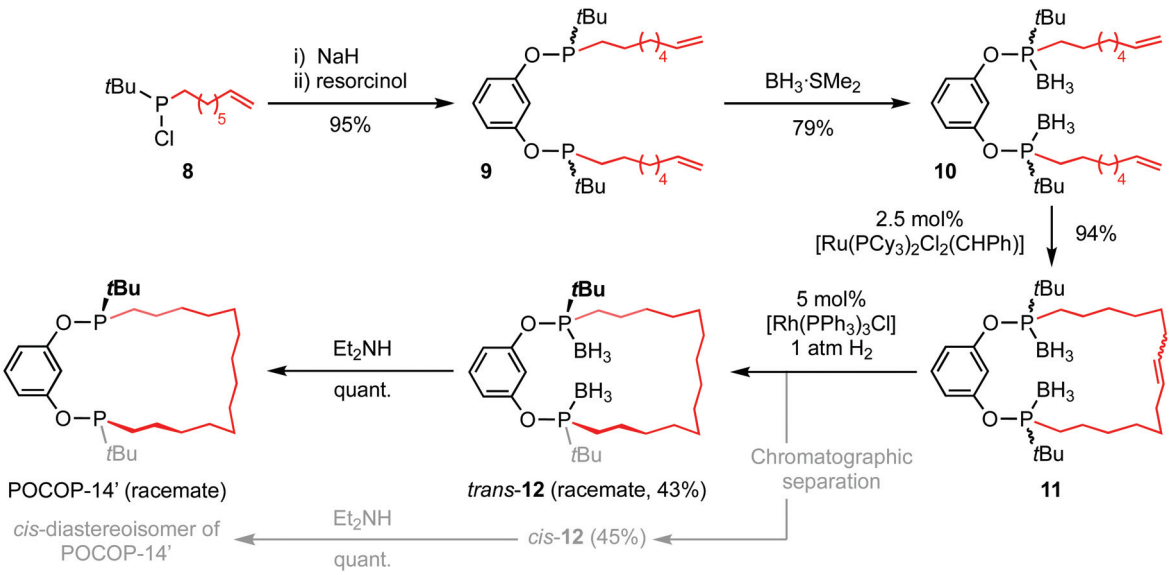
† Electronic supplementary information (ESI) available: Additional experimental details; NMR, IR and ESI-MS spectra of new compounds, and selected reactions (PDF); primary NMR data (MNOVA). CCDC 1972811–1972820. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9dt04835a



Scheme 1 Asymmetric synthesis of PCP-14′.

reduction of the mesylate with tetrabutylammonium borohydride and isolated in 65% overall yield from **1**. Isolated **4** is unstable at room temperature, presumably due to a propensity to undergo hydrophosphination,[8] and is best converted directly into the corresponding phosphide by deprotonation with *n*BuLi at −78 °C. Reaction thereafter with 1,3-bis(bromomethyl)benzene afforded **5** (δ_{31P} 32.3), which was cyclised by portion-wise treatment with Grubbs' 1st generation catalyst (totalling 10 mol%) under dilute conditions in CH_2Cl_2 (5 mmol L^{-1}) to afford the corresponding unsaturated macrocycle **6** (δ_{31P} 31.3–33.4). Subsequent hydrogenation using Wilkinson's catalyst (producing PCP-14′·2BH_3 **7**, δ_{31P} 32.5) and deprotection by borane transfer in neat diethylamine afforded the proligand (δ_{31P} 3.2) as the (*R*,*R*)-diastereomer with a respectable overall yield of 48% and >95% ee, as determined by ^{1}H and ^{31}P NMR spectroscopic analysis of the oxide derivative using the chiral shift reagent (−)-3,5-dinitro-*N*-(1-phenylethyl)benzamide (see ESI†).[9]

Attempts to develop an asymmetric procedure for the preparation of the proligand POCOP-14′ starting from enantiopure **3**, involving reaction of the mesylate with disodium resorcinolate or nucleophilic aromatic substitution of 1,3-difluorobenzene by the conjugate base, were unsuccessful (see ESI† for details). Likewise, attempted conversion of **2** to the corresponding borane protected chlorodialkylphosphine by acidolysis with HCl was unsuccessful. Instead the five step racemic synthesis outlined in Scheme 2, adapted from our work with PNP-14 and PONOP-14 and also involving ring-closing olefin metathesis,[6] was employed with the borane protected (saturated) macrocycle **12** proving to be the most conducive to resolution of the two diastereoisomers by column chromatography (*cis*-**12**, δ_{31P} 143.7; *trans*-**12**, δ_{31P} 143.8) and enabling



Scheme 2 Preparation of POCOP-14′.

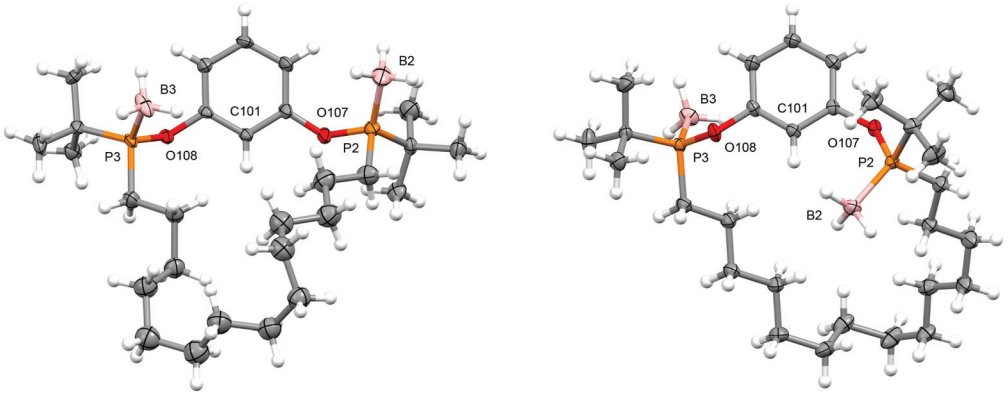


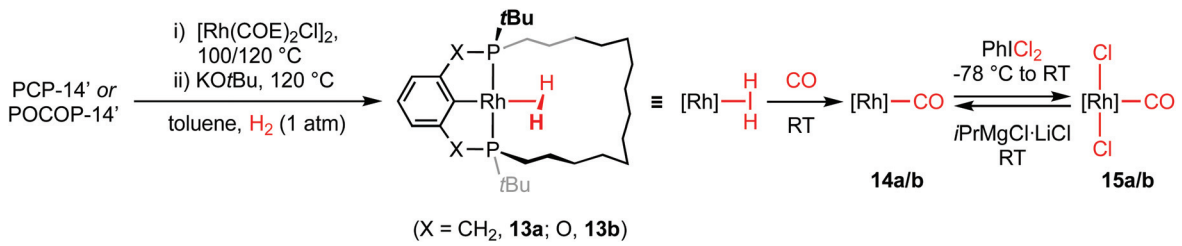
Fig. 1 Solid-state structures of *cis*-**12** (left) and *trans*-**12** (right; not unique, $Z' = 2$). Thermal ellipsoids drawn at 30% and 50% probability, respectively; minor disordered components omitted (*cis*-**12**; *t*Bu groups and methylene chain). Selected bond lengths (Å): *cis*-**12**, P2–B2, 1.915(8); P3–B3, 1.896(7); P2–O107, 1.617(4); P3–O108, 1.630(4); *trans*-**12**, B2–P2, 1.908(2); B3–P3, 1.905(2); P2–O107, 1.6323(9); P3–O108, 1.6270(9); B12–P12, 1.901(2); B13–P13, 1.904(2); P12–O207, 1.6284(10); P13–O208, 1.6274(10).

determination of their respective configurations by single crystal X-ray diffraction (Fig. 1). In this way POCOP-14′ was obtained as an analytically pure racemate in 30% overall yield (δ_{31P} 141.6). Use of the chiral shift reagent (−)-3,5-dinitro-*N*-(1-phenylethyl)benzamide enabled the component phosphine oxide enantiomers to be resolved by ^{31}P NMR spectroscopy (see ESI†).[9]

Rhodium complexes

With the new macrocyclic proligands in hand, the synthesis of rhodium derivatives was targeted (Scheme 3). Using an adapted literature procedure,[10] rhodium dihydrogen complexes [Rh(pincer)(H_2)] (pincer = PCP-14, **13a**; POCOP-14, **13b**) were prepared in quantitative spectroscopic yield using a one-pot procedure involving metalation of the proligands with $[Rh(COE)_2Cl]_2$ (COE = cyclooctene) in toluene at elevated temperature and subsequent treatment with KO*t*Bu at 120 °C under an atmosphere of dihydrogen. Complexes **13a/b** were characterised *in situ* and are notable for the adoption of C_2 symmetry, ^{31}P resonances at δ 70.4 ($^1J_{RhP}$ = 153 Hz)/198.4 ($^1J_{RhP}$ = 165 Hz) displaying large coupling to ^{103}Rh, and broad 2H hydride signals at δ −4.36/−2.87 (298 K), which exhibit fast spin–lattice relaxation (T_1 = 74 ± 4/42 ± 2 ms at 298 K; T_1 = 117 ± 15/89 ± 11 ms at 200 K; 600 MHz, Ar) consistent with the assignment as dihydrogen complexes.[11,12] The formulation of **13a/b** as σ-complexes is further substantiated by their instability to vacuum and onward reactivity with CO (1 atm), conferring C_2 symmetric Rh(I) carbonyl complexes [Rh(pincer)(CO)] (pincer = PCP-14, **14a**; POCOP-14, **14b**), which are characterised by ^{31}P resonances at δ 75.0 ($^1J_{RhP}$ = 146 Hz)/201.6 ($^1J_{RhP}$ = 156 Hz) with $^1J_{RhP}$ coupling constants of similar magnitude. Complexes **14a/b** were thereafter oxidised to the corresponding C_2 symmetric Rh(III) carbonyl complexes **15a/b** by reaction with $PhICl_2$, as evidenced by ^{31}P resonances at δ 64.9 ($^1J_{RhP}$ = 87 Hz)/181.0 ($^1J_{RhP}$ = 92 Hz) with the expected reductions in $^1J_{RhP}$ values, isolated as analytically pure materials in 80/48% overall yield, following purification by silica chromatography (CH_2Cl_2–pentane), and fully characterised (Fig. 2, Table 1).[13] Analytically pure samples of very alkane soluble **14a/b** were secured from the reaction of **15a/b** with 3 equivalents *i*PrMgCl·LiCl in THF and subsequent recrystallisation from $SiMe_4$ in 85/94% yield; as confirmed by combustion analysis.

The solid-state structures of **14a/b** have been determined by single crystal X-ray diffraction and demonstrate the adoption of distorted square planar metal coordination geometries, with the tetradecamethylene linker of the pincer ligands considerably skewed to one side of the coordination plane conferring overall C_1 symmetry and inducing an appreciable deviation of the C101–Rh1–C4 angles from linearity, especially in the case of the phosphinite pincer (171.38(10)°, **14a**; 165.3(3)°, **14b**). The methylene chains of the macrocycles are also non-symmetrically positioned in the Rh(III) congeners, but in this



(X = CH_2, **13a**; O, **13b**)

Scheme 3 Synthesis of rhodium PCP-14 and POCOP-14 complexes **13–15**.

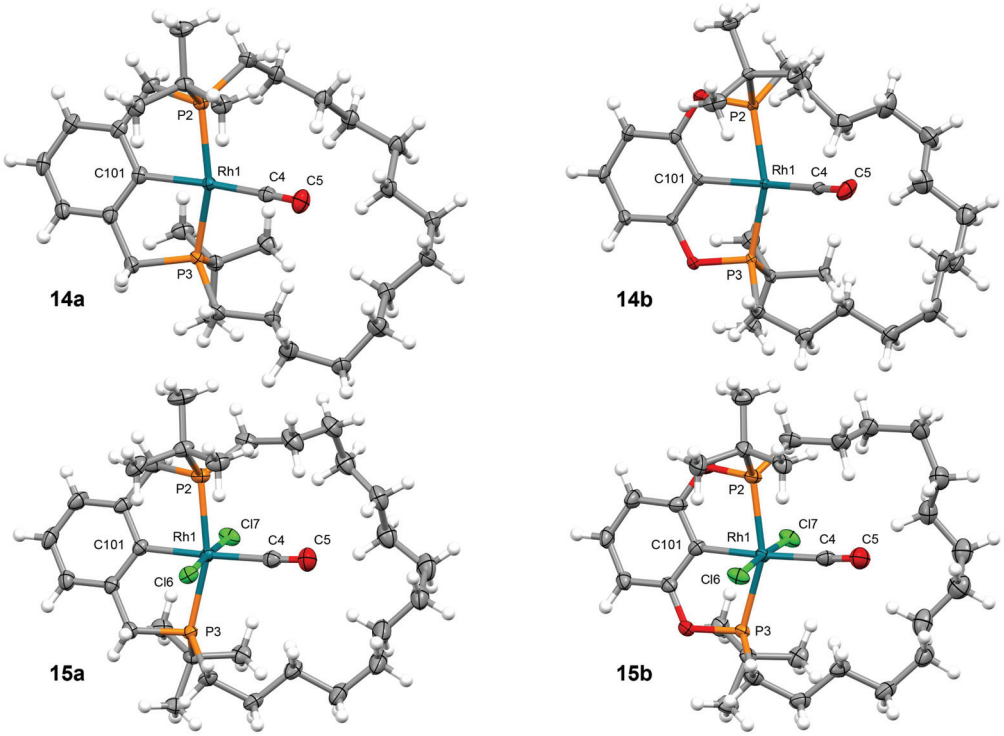


Fig. 2 Solid-state structures of **14** and **15**. Thermal ellipsoids drawn at 50% probability; minor disordered components omitted (**15a/b**; methylene chains). Selected metrics provided in Table 1.

Table 1 Selected bond lengths (Å) and angles (°) for **14**, **15**, **18** and **19**

	M = Rh				M = Ir			
	14a	**14b**	**15a**	**15b**	**18a**	**18b**	**19a**	**19b**
M1–P2	2.2844(6)	2.2704(15)	2.3615(7)	2.3324(12)	2.2817(7)	2.2694(11)	2.3637(9)	2.336(2)
M1–P3	2.2731(6)	2.2856(13)	2.3938(6)	2.3768(11)	2.2760(7)	2.2798(10)	2.3922(8)	2.377(2)
M1–C4	1.865(3)	1.879(6)	2.005(3)	1.996(6)	1.862(3)	1.879(4)	1.940(3)	1.926(9)
M1–C101	2.083(3)	2.037(6)	2.061(3)	2.018(5)	2.085(3)	2.048(4)	2.089(3)	2.034(10)
M1–Cl6	—	—	2.3656(5)	2.3616(12)	—	—	2.3828(7)	2.380(2)
M1–Cl7	—	—	2.3591(6)	2.3521(12)	—	—	2.3793(8)	2.371(2)
P2–M1–P3	160.83(2)	155.98(5)	162.17(2)	156.80(5)	161.16(2)	156.21(3)	160.81(3)	156.18(9)
C101–M1–C4	171.38(10)	165.3(3)	177.22(11)	174.6(2)	171.91(12)	165.6(2)	177.24(14)	174.9(4)
Cl6–M1–Cl7	—	—	176.92(2)	176.32(5)	—	—	178.81(3)	177.37(9)
Aryl twist[a]	14.30(6)	6.7(2)	18.52(7)	12.34(13)	13.95(8)	6.49(14)	17.93(9)	11.3(3)

[a] Angle between the least-squares mean planes of the aryl group and the MP_2C(aryl) atoms.

case contortion is counteracted by buttressing with the ancillary chloride ligands and more ideal C101–Rh1–C4 angles are observed (177.22(11)°, **15a**; 174.6(2)°, **15b**). These asymmetric configurations are not retained in solution, where time averaged C_2 symmetry is observed at 298 K (500–600 MHz) consistent with the tetradecamethylene linker being sufficiently large and flexible to accommodate the carbonyl ligand within the annulus of the macrocycle. The more obtuse P2–Rh1–P3 bite angles and rigid backbone conformations observed in the complexes of POCOP-14 in the solid state, compared to those of PCP-14, are fully in line with expectations for these pincer architectures.[14] This homologous series of complexes showcases the effect of increased steric crowding on the latter, where C_2 symmetric twisting of the central aryl donor is considerably more pronounced in the octahedral Rh(III) congeners. Finally, the observed differences in Rh–P, Rh–CO, and Rh–aryl contacts for the Rh(I) and Rh(III) congeners are consistent with the nature of associated donors (*vide infra* for further discussion on the carbonyl ligand).

Iridium complexes

In a similar manner to that employed for the rhodium analogues, iridium tetrahydride complexes [Ir(pincer)H_4] (pincer = PCP-14, **16a**; POCOP-14, **16b**) were prepared using a one-pot

procedure involving metalation of the macrocyclic proligands with $[Ir(COE)_2Cl]_2$ (**16a**) or $[Ir(COD)Cl]_2$ (**16b**, COD = cyclooctadiene) in toluene at elevated temperature and subsequent treatment with KO*t*Bu at 120 °C under an atmosphere of dihydrogen (Scheme 4). Complexes **16a/b** were characterised *in situ* and are notable for the adoption of C_2 symmetry, ^{31}P resonances at δ 49.9/165.0, and relatively sharp triplet 4H hydride signals at δ −8.99 ($^2J_{PH}$ = 9.8 Hz)/−8.26 ($^2J_{PH}$ = 9.9 Hz) at 298 K that only broaden slightly on cooling to 200 K, with moderate spin–lattice relaxation (T_1 = 300 ± 10/194 ± 4 ms at 298 K; T_1 = 626 ± 15/242 ± 15 ms at 200 K; 600 MHz, Ar). These data are consistent with fluxional hydride ligands, where dynamic interconversion between classical tetrahydride and dihydride dihydrogen formulations occurs on the NMR timescale.[11,15] Evidencing the presence of the latter, reaction with CO (1 atm) resulted in immediate substitution of one equivalent of dihydrogen and formation of *cis*-**17a/b** [δ_{1H}(hydride) −10.66, −11.59; δ_{31P} 51.0, 45.8 ($^2J_{PP}$ = 286 Hz)/δ_{1H}(hydride) −9.82, −10.75; δ_{31P} 160.4, 154.6 ($^2J_{PP}$ = 305 Hz)]. Prolonged thermolysis at 120 °C under CO (1 atm) in the presence of *tert*-butylethylene (TBE) followed by removal of CO resulted in the formation of C_2 symmetric Ir(I) carbonyl complexes [Ir(pincer)(CO)] (pincer = PCP-14, δ_{31P} 68.1, **18a**; POCOP-14, δ_{31P} 186.7, **18b**). Transient formation of *trans*-**17a/b** [δ_{1H}(hydride) −9.65; δ_{31P} 54.1/δ_{1H}(hydride) −9.76; δ_{31P} 167.3] and generation of [Ir(pincer)(CO)$_2$] (pincer = PCP-14, δ_{31P} 51.6; POCOP-14, δ_{31P} 164.8) were noted during this transformation. Complexes **18a/b** were thereafter oxidised to the corresponding C_2 symmetric Ir(III) carbonyl complexes **19a/b** (δ_{31P} 33.8/144.4) by reaction with $PhICl_2$ and isolated as analytically pure and air-stable materials in 51/73% overall yield, following purification by silica chromatography (CH_2Cl_2–hexane), and fully characterised. Analytically pure samples of very alkane soluble **18a/b** were secured from the reaction of **19a/b** with 10 equivalents of KC_8 in pentane and subsequent recrystallisation from neohexane/$SiMe_4$ in 84/79% yield; as confirmed by combustion analysis.[16]

The solid-state structures of **18a/b** and **19a/b** have all been determined by single crystal X-ray diffraction and are isomorphous to the corresponding rhodium congeners **14a/b** and **15a/b**, respectively (Table 1).

Carbonyl stretching frequencies

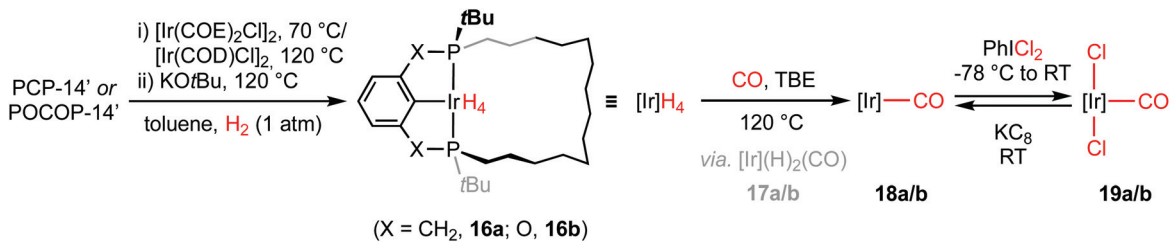
The ν(CO) bands of metal carbonyl derivatives are established reporter groups for donor properties of ligands.[17] In the case of pincer ligands, group 9 examples have an established track record in the literature.[18] The carbonyl stretching frequencies of **14**, **15**, **18** and **19** and those of known acyclic pincer complexes [M(pincer)(CO)] (M = Rh, Ir; pincer = 2,6-(tBu$_2$PCH$_2$)$_2$C$_6$H$_3$═PCP-*t*Bu, 2,6-(tBu$_2$PO)$_2$C$_6$H$_3$═POCOP-*t*Bu) have all been determined by IR spectroscopy under the same conditions and compiled in Table 2. These data suggest that PCP-14 and POCOP-14 are marginally weaker donors than PCP-*t*Bu and POCOP-*t*Bu, respectively, consistent with similar findings for the neutral PNP and PONOP analogues and attributed to changes in the phosphine/phosphinite substituents alone.[6] Other trends apparent in the IR data associated with the extent of π-backbonding increasing in the order Ir > Rh, M(I) > M(III) and PCP > POCOP are fully in line with expectation and reinforced by similar trends in the X-ray derived metrics (Table 1) and NMR data (see Experimental section).

Table 2 Carbonyl stretching frequencies for rhodium and iridium complexes of macrocyclic PCP-14 and POCOP-14, and acyclic PCP-*t*Bu and POCOP-*t*Bu (toluene, cm^{-1})

	Macrocyclic	Acyclic
[Rh(PCP)(CO)]	1939	1933
[Rh(POCOP)(CO)]	1958	1954
[Rh(PCP)Cl$_2$(CO)]	2069	—
[Rh(POCOP)Cl$_2$(CO)]	2083	—
[Ir(PCP)(CO)]	1925	1918
[Ir(POCOP)(CO)]	1943	1939
[Ir(PCP)Cl$_2$(CO)]	2034	—
[Ir(POCOP)Cl$_2$(CO)]	2049	—

Conclusions

Procedures that enable the preparation of two phosphine-based macrocyclic pincer (pro)ligands PCP-14 and POCOP-14, where the chiral P-donors are *trans*-substituted with a tetradecamethylene linker, have been developed. The synthesis of *meta*-xylene-based proligand PCP-14′ was achieved using a seven-step asymmetric protocol involving (−)-*cis*-1-amino-2-indanol as a chiral auxiliary and ring-closing olefin metathesis, affording the (*R*,*R*)-diastereomer in 48% overall yield and >95% ee. Whilst we were unable to apply this methodology to the synthesis of resorcinol-based POCOP-14′, this proligand was obtained as analytically pure racemate in 30% overall yield using a non-diastereoselective route, where separation from



Scheme 4 Synthesis of iridium PCP-14 and POCOP-14 complexes **16–19**.

the unwanted *cis*-substituted by-product was achieved by chromatography. Rhodium and iridium complexes of these new macrocyclic pincer ligands have been obtained through metalation of the proligands with dimeric rhodium(I) and iridum(I) halide precursors and subsequent dehydrohalogenation under a dihydrogen atmosphere. The resulting hydride complexes were characterised *in situ* by NMR spectroscopy and reacted on to generate isolatable $M^{I}(CO)$ and $M^{III}Cl_2(CO)$ derivatives that have been extensively characterised in solution and the solid state, including all eight complexes by single crystal X-ray diffraction. By comparison of the ν(CO) bands of the rhodium(I) and iridum(I) carbonyl adducts, determined by IR spectroscopy in toluene, PCP-14 and POCOP-14 can be considered to be marginally weaker net donors than their respective homoleptic *tert*-butyl substituted congeners PCP-*t*Bu and POCOP-*t*Bu, respectively. Work exploring the organometallic chemistry of these novel macrocyclic pincer ligands is ongoing in our laboratories and will be reported in due course.

Experimental

General methods

All manipulations were performed under an atmosphere of argon using Schlenk and glove box techniques unless otherwise stated. Hydrogen was dried by passage through a stainless-steel column of activated 3 Å molecular sieves. Carbon monoxide was used as received. 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. CD_2Cl_2 was freeze–pump–thaw degassed and dried over 3 Å molecular sieves. Toluene-d_8 and C_6D_6 were dried over sodium overnight, distilled, freeze–pump–thaw degassed and stored over 3 Å molecular sieves. THF was distilled from sodium and benzophenone and stored over 3 Å molecular sieves. Et_2NH was distilled from CaH_2. *tert*-Butylethylene was freeze–pump–thaw degassed and stored over 3 Å molecular sieves. $SiMe_4$ was distilled from liquid Na/K alloy and stored over a potassium mirror. Neohexane (2,2-dimethylbutane) was distilled from liquid Na/K alloy and stored over 3 Å molecular sieves. Other anhydrous solvents were purchased from Acros Organics or Sigma-Aldrich, freeze–pump–thaw degassed and stored over 3 Å molecular sieves. The concentration of *n*BuLi was titrated by ^{1}H NMR spectroscopy before use.[19] Oxazaphospholidine **1**,[7] $MgBr(C_8H_{15})$,[20] **8**,[6] $PhICl_2$,[21] $[Rh(PPh_3)_3Cl]$,[22] $[Rh(COE)_2Cl]_2$,[23] $[Ir(COD)Cl]_2$,[24] $[Ir(COE)_2Cl]_2$,[24] [M(pincer)(CO)] (M = Rh, Ir; pincer = PCP-*t*Bu, POCOP-*t*Bu)[2,14d,25] were synthesised according to published procedures. 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.[26] NMR spectra in toluene-d_0 were recorded using an internal capillary of C_6D_6. HR ESI-MS were recorded on a Bruker MaXis mass spectrometer. IR spectra were recorded on a Bruker Alpha Platinum ATR FT-IR spectrometer at RT (for full details see ESI†). Microanalyses were performed at the London Metropolitan University by Stephen Boyer in all cases, except for samples of **14a/b** and **18a/b**, which were analysed by Elemental Microanalysis Ltd.

Synthesis of PCP-14′

Preparation of 2. A solution of $MgBr(C_8H_{15})$ in THF (0.37 M, 45 mL, 17 mmol) was added dropwise in three equal portions separated by 30 minutes to a solution of **1** (1.39 g, 5.57 mmol) in toluene at 80 °C. The solution was concentrated under reduced pressure and the residue re-dissolved in a minimal amount of toluene (20 mL) and heated at reflux for 3 days. The reaction mixture was cooled to 0 °C, exposed to air and quenched with saturated aqueous NH_4Cl (10 mL). The aqueous phase was extracted with EtOAc (3 × 20 mL) and the combined organic fractions dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give a pale-yellow oil. Purification by flash column chromatography (silica, 8% EtOAc in hexane, R_f = 0.15) afforded **2** as a colourless oil. Yield: 1.92 g (95%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35–7.42 (m, 1H, Ar), 7.23–7.28 (m, 3H, Ar), 5.81 (ddt, $^3J_{HH}$ = 16.9, 10.1, 6.5, 1H, C$\underline{H}$=CH$_2$), 5.01 (app dq, $^3J_{HH}$ = 16.9, J_{HH} = 2, 1H, CH=C$\underline{H}_2$), 4.95 (ddt, $^3J_{HH}$ = 10.1, $^2J_{HH}$ = 2.2, $^4J_{HH}$ = 1.2, 1H, CH=C$\underline{H}_2$), 4.77 (app td, J = 10, $^3J_{HH}$ = 4.5, 1H, NC$\underline{H}$), 4.51 (app q, $^3J_{HH}$ = 5, 1H, OC$\underline{H}$), 3.10 (dd, $^2J_{HH}$ = 16.6, $^3J_{HH}$ = 4.7, 1H, OCHC$\underline{H}_2$), 2.90 (d, $^2J_{HH}$ = 16.6, 1H, OCHC$\underline{H}_2$), 2.11 (d, $^3J_{HH}$ = 10.0, NH), 2.05 (app q, $^3J_{HH}$ = 7, 2H, C$\underline{H}_2$CH=CH$_2$), 1.81 (d, $^3J_{HH}$ = 4.4, 1H, OH), 1.56–1.83 (m, 4H, CH_2), 1.30–1.49 (m, 6H, CH_2), 1.26 (d, $^3J_{PH}$ = 13.6, 9H, *t*Bu), 0.55 (partially collapsed quartet, fwhm = 310 Hz, 3H, BH_3).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 142.9 (d, $^3J_{PC}$ = 7, Ar{C}), 139.9 (s, Ar{C}), 139.1 (s, C$\underline{H}$=CH$_2$), 128.1 (s, Ar), 127.1 (s, Ar), 125.6 (s, Ar), 124.3 (s, Ar), 114.5 (s, CH=C$\underline{H}_2$), 74.8 (s, OCH), 62.3 (d, $^2J_{PC}$ = 3, NCH), 39.4 (s, OCH$\underline{C}$H$_2$), 33.8 (s, C$\underline{H}_2$CH=CH$_2$), 31.9 (d, $^1J_{PC}$ = 39, *t*Bu{C}), 31.5 (d, $^2J_{PC}$ = 13, CH_2), 28.9 (s, CH_2), 28.8 (s, CH_2), 25.1 (d, $^2J_{PC}$ = 2, *t*Bu{CH_3}), 24.1 (d, $^1J_{PC}$ = 36, PCH_2), 23.0 (s, CH_2).

^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 76.5 (partially collapsed quartet, fwhm = 200 Hz).

HR ESI-MS (positive ion, 4 kV): 384.2603, $[M + Na]^+$ (calcd 384.2602) *m*/*z*.

Preparation of 3. H_2SO_4 (98%, 5.4 mL, 99 mmol) was added dropwise to a solution of **2** (4.52 g, 12.5 mmol) in a MeOH–water mixture (140 mL : 45 mL). The reaction mixture was heated at 70 °C for 4 days, with periodic monitoring by TLC. The mixture was allowed to cool to RT, exposed to air, and CH_2Cl_2 (40 mL) and saturated aqueous NaCl (20 mL) added. The aqueous phase was extracted with CH_2Cl_2 (3 × 15 mL) and the combined organic extracts dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give a colourless opaque oil. The crude material was dissolved in a minimal amount of CH_2Cl_2 and run through a short silica plug, eluting with CH_2Cl_2 (R_f = 0.6). The volatiles were removed under reduced pressure to afford **3** as a colourless oil. Yield: 2.51 g (87%).

^{1}H NMR (500 MHz, toluene-d_8): δ 5.75 (ddt, $^3J_{HH}$ = 17.0, 10.2, 6.7, 1H, C$\underline{H}$=CH$_2$), 5.02 (br d, $^3J_{HH}$ = 17.1, 1H, CH=C$\underline{H}_2$), 4.97 (br d, $^3J_{HH}$ = 10.1, 1H, CH=C$\underline{H}_2$), 3.14 (br, 1H,

OH), 1.95 (app q, $^3J_{HH}$ = 7, 2H, C$\underline{H}_2$CH=CH$_2$), 1.60–1.75 (m, 1H, CH$_2$), 1.39–1.56 (m, 2H, CH$_2$), 1.03–1.38 (m, 7H, CH$_2$), 0.95 (d, $^3J_{PH}$ = 13.7, 9H, *t*Bu), 0.63–1.30 (obscured, 3H, BH$_3$).

^{13}C{^{1}H} NMR (126 MHz, toluene-d_8): δ 139.1 (s, $\underline{C}$H=CH$_2$), 114.6 (s, CH=$\underline{C}$H$_2$), 34.2 (s, $\underline{C}$H$_2$CH=CH$_2$), 31.5 (d, $^2J_{PC}$ = 12, CH$_2$), 31.0 (d, $^1J_{PC}$ = 38, *t*Bu{C}), 29.24 (s, CH$_2$), 29.15 (s, CH$_2$), 24.5 (d, $^1J_{PC}$ = 35, PCH$_2$), 24.0 (d, $^2J_{PC}$ = 3, *t*Bu{CH$_3$}), 22.8 (s, CH$_2$).

^{31}P{^{1}H} NMR (121 MHz, toluene-d_8): δ 125.6 (partially collapsed quartet, fwhm = 200 Hz).

Preparation of 4. Triethylamine (3.79 mL, 27.2 mmol) was added dropwise to a solution of **3** (2.51 g, 10.9 mmol) and methanesulfonic anhydride (2.84 g, 16.3 mmol) in dichloromethane (15 mL) at −20 °C and the resulting solution stirred at this temperature for 1 h. A solution of tetrabutylammonium borohydride (2.81 g, 10.9 mmol) in CH_2Cl_2 (10 mL) was added at −20 °C and the reaction mixture stirred for a further 16 h at −20 °C. The mixture was allowed to warm to 0 °C and HCl (0.5 M, 20 mL) added slowly. The mixture was exposed to air, diluted with distilled water, and the aqueous phase extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure to give a colourless oil. Purification by flash column chromatography (silica, 5% EtOAc in hexane, R_f = 0.42) afforded **4** as a colourless oil. Yield: 1.83 g (79%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.80 (ddt, $^3J_{HH}$ = 17.0, 10.0, 6.5, 1H, C$\underline{H}$=CH$_2$), 4.99 (app dq, $^3J_{HH}$ = 17.0, J_{HH} = 2, 1H, CH=C$\underline{H}_2$), 4.94 (ddt, $^3J_{HH}$ = 10.0, $^2J_{HH}$ = 2.3, $^4J_{HH}$ = 1.2, 1H, CH=C$\underline{H}_2$), 4.23 (dm, $^1J_{PH}$ = 350.6, 1H, PH), 2.04 (app q, $^3J_{HH}$ = 7, 2H, C$\underline{H}_2$CH=CH$_2$), 1.65–1.90 (m, 2H, CH$_2$), 1.45–1.60 (m, 2H, CH$_2$), 1.24–1.40 (m, 6H, CH$_2$), 1.21 (d, $^3J_{PH}$ = 14.2, 9H, *t*Bu), 0.46 (partially collapsed quartet, fwhm = 330, 3H, BH$_3$).

^{13}C{^{1}H} NMR (126 MHz $CDCl_3$): δ 139.0 (s, $\underline{C}$H=CH$_2$), 114.5 (s, CH=$\underline{C}$H$_2$), 33.8 (s, CH$_2$), 30.9 (d, $^2J_{PC}$ = 11, CH$_2$), 28.8 (s, CH$_2$), 28.7 (s, CH$_2$), 26.9 (d, $^2J_{PC}$ = 2, *t*Bu{CH$_3$}), 26.8 (d, $^1J_{PC}$ = 35, *t*Bu{C}), 25.0 (d, $^3J_{PC}$ = 2, CH$_2$), 17.6 (d, $^1J_{PC}$ = 32, PCH$_2$).

^{31}P NMR (202 MHz, $CDCl_3$): δ 22.2 (br d, $^1J_{PH}$ = 352).

^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 22.2 (partially collapsed quartet, fwhm = 165 Hz).

Preparation of 5. *n*BuLi (1.60 M, 4.11 mL, 6.59 mmol) was added dropwise to a solution of **4** (1.41 g, 6.59 mmol) in THF (15 mL) at −78 °C. The reaction mixture was stirred for 30 min at this temperature and a solution of 1,3-bis(bromomethyl) benzene (870 mg, 3.30 mmol) in THF (3 mL) was added at −78 °C. The reaction mixture was stirred at −78 °C for 1 h, allowed to warm to RT over 3 h, then quenched by slow addition of water (10 mL) at 0 °C in air. THF was removed under reduced pressure and aqueous mixture extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure to give a colourless oil. Purification by flash column chromatography (silica, 5% EtOAc in hexane, R_f = 0.33) afforded **5** as a colourless oil, which was carried forward directly. Yield: 1.60 g (91%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.12–7.24 (m, 4H, Ar), 5.78 (ddt, $^3J_{HH}$ = 16.9, 10.2, 6.8, 2H, C$\underline{H}$=CH$_2$), 4.88–5.03 (m, 4H, CH=C$\underline{H}_2$), 2.85–3.10 (m, 4H, PCH$_2$), 2.01 (app q, $^3J_{HH}$ = 7.0, 4H, C$\underline{H}_2$CH=CH$_2$), 1.10–1.65 (m, 24H, CH$_2$), 1.17 (d, $^3J_{PH}$ = 13.1, 18H, *t*Bu), 0.44 (partially collapsed quartet, fwhm = 270 Hz, 6H, BH$_3$).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 32.3 (partially collapsed quartet, fwhm = 140 Hz).

HR ESI-MS (positive ion, 4 kV): 553.4469, [M + Na]$^+$ (calcd 553.4416) *m*/*z*.

Preparation of 6. A solution of **5** (1.60 g, 3.01 mmol) in CH_2Cl_2 (5 mmol L^{-1}, 600 mL) was treated with a solution of [Ru(PCy$_3$)$_2$Cl$_2$(CHPh)] (248 mg, 301 μmol, 10 mol%) in CH_2Cl_2 (2 mL) in 4 equal portions – every 12 h – over 2 days with periodic argon sparging (*ca.* 10 min). Volatiles were removed *in vacuo* and the crude mixture was purified by flash column chromatography in air (silica, 8% EtOAc in hexane, R_f = 0.26) to afford **6** (mixture of alkene isomers) as a colourless oil, which was carried forward directly. Yield: 1.37 g (91%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.14–7.25 (m, 4H, Ar), 5.21–5.29 (m, 0.6H, CH=CH minor), 5.21–5.29 (m, 1.4H, CH=CH major), 3.02 (dd, $^2J_{HH}$ = 13.8, $^2J_{PH}$ = 9.0, 2H, ArC$\underline{H}_2$), 2.92 (app t, ^2J = 14, 1.4H, ArC$\underline{H}_2$ major), 2.92 (app t, ^2J = 14, 1.4H, ArC$\underline{H}_2$ major), 2.91 (app t, ^2J = 14, 0.6H, ArC$\underline{H}_2$ minor), 1.88–2.05 (m, 4H, CH$_2$), 0.93–1.70 (m, 20H, CH$_2$), 1.21 (d, $^3J_{PH}$ = 13.0, 5.4H, *t*Bu minor), 1.20 (d, $^3J_{PH}$ = 13.0, 12.6H, *t*Bu major), 0.45 (partially collapsed quartet, fwhm = 270 Hz, 6H, BH$_3$).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 31.3–33.4 (br m).

HR ESI-MS (positive ion, 4 kV): 525.4105, [M + Na]$^+$ (calcd 525.4102) *m*/*z*.

Preparation of PCP-14′·2BH$_3$ (7). A suspension of [Rh(PPh$_3$)$_3$Cl] (126 mg, 136 μmol, 5 mol%) in benzene (5 mL) was added to a stirred solution of **6** (1.37 g, 2.73 mmol) in benzene (20 mL). The suspension was freeze–pump–thaw degassed, placed under dihydrogen and the resulting solution stirred at 50 °C for 2 days. Volatiles were removed under reduced pressure and the crude product purified by flash column chromatography in air (silica, 5% EtOAc in hexane, R_f = 0.25) to afford **7** as a colourless oil. Yield: 1.21 g (88%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.25 (s, 1H, Ar{2-CH}), 7.22 (t, $^3J_{HH}$ = 7.6, 1H, Ar), 7.17 (d, $^3J_{HH}$ = 7.6, 2H, Ar), 3.03 (dd, $^2J_{HH}$ = 14.0, $^2J_{PH}$ = 9.9, 2H, ArC$\underline{H}_2$), 3.03 (app t, ^2J = 14, 2H, ArC$\underline{H}_2$), 1.50–1.61 (m, 4H, PCH$_2$), 1.40–1.50 (m, 2H, CH$_2$), 1.13–1.35 (m, 22H, CH$_2$), 1.17 (d, $^3J_{PH}$ = 13.1, 18H, *t*Bu), 0.46 (partially collapsed quartet, fwhm = 270 Hz, 6H, BH$_3$).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 133.9 (dd, $^2J_{PC}$ = 5, $^4J_{PC}$ = 2, Ar{C}), 132.0 (t, $^3J_{PC}$ = 4, Ar{2-CH}), 128.7 (dd, $^3J_{PC}$ = 4, $^5J_{PC}$ = 3, Ar), 128.5 (t, $^4J_{PC}$ = 2, Ar), 30.8 (d, $^2J_{PC}$ = 12, CH$_2$), 28.8 (d, $^1J_{PC}$ = 31, *t*Bu{C}), 28.7 (d, $^1J_{PC}$ = 27, Ar$\underline{C}$H$_2$), 27.8 (s, CH$_2$), 27.6 (s, 2 × CH$_2$), 27.4 (s, CH$_2$), 25.8 (d, $^2J_{PC}$ = 1, *t*Bu{CH$_3$}), 23.3 (s, CH$_2$), 20.2 (d, $^1J_{PC}$ = 31, PCH$_2$).

^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ 32.5 (partially collapsed quartet, fwhm = 155 Hz).

HR ESI-MS (positive ion, 4 kV): 527.4250, [M + Na]$^+$ (calcd 527.4259) *m*/*z*.

Anal. Calcd for $C_{30}H_{60}B_2P_2$ (508.32 g mol^{-1}): C, 71.44; H, 11.99; found: C, 71.37; H, 12.10.

Preparation of PCP-14′. A solution of **7** (26.3 mg, 52.1 μmol) in Et$_2$NH (2 mL) was heated at 80 °C for 3 days. Volatiles were

removed *in vacuo* to afford PCP-14′ as a colourless oil. Yield: 24.8 mg (>99%).

^{1}H NMR (600 MHz, toluene-d_8): δ 7.34 (s, 1H, Ar{2-CH}), 7.06 (br, 3H, Ar), 2.75 (d, $^2J_{HH}$ = 13.5, 2H, ArC$\underline{H}_2$), 2.51 (dd, $^2J_{HH}$ = 13.5, $^2J_{PH}$ = 3.0, 2H, ArC$\underline{H}_2$), 1.10–1.50 (m, 28H, CH_2), 0.98 (d, $^3J_{PH}$ = 10.9, 18H, *t*Bu).

^{13}C{^{1}H} NMR (151 MHz, toluene-d_8): δ 140.2 (d, $^2J_{PC}$ = 8, Ar{C}), 130.9 (t, $^3J_{PC}$ = 7, Ar{2-CH}), 128.5 (s, Ar), 127.1 (dd, $^3J_{PC}$ = 7, $^5J_{PC}$ = 2, Ar), 32.6 (d, $^1J_{PC}$ = 23, Ar$\underline{C}H_2$), 30.8 (d, $^2J_{PC}$ = 12, CH_2), 28.6 (s, CH_2), 28.3 (s, CH_2), 28.23 (d, $^1J_{PC}$ = 15, *t*Bu{C}), 28.21 (s, CH_2), 28.1 (s, CH_2), 27.5 (d, $^2J_{PC}$ = 13, *t*Bu{CH_3}), 27.3 (s, CH_2), 24.4 (d, $^1J_{PC}$ = 20, PCH_2).

^{31}P{^{1}H} NMR (243 MHz, toluene-d_8): δ 3.2 (s).

Preparation of PCP-14′·O_2. Following an adapted literature procedure.[27] To a stirred solution of PCP-14′ (24.8 mg, 52.0 μmol) in EtOH (1 mL) cooled to −78 °C was added H_2O_2 (30% w/w in H_2O, 16 μL, 0.16 mmol). The mixture was allowed to warm to RT overnight before the volatiles were removed *in vacuo*. Toluene (0.5 mL) was added and the solution was stirred over 3 Å molecular sieves (15 mg) overnight. The solution was filtered, extracting the sieves with additional toluene (3 × 1 mL), and reduced to dryness to afford PCP-14′·O_2 as a colourless oil, which crystallised upon standing. Yield: 22.3 mg (84%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.37 (s, 1H, Ar), 7.23–7.28 (m, 1H, Ar), 7.21 (d, $^3J_{HH}$ = 7.6, 2H, Ar), 3.12 (app t, ^2J = 14, 2H, ArC$\underline{H}_2$), 3.02 (dd, $^2J_{HH}$ = 14.5, $^2J_{PH}$ = 10.1, 2H, ArC$\underline{H}_2$), 1.61–1.76 (m, 2H, PCH_2), 1.50–1.61 (m, 2H, PCH_2), 1.39–1.50 (m, 2H, CH_2), 1.10–1.50 (m, 22H, CH_2), 0.98 (d, $^3J_{PH}$ = 10.9, 18H, *t*Bu).

^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 134.2 (dd, $^2J_{PC}$ = 8, $^4J_{PC}$ = 2, Ar{C}), 131.9 (t, $^3J_{PC}$ = 5, Ar{2-CH}), 128.8 (t, $^4J_{PC}$ = 2, Ar), 128.6 (app t, J_{PC} = 3, Ar), 33.2 (d, $^1J_{PC}$ = 65, *t*Bu{C}), 32.9 (d, $^1J_{PC}$ = 55, Ar$\underline{C}H_2$), 30.9 (d, $^2J_{PC}$ = 12, CH_2), 28.3 (s, CH_2), 28.2 (s, CH_2), 28.14 (s, CH_2), 28.08 (s, CH_2), 24.9 (s, *t*Bu{CH_3}), 24.4 (d, $1J_{PC}$ = 62, PCH_2), 22.0 (d, $^3J_{PC}$ = 5, CH_2).

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 52.2 (s).

HR ESI-MS (positive ion, 4 kV): 531.3490, $[M + Na]^+$ (calcd 531.3491) *m*/*z*.

Preparation of POCOP-14′

Preparation of 9. A solution of resorcinol (3.53 g, 32.1 mmol) in THF (10 mL) was added to a suspension of NaH (1.62 g, 67.3 mmol) in THF (10 mL). The resulting suspension was heated at reflux for 1 h, allowed to cool to RT and a solution of **8** (16.6 g, 70.5 mmol) in THF (10 mL) added. The reaction mixture was then heated at reflux for a further 1 h. Volatiles were removed *in vacuo* and the residue extracted with hexane (3 × 10 mL) to afford **9** (1 : 1 mixture of diastereoisomers) as a colourless oil on drying. Yield: 16.1 g (95%).

^{1}H NMR (300 MHz, C_6D_6): δ 7.43 (s, 1H, Ar{2-CH}), 7.04 (t, $^3J_{HH}$ = 8.0, 1H, Ar), 6.95 (d, $^3J_{HH}$ = 8.4, 2H, Ar), 5.76 (ddt, $^3J_{HH}$ = 16.8, 11.8, 6.7, 2H, C$\underline{H}$=CH_2), 4.95–5.10 (m, 4H, CH=C$\underline{H}_2$), 1.95 (app q, $^3J_{HH}$ = 7, 4H, C$\underline{H}_2$CH=CH_2), 1.75–1.90 (m, 2H, CH_2), 1.61 (app sex, J = 8, 4H, CH_2), 1.15–1.40 (m, 14H, CH_2), 1.04 (d, $^3J_{PH}$ = 12.0, 18H, *t*Bu).

^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ 161.0 (d, $^2J_{PH}$ = 9.0, Ar{C}), 139.2 (s, $\underline{C}$H=CH_2), 130.2 (s, Ar), 114.6 (s, CH=$\underline{C}H_2$), 112.4 (d, $^3J_{PH}$ = 11, Ar), 109.6 (t, $^3J_{PH}$ = 12, Ar{2-CH}), 34.2 (s, $\underline{C}H_2$CH=CH), 32.7 (d, $^1J_{PH}$ = 16, *t*Bu{C}), 31.5 (d, $^2J_{PH}$ = 12, CH_2), 29.3 (s, CH_2), 29.2 (s, CH_2), 29.2 (d, $^1J_{PH}$ = 24, PCH_2), 25.9 (d, $^3J_{PH}$ = 16, CH_2), 25.4 (d, $^2J_{PH}$ = 16, *t*Bu{CH_3})

^{31}P{^{1}H} NMR (121 MHz, C_6D_6): δ 142.40 (s, 1P), 142.36 (s, 1P).

HR ESI-MS (positive ion, 4 kV): 561.3231, $[M + 2O + Na]^+$ (calcd 561.3233) *m*/*z*.

Preparation of 10. BH_3·SMe_2 (4.63 g, 5.78 mL, 61.0 mmol) was added dropwise to a stirred solution of **9** (15.4 g, 30.5 mmol) in THF (50 mL) at −78 °C. The reaction mixture was warmed to RT overnight and volatiles removed *in vacuo* to afford the crude material as an opaque colourless oil. Purification by flash column chromatography in air (silica, 8% EtOAc in hexane, R_f = 0.41) afforded **10** (1 : 1 mixture of diastereoisomers) as a colourless oil. Yield: 12.9 g (79%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.19 (t, $^3J_{HH}$ = 8.2, 1H, Ar), 6.99 (app q, J = 2, 1H, Ar{2-CH}), 6.90 (app dt, $^3J_{HH}$ = 8.4, J = 2, 2H, Ar), 5.79 (app ddt, $^3J_{HH}$ = 16.9, 10.1, 6.7, 2H, C$\underline{H}$=CH_2), 4.99 (app dq, $^3J_{HH}$ = 17.0, J_{HH} = 2, 2H, CH=C$\underline{H}_2$), 4.93 (app dq, $^3J_{HH}$ = 10.2, J_{HH} = 2, 2H, CH=C$\underline{H}_2$), 2.04 (app q, $^3J_{HH}$ = 7, 4H, C$\underline{H}_2$CH=CH_2), 1.92–2.01 (m, 2H, PCH_2), 1.68–1.79 (m, 4H, CH_2), 1.55–1.65 (m, 2H, CH_2), 1.28–1.44 (m, 12H, CH_2), 1.26 (d, $^3J_{PH}$ = 14.0, 18H, *t*Bu), 0.53 (partially collapsed quartet, fwhm = 300 Hz, 6H, BH_3).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 154.2 (d, $^2J_{PC}$ = 6, Ar{C}), 139.1 (s, $\underline{C}$H=CH_2), 129.6 (s, Ar), 117.0 (d, $^3J_{PC}$ = 3, Ar), 114.5 (s, CH=$\underline{C}H_2$), 114.1 (t, $^3J_{PC}$ = 3.0, Ar{2-CH}), 33.8 (s, $\underline{C}H_2$CH=CH_2), 32.9 (d, $^1J_{PC}$ = 37, *t*Bu{C}), 31.4 (d, $^2J_{PC}$ = 13.0, CH_2), 28.9 (d, $^4J_{PC}$ = 3, CH_2), 28.7 (s, CH_2), 25.4 (d, $^1J_{PC}$ = 33, PCH_2), 24.9 (d, $^2J_{PC}$ = 3, *t*Bu{CH_3}), 22.8 (s, CH_2).

^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 143.7 (partially collapsed quartet, fwhm = 165 Hz).

HR ESI-MS (positive ion, 4 kV): 557.4000, $[M + Na]^+$ (calcd 557.3990) *m*/*z*.

Preparation of 11. A solution of $[Ru(PCy_3)_2Cl_2(CHPh)]$ (36.0 mg, 43.7 μmol, 2.5 mol%) in CH_2Cl_2 (3 mL) was added at RT to a solution of **10** (930 mg, 1.74 mmol) in CH_2Cl_2 (350 mL, 5 mmol L^{-1}). The solution was stirred at RT with periodic (every 12 h) argon sparging (*ca.* 10 min) for 2 days. Volatiles were removed *in vacuo* and the crude mixture was purified by flash column chromatography in air (silica, 10% EtOAc in hexane, R_f = 0.40) to afford **11** (1 : 1 mixture of diastereoisomers) as a colourless oil. Yield: 832 mg (94%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.20 (t, $^3J_{HH}$ = 8.3, 0.5H, Ar *cis*), 7.19 (t, $^3J_{HH}$ = 8.3, 0.5H, Ar *trans*), 7.03 (dd, $^3J_{HH}$ = 8.3, $^4J_{HH}$ = 2.4, 1H, Ar *cis*), 6.97 (t, $^4J_{HH}$ = 2.3, 0.5H, Ar{2-CH} *trans*), 6.89 (dd, $^3J_{HH}$ = 8.3, $^4J_{HH}$ = 2.3, 1H, Ar *trans*), 6.74 (t, $^4J_{HH}$ = 2.4, 0.5H, Ar{2-CH} *cis*), 5.26–5.36 (m, 2H, CH=CH), 1.93–2.10 (m, 6H, CH_2), 1.61–1.81 (m, 4H, CH_2), 1.24–1.60 (m, 14H, CH_2), 1.27 (d, $^3J_{PH}$ = 14.0, 18H, *t*Bu), 0.55 (partially collapsed quartet, fwhm = 300 Hz, 6H, BH_3).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 154.4 (d, $^2J_{PC}$ = 6, Ar{C} *cis*), 154.1 (d, $^2J_{PC}$ = 6, Ar{C} *trans*), 130.9 (s, CH=CH *trans*), 130.8 (s, CH=CH *cis*), 129.7 (s, Ar *cis*), 129.5 (s, Ar *trans*), 117.0

(d, $^3J_{PC}$ = 4, Ar *trans*), 116.4 (d, $^3J_{PC}$ = 3, Ar *cis*), 114.4 (t, $^3J_{PC}$ = 3, Ar{2-CH} *trans*), 113.3 (t, $^3J_{PC}$ = 4, Ar{2-CH} *cis*), 32.8 (d, $^1J_{PC}$ = 37, *t*Bu{C} *cis*), 32.7 (d, $^1J_{PC}$ = 38, *t*Bu{C} *trans*), 32.10 (s, $\underline{C}H_2CH{=}CH$ *trans*), 32.06 (s, $\underline{C}H_2CH{=}CH$ *cis*), 31.6 (d, $^2J_{PC}$ = 13, CH_2 *trans*), 31.2 (d, $^2J_{PC}$ = 13, CH_2 *cis*), 28.8 (s, CH_2 *trans*), 28.7 (s, CH_2 *cis*), 28.1 (s, CH_2 *trans*), 27.9 (s, CH_2 *cis*), 25.5 (d, $^1J_{PC}$ = 33, PCH_2 *cis*), 25.4 (d, $^1J_{PC}$ = 33, PCH_2 *trans*), 24.9 (d, $^2J_{PC}$ = 3, *t*Bu{CH_3} *cis*), 24.8 (d, $^2J_{PC}$ = 3, *t*Bu{CH_3} *trans*), 23.0 (d, $^3J_{PC}$ = 2, CH_2 *trans*), 22.7 (d, $^3J_{PC}$ = 2, CH_2 *cis*). Data for major alkene isomer only.

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 142.0–144.6 (br m).

HR ESI-MS (positive ion, 4 kV): 529.3689, $[M + Na]^+$ (calcd 529.3687) *m*/*z*.

Preparation of 12. A suspension of $[Rh(PPh_3)_3Cl]$ (201 mg, 220 μmol, 5 mol%) in benzene (20 mL) was added to a stirred solution of **11** (2.20 g, 4.34 mmol) in benzene. The suspension was freeze–pump–thaw degassed and placed under a hydrogen atmosphere and the resulting solution stirred at 50 °C for 2 days. Volatiles were removed under reduced pressure and the crude mixture was eluted through a short silica plug in air (5% EtOAc in hexane) to afford **12** as a mixture of diastereomers (2.02 g, 3.97 mmol, 92%). Subsequent purification by repeated flash column chromatography in air (silica, 5% EtOAc in hexane) enabled separation of the *cis*- and *trans*-diastereomers.

POCOP-14′·2BH_3 (*trans*-**12**, R_f = 0.45). Yield: 951 mg (43%, colourless oil which slowly crystallised upon standing).

^1H NMR (600 MHz, $CDCl_3$): δ 7.19 (t, $^3J_{HH}$ = 8.2, 1H, Ar), 7.03 (t, $^4J_{HH}$ = 2.5, 1H, Ar{2-CH}), 6.93 (dd, $^3J_{HH}$ = 8.2, $^4J_{HH}$ = 2.5, 2H, Ar), 1.94–2.04 (m, 2H, PCH_2), 1.67–1.76 (m, 4H, CH_2), 1.50–1.61 (m, 2H, CH_2), 1.36–1.44 (m, 4H, CH_2), 1.22–1.34 (m, 16H, CH_2), 1.26 (d, $^3J_{PH}$ = 13.8, 18H, *t*Bu), 0.58 (partially collapsed quartet, fwhm = 300 Hz, 6H, BH_3).

$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 154.2 (d, $^2J_{PC}$ = 6, Ar{C}), 129.6 (s, Ar), 116.9 (d, $^3J_{PC}$ = 3, Ar), 114.1 (t, $^3J_{PC}$ = 3, Ar{2-CH}), 32.8 (d, $^1J_{PC}$ = 37, *t*Bu{C}), 30.7 (d, $^2J_{PC}$ = 12, CH_2), 28.1 (s, CH_2), 28.0 (s, CH_2), 27.6 (s, CH_2), 27.5 (s, CH_2), 25.1 (d, $^1J_{PC}$ = 33, PCH_2), 24.8 (d, $^3J_{PC}$ = 3, *t*Bu{CH_3}), 22.3 (s, CH_2).

$^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 143.8 (partially collapsed quartet, fwhm = 165 Hz).

HR ESI-MS (positive ion, 4 kV): 531.3840, $[M + Na]^+$ (calcd 531.3844) *m*/*z*.[28]

Anal. Calcd for $C_{28}H_{56}B_2O_2P_2$ (508.32 g mol^{-1}): C, 66.16; H, 11.10; found: C, 66.09; H, 11.26.[28]

cis-**12** (R_f = 0.42). Yield: 984 mg (45%, white crystalline solid).

^1H NMR (500 MHz, $CDCl_3$): δ 7.20 (t, $^3J_{HH}$ = 8.3, 1H, Ar), 7.03 (dd, $^3J_{HH}$ = 8.3, $^4J_{HH}$ = 2.3, 2H, Ar), 6.82 (t, $^4J_{HH}$ = 2.5, 1H, Ar{2-CH}), 1.90–2.06 (m, 2H, PCH_2), 1.67–1.81 (m, 4H, CH_2), 1.53–1.66 (m, 2H, CH_2), 1.20–1.50 (m, 20H, CH_2), 1.26 (d, $^3J_{PH}$ = 14.0, 18H, *t*Bu), 0.61 (partially collapsed quartet, fwhm = 285 Hz, 6H, BH_3).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 154.4 (d, $^2J_{PC}$ = 6, Ar{C}), 129.7 (s, Ar), 116.6 (d, $^3J_{PC}$ = 3, Ar), 113.4 (t, $^3J_{PC}$ = 4, Ar{2-CH}), 32.9 (d, $^1J_{PC}$ = 37, *t*Bu{C}), 30.5 (d, $^2J_{PC}$ = 12, CH_2), 28.2 (s, CH_2), 27.9 (s, CH_2), 27.8 (s, CH_2), 27.6 (s, CH_2), 25.2 (d, $^1J_{PC}$ = 33, PCH_2), 24.9 (d, $^3J_{PC}$ = 3, *t*Bu{CH_3}), 22.0 (d, $^3J_{PC}$ = 2, CH_2).

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 143.7 (br, fwhm = 175 Hz).

HR ESI-MS (positive ion, 4 kV): 531.3840, $[M + Na]^+$ (calcd 531.3844) *m*/*z*.[28]

Anal. Calcd for $C_{28}H_{56}B_2O_2P_2$ (508.32 g mol^{-1}): C, 66.16; H, 11.10; found: C, 66.09; H, 11.26.[28]

Preparation of POCOP-14′. A solution of *trans*-**12** (231 mg, 455 μmol) in Et_2NH (7 mL) was heated at 60 °C for 2 days. Volatiles were removed *in vacuo* to afford POCOP-14′ as a colourless oil. Yield: 217 mg (>99%).

^1H NMR (500 MHz, toluene-d_8): δ 7.30 (app p, J = 2, 1H, Ar{2-CH}), 6.97 (t, $^3J_{HH}$ = 8.1, 1H, Ar), 6.87 (app dt, $^3J_{HH}$ = 8.2, J = 2, 2H, Ar), 1.84 (dtd, $^2J_{HH}$ = 14.4, $^3J_{HH}$ = 7.3, $^2J_{PH}$ = 3.2, 2H, PCH_2), 1.54–1.67 (m, 4H, CH_2), 1.15–1.50 (m, 22H, CH_2), 1.00 (d, $^3J_{PH}$ = 12.1, 18H, *t*Bu).

$^{13}C\{^1H\}$ NMR (126 MHz, toluene-d_8): δ 160.9 (d, $^2J_{PC}$ = 9, Ar{C}), 129.9 (s, Ar), 112.2 (d, $^3J_{PC}$ = 11, Ar), 109.2 (t, $^3J_{PC}$ = 12, Ar{2-CH}), 32.5 (d, $^1J_{PC}$ = 16, *t*Bu{C}), 31.1 (d, $^2J_{PC}$ = 11, CH_2), 29.0 (d, $^1J_{PC}$ = 24, PCH_2), 28.9 (s, CH_2), 28.5 (s, CH_2), 28.2 (s, CH_2), 28.0 (s, CH_2), 25.5 (d, $^3J_{PC}$ = 15, CH_2), 25.3 (d, $^2J_{PC}$ = 15, *t*Bu{CH_3}).

$^{31}P\{^1H\}$ NMR (162 MHz, toluene-d_8): δ 141.6 (s).

Preparation of the *cis*-diastereoisomer of POCOP-14′. A solution of *cis*-**12** (10.0 mg, 19.7 μmol) in Et_2NH (0.5 mL) was heated at 80 °C for 2 days. Volatiles were removed *in vacuo* to afford the *cis*-diastereoisomer of POCOP-14′ as a colourless oil. Yield: 9.4 mg (>99%).

^1H NMR (500 MHz, toluene-d_8): δ 7.21 (app p, J = 2, 1H, Ar{2-CH}), 6.97 (t, $^3J_{HH}$ = 7.9, 1H, Ar), 6.91 (app dt, $3J_{HH}$ = 7.9, J = 2, 2H, Ar), 1.85 (dtd, $^2J_{HH}$ = 14.2, $^3J_{HH}$ = 7.4, $^2J_{PH}$ = 3.1, 1H, PCH_2), 1.58–1.68 (m, 4H, CH_2), 1.41–1.52 (m, 2H, CH_2), 1.16–1.40 (m, 20H, CH_2), 1.01 (d, $^3J_{PH}$ = 12.0, 18H, *t*Bu).

$^{13}C\{^1H\}$ NMR (126 MHz, toluene-d_8): δ 160.8 (d, $^2J_{PC}$ = 9, Ar{C}), 129.9 (s, Ar), 111.7 (d, $^3J_{PC}$ = 13, Ar), 109.4 (t, $^3J_{PC}$ = 11, Ar{2-CH}), 32.5 (d, $^1J_{PC}$ = 16, *t*Bu{C}), 30.9 (d, $^2J_{PC}$ = 11, CH_2), 29.1 (d, $^1J_{PC}$ = 24, PCH_2), 28.9 (s, CH_2), 28.5 (s, CH_2), 28.2 (s, CH_2), 28.1 (s, CH_2), 25.4 (d, $^3J_{PC}$ = 15, CH_2), 25.3 (d, $^3J_{PC}$ = 15, *t*Bu{CH_3}).

$^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ 140.5 (s).

Preparation of POCOP-14′·O_2. Following an adapted literature procedure.[27] To a stirred solution of POCOP-14′ (25.1 mg, 52.2 μmol) in EtOH (2 mL) cooled to −78 °C was added H_2O_2 (30% w/w in H_2O, 16 μL, 0.16 mmol). The mixture was allowed to warm to RT overnight before the volatiles were removed *in vacuo*. Toluene (1 mL) was added and the solution was stirred over 3 Å molecular sieves (45.2 mg) overnight. The solution was filtered, extracting the sieves with additional toluene (3 × 1 mL), and reduced to dryness to afford POCOP-14′·O_2 as a colourless oil, which crystallised upon standing. Yield: 26.2 mg (95%).

^1H NMR (500 MHz, CD_2Cl_2): δ 7.23 (t, $^3J_{HH}$ = 8.3, 1H, Ar), 7.19 (t, $^4J_{HH}$ = 2.4, 1H, Ar{2-CH}), 7.04 (dd, $^3J_{HH}$ = 8.3, $^4J_{HH}$ = 7.1, 2H, Ar), 1.75–1.91 (m, 4H, CH_2), 1.16–1.73 (m, 24H, CH_2), 1.22 (d, $^3J_{PH}$ = 15.5, 18H, *t*Bu).

$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ 153.6 (d, $^2J_{PC}$ = 10, Ar{C}), 130.2 (s, Ar), 116.4 (d, $^3J_{PC}$ = 4, Ar), 113.3 (t, $^3J_{PC}$ = 4, Ar{2-CH}), 33.9 (d, $^1J_{PC}$ = 91, *t*Bu{C}), 30.9 (d, $^2J_{PC}$ = 14, CH_2),

28.5 (s, CH_2), 28.3 (s, CH_2), 28.0 (s, CH_2), 27.7 (s, CH_2), 24.6 (s, *t*Bu{CH_3}), 24.4 (d, $^1J_{PC}$ = 83, PCH_2), 21.9 (d, $^3J_{PC}$ = 6, CH_2).

$^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 64.1 (s).

HR ESI-MS (positive ion, 4 kV): 535.3078, $[M + Na]^+$ (calcd 535.3077) *m*/*z*.

Synthesis of rhodium complexes of PCP-14

A solution of PCP-14′ (118.2 mg, 248 μmol) and $[Rh(COE)_2Cl]_2$ (88.9 mg, 124 μmol) in toluene (5 mL) within a reaction flask fitted with a J Young's value was freeze–pump–thaw-degassed and placed under dihydrogen (1 atm), sealed, and heated at 100 °C for 18 h. The solution was cooled to RT and cannula transferred under dihydrogen into a reaction flask fitted with a J Young's value and charged with KO*t*Bu (34.0 mg, 303 μmol). The flask was then sealed and heated at 120 °C for 2 h to generate **13a**, which was characterised *in situ*. The solution was freeze–pump–thaw degassed and placed under carbon monoxide (1 atm) resulting in immediate formation of **14a**, which was isolated by removal of the volatiles *in vacuo* and extraction of the residue with hexane. Crude **14a** obtained in this way was dissolved in toluene (5 mL) and then slowly added to a suspension of $PhICl_2$ (68.7 mg, 250 μmol) in toluene (2 mL) at −78 °C. The reaction mixture was allowed to warm to RT overnight, the volatiles removed *in vacuo*, and the resulting residue extracted with hexane to afford the crude product, which was purified by alumina chromatography in air (20% CH_2Cl_2 in hexane, R_f = 0.55) to afford analytically pure **15a**. Yield: 136.4 mg (80%). Complex **15a** is stable in the solid state, but partial loss of CO was observed in solution over time.

[Rh(PCP-14)(H_2)] (13a). This complex is unstable to vacuum but was characterised *in situ* using a sample (*ca.* 10 μmol) prepared in a similar manner within a J Young's valve NMR tube following removal of volatiles, addition of toluene-d_8 (0.5 mL) under argon, freeze–pump–thaw-degassing, and placing under dihydrogen (1 atm). T_1 values were subsequently determined following rapid freeze–pump–thaw-degassing and placing under argon.

^1H NMR (500 MHz, toluene-d_8, H_2): δ 7.12 (d, $^3J_{HH}$ = 7.4, 2H, Ar), 7.05 (t, $^3J_{HH}$ = 7.4, 1H, Ar), 3.08 (vt, J_{PH} = 3.9, 4H, $ArCH_2$), 1.87–2.00 (m, 2H, CH_2), 1.74–1.84 (m, 2H, CH_2), 1.17–1.67 (m, 24H, CH_2), 1.01 (vt, J_{PH} = 6.5, 18H, *t*Bu), −4.36 (br, 2H, RhH).

$^{13}C\{^1H\}$ NMR (126 MHz, toluene-d_8, H_2): δ 176.3 (dt, $^1J_{RhC}$ = 40, $^2J_{PC}$ = 6, Ar{CRh}), 151.6 (vtd, J_{PC} = 12, $^2J_{RhC}$ = 3, Ar{C}), 124.1 (s, Ar), 120.7 (vt, J_{PC} = 10, Ar), 39.9 (vtd, J_{PC} = 10, $^2J_{RhC}$ = 4, $ArCH_2$), 31.9 (vt, J_{PC} = 11, *t*Bu{C}), 29.5 (vt, J_{PC} = 4, CH_2), 29.2 (s, CH_2), 29.0 (s, CH_2), 28.6 (s, CH_2), 28.4 (vt, J_{PC} = 3, *t*Bu{CH_3}), 27.7 (s, CH_2), 25.6 (vt, J_{PC} = 4, CH_2), 22.9 (vt, J_{PC} = 8, PCH_2).

$^{31}P\{^1H\}$ NMR (162 MHz, toluene-d_8, H_2): δ 70.4 (d, $^1J_{RhP}$ = 153).

^1H NMR (600 MHz, toluene-d_8, Ar, selected data): δ −4.36 (br d, $^1J_{RhH}$ = 17.9, 2H, RhH, T_1 = 74 ± 4 ms).

^1H NMR (600 MHz, toluene-d_8, Ar, 200 K, selected data): δ −4.26 (br, 2H, RhH, T_1 = 117 ± 15 ms).

[Rh(PCP-14)Cl_2(CO)] (15a)

^1H NMR (600 MHz, toluene-d_8, CO): δ 6.95 (t, $^3J_{HH}$ = 7.4, 1H, Ar), 6.90 (d, $^3J_{HH}$ = 7.4, 2H, Ar) 3.71 (dvt, $^2J_{HH}$ = 15.6, J_{PH} = 4.8, 2H, $ArCH_2$), 2.96–3.04 (m, 2H, PCH_2), 2.91 (dvt, $^2J_{HH}$ = 15.6, J_{PH} = 4.1, 2H, $ArCH_2$), 1.84–1.95 (m, 2H, CH_2), 1.25–1.78 (m, 24H, CH_2), 1.16 (vt, J_{PH} = 6.9, 18H, *t*Bu).

$^{13}C\{^1H\}$ NMR (151 MHz, toluene-d_8, CO): δ 189.1 (dt, $^1J_{RhC}$ = 39, $^2J_{PC}$ = 7, CO), 163.7 (d, $^1J_{RhC}$ = 21, Ar{CRh}), 147.4 (vt, J_{PC} = 8, Ar{C}), 125.6 (s, Ar), 122.6 (vt, J_{PC} = 9, Ar), 38.1 (vt, J_{PC} = 14, $ArCH_2$), 34.9 (vt, J_{PC} = 10, *t*Bu{C}), 30.9 (vt, J_{PC} = 5, CH_2), 29.2 (s, CH_2), 29.1 (s, CH_2), 28.9 (s, CH_2), 28.6 (s, CH_2), 27.6 (s, *t*Bu{CH_3}), 26.4 (s, CH_2), 22.3 (vt, J_{PC} = 11, PCH_2).

$^{31}P\{^1H\}$ NMR (243 MHz, toluene-d_8, CO): δ 64.9 (d, $^1J_{RhP}$ = 87).

IR (toluene): ν(CO) 2069 cm^{-1}.

Anal. Calcd for $C_{31}H_{53}Cl_2OP_2Rh$ (677.52 g mol^{-1}): C, 54.96; H, 7.89; found: C, 54.99; H, 8.06.

Synthesis of rhodium complexes of POCOP-14

A solution of POCOP-14′ (217 mg, 452 μmol) and $[Rh(COE)_2Cl]_2$ (163 mg, 227 μmol) in toluene (5 mL) within a reaction flask fitted with a J Young's value was freeze–pump–thaw-degassed and placed under dihydrogen (1 atm), sealed, and heated at 120 °C for 3 days. The solution was cooled to RT and cannula transferred under dihydrogen into a reaction flask fitted with a J Young's value and charged with KO*t*Bu (61.1 mg, 545 μmol). The flask was then sealed and heated at 120 °C for 1 h to generate **13b**, which was characterised *in situ*. The solution was freeze–pump–thaw degassed and placed under carbon monoxide (1 atm) resulting in immediate formation of **14b**, which was isolated by removal of the volatiles *in vacuo* and extraction of the residue with hexane. Crude **14b** obtained in this way was dissolved in toluene (5 mL) and then slowly added to a suspension of $PhICl_2$ (125 mg, 455 μmol) in toluene (2 mL) at −78 °C. The reaction mixture was allowed to warm to RT overnight, the volatiles removed *in vacuo*, and the resulting residue extracted with hexane to afford the crude product, which was purified by alumina chromatography in air (20% CH_2Cl_2 in hexane, R_f = 0.45) to afford analytically pure **15b**. Yield: 149.3 mg (48%). Complex **15b** is stable in the solid state, but partial loss of CO was observed in solution over time.

[Rh(POCOP-14)(H_2)] (13b). This complex is unstable to vacuum but was characterised *in situ* using a sample (*ca.* 10 μmol) prepared in a similar manner within a J Young's valve NMR tube following removal of volatiles, addition of toluene-d_8 (0.5 mL) under argon, freeze–pump–thaw-degassing, and placing under dihydrogen (1 atm). T_1 values were subsequently determined following rapid freeze–pump–thaw-degassing and placing under argon.

^1H NMR (500 MHz, toluene-d_8, H_2): δ 6.94 (t, $^3J_{HH}$ = 7.9, 1H, Ar), 6.76 (d, $^3J_{HH}$ = 7.9, 2H, Ar), 1.93–2.04 (m, 4H, CH_2), 1.83–1.92 (m, 2H, PCH_2), 1.17–1.67 (m, 22H, CH_2), 1.15 (vt, J_{PH} = 7.1, 18H, *t*Bu), −2.87 (br d, $^1J_{RhH}$ = 18.8, 2H, RhH).

$^{13}C\{^1H\}$ NMR (126 MHz, toluene-d_8, H_2): δ 167.3 (vt, J_{PC} = 10, Ar{C}), 143.1 (dt, $^1J_{RhC}$ = 35, $^2J_{PC}$ = 10, Ar{CRh}), 126.7 (s, Ar), 104.8 (vt, J_{PC} = 7, Ar), 36.7 (vtd, J_{PC} = 12, $^2J_{RhC}$ = 2, *t*Bu{C}), 29.0 (vt, J_{PC} = 2, CH_2), 28.9 (s, CH_2), 28.7 (s, CH_2), 28.6 (s, CH_2), 28.1 (vtd, J_{PC} = 9, $^2J_{RhC}$ = 2, PCH_2), 27.7 (s, CH_2), 26.8 (vt, J_{PC} = 4, *t*Bu{CH_3}), 25.0 (vt, J_{PC} = 4, CH_2).

$^{31}P\{^1H\}$ NMR (162 MHz, toluene-d_8, H_2): δ 198.4 (d, $^1J_{RhP}$ = 165).

^{1}H NMR (600 MHz, toluene-d_8, Ar, selected data): δ −2.87 (br d, $^1J_{RhH}$ = 18.9, 2H, RhH, T_1 = 42 ± 2 ms).

^{1}H NMR (600 MHz, toluene-d_8, Ar, 200 K, selected data): δ −2.72 (br, 2H, RhH, T_1 = 89 ± 11 ms).

[Rh(POCOP-14)Cl$_2$(CO)] (15b)

^{1}H NMR (500 MHz, toluene-d_8, CO): δ 6.80 (t, $^3J_{HH}$ = 7.9, 1H, Ar), 6.61 (d, $^3J_{HH}$ = 7.9, 2H, Ar), 3.63 (app dp, $^2J_{HH}$ = 14.1, J = 7, 2H, PCH$_2$), 1.87–1.94 (m, 2H, CH$_2$), 1.78–1.87 (m, 2H, PCH$_2$), 1.29 (vt, J_{PH} = 7.6, 18H, *t*Bu), 1.11–1.72 (m, 22H, CH$_2$).

^{13}C{^{1}H} NMR (126 MHz, toluene-d_8, CO): δ 187.2 (dt, $^1J_{RhC}$ = 41, $^2J_{PC}$ = 5, CO), 163.6 (vt, J_{PC} = 6, Ar{C}), 136.1 (dt, $^1J_{RhC}$ = 22, $^2J_{PC}$ = 6, Ar{CRh}), 128.4 (s, Ar), 107.6 (vt, J_{PC} = 6, Ar), 41.5 (vt, J_{PC} = 11, *t*Bu{C}), 30.7 (vt, J_{PC} = 6, CH$_2$), 29.5 (s, CH$_2$), 29.4 (s, CH$_2$), 29.2 (s, CH$_2$), 28.2 (s, CH$_2$), 26.5 (s, *t*Bu{CH$_3$}), 24.1 (vt, J_{PC} = 3, CH$_2$), 23.8 (vt, J_{PC} = 13, PCH$_2$).

^{31}P{^{1}H} NMR (162 MHz, toluene-d_8, CO): δ 181.0 (d, $^1J_{RhP}$ = 92).

IR (toluene): ν(CO) 2083 cm^{-1}.

Anal. Calcd for $C_{29}H_{49}Cl_2O_3P_2Rh$ (681.46 g mol^{-1}): C, 51.11; H, 7.25; found: C, 51.09; H, 7.31.

Synthesis of iridium complexes of PCP-14

A solution of PCP-14′ (57.6 mg, 121 μmol) and [Ir(COE)$_2$Cl]$_2$ (54.1 mg, 60.4 μmol) in toluene (5 mL) within a reaction flask fitted with a J Young's value was freeze–pump–thaw-degassed and placed under dihydrogen (1 atm), sealed, and heated at 70 °C for 18 h. The solution was cooled to RT and cannula transferred under dihydrogen into a reaction flask fitted with a J Young's value and charged with KO*t*Bu (16.3 mg, 145 μmol). The flask was then sealed and heated at 120 °C for 18 h to generate **16a**, which was characterised *in situ*. The solution was freeze–pump–thaw degassed and placed under carbon monoxide (1 atm) resulting in immediate formation of *cis*-**17a**, which was characterised *in situ*. To this solution *tert*-butylethylene (78 μL, 0.60 mmol) was added and the reaction mixture heated under carbon monoxide (1 atm, sealed flask) at 120 °C for 18 h, resulting in partial conversion to *trans*-**17a** but ultimately affording [Ir(PCP-14)(CO)$_2$] (δ_{31P} 51.6). The solution was freeze–pump–thaw degassed and placed under argon to generate **18a**, filtered, and slowly added to a suspension of PhICl$_2$ (33.3 mg, 121 μmol) in toluene (1 mL) at −78 °C. The reaction mixture was allowed to warm to RT overnight, the volatiles removed *in vacuo*, and the resulting residue extracted with hexane to afford the crude product, which was purified by silica chromatography in air (40% CH$_2$Cl$_2$ in hexane, R_f = 0.43) to afford analytically pure **19a**. Yield: 76.9 mg (51%).

[Ir(PCP-14)H$_4$] (16a). This complex is unstable to vacuum but was characterised *in situ* using a sample (*ca.* 10 μmol) prepared in a similar manner within a J Young's valve NMR tube following concentration *in vacuo*, placing under dihydrogen (1 atm), concentration to dryness *in vacuo*, addition of toluene-d_8 (0.5 mL) under argon, freeze–pump–thaw-degassing, and placing under dihydrogen (1 atm). NB: Long term storage in toluene-d_8 resulted in extensive H/D exchange of the hydride ligands, pincer backbone and some positions of the tetramethylene linker. T_1 values were subsequently determined following rapid freeze–pump–thaw-degassing and placing under argon.

^{1}H NMR (600 MHz, toluene-d_8, H$_2$): δ 6.99–7.03 (m, 3H, Ar), 3.50 (dvt, $^2J_{HH}$ = 16.1, J_{PH} = 3.6, 2H, ArCH$_2$), 2.89 (dvt, $^2J_{HH}$ = 16.6, J_{PH} = 4.6, 2H, ArCH$_2$), 1.78–1.88 (m, 2H, PCH$_2$), 1.67–1.77 (m, 2H, CH$_2$), 1.53–1.63 (m, 2H, CH$_2$), 1.27–1.53 (m, 22H, CH$_2$), 0.94 (vt, J_{PH} = 6.8, 18H, *t*Bu), −8.99 (t, $^2J_{PH}$ = 9.8, 4H, IrH).

^{13}C{^{1}H} NMR (151 MHz, toluene-d_8, H$_2$): δ 151.7 (s, Ar{CIr}), 147.7 (vt, J_{PC} = 8, Ar{C}), 123.3 (s, Ar), 120.1 (vt, J_{PC} = 8, Ar), 46.1 (vt, J_{PC} = 17, ArCH$_2$), 30.0 (vt, J_{PC} = 4, CH$_2$), 29.7 (s, CH$_2$), 29.3 (vt, J_{PC} = 15, *t*Bu{C}), 29.1 (s, CH$_2$), 28.9 (s, CH$_2$), 28.2 (s, CH$_2$), 27.4 (br, CH$_2$), 27.2 (vt, J_{PC} = 15, PCH$_2$), 25.7 (vt, J_{PC} = 3, *t*Bu{CH$_3$}).

^{31}P{^{1}H} NMR (243 MHz, toluene-d_8, H$_2$): δ 49.9 (s).

^{1}H NMR (600 MHz, toluene-d_8, Ar, selected data): δ −8.99 (t, $^2J_{PH}$ = 9.8, 4H, IrH, T_1 = 300 ± 10 ms).

^{1}H NMR (600 MHz, toluene-d_8, Ar, 200 K, selected data): δ −8.95 (br, 4H, IrH, T_1 = 626 ± 15 ms).

***cis*-[Ir(PCP-14)(H)$_2$(CO)] (*cis*-17a).** This complex is most conveniently characterised *in situ* by placing a toluene-d_8 (0.5 mL) solution of analytically pure **18a** (6.0 mg, 8.6 μmol) under dihydrogen (1 atm) in a J Young's valve NMR tube.

^{1}H NMR (500 MHz, toluene-d_8): δ 6.99–7.04 (m, 3H, Ar), 3.50–3.65 (m, 2H, ArCH$_2$), 2.98 (dd, $^2J_{HH}$ = 16.0, $^2J_{PH}$ = 7.3, 1H, ArCH$_2$), 2.86 (dd, $^2J_{HH}$ = 16.8, $^2J_{PH}$ = 8.8, 1H, ArCH$_2$), 2.06–2.16 (m, 1H, PCH$_2$), 1.92–2.04 (m, 2H, CH$_2$), 1.14–1.91 (m, 25H, CH$_2$), 0.96 (d, $^2J_{PH}$ = 13.3, 9H, *t*Bu), 0.89 (d, $^2J_{PH}$ = 13.6, 9H, *t*Bu), −10.66 (ddd, $^2J_{PH}$ = 23.4, $^2J_{PH}$ = 10.5, $^2J_{HH}$ = 3.0, 1H, IrH), −11.59 (app td, $^2J_{PH}$ = 12, $^2J_{HH}$ = 3.0, 1H, IrH).

^{13}C{^{1}H} NMR (126 MHz, toluene-d_8): δ 183.3 (m, CO), 155.1 (br, Ar{CIr}), 148.8 (dd, $^2J_{PC}$ = 10, J_{PC} = 4, Ar{C}), 148.1 (dd, $^2J_{PC}$ = 9, J_{PC} = 4, Ar{C}), 123.5 (s, Ar), 120.0 (d, $^3J_{PC}$ = 14, Ar), 119.8 (d, $^3J_{PC}$ = 16, Ar), 48.4 (d, $^1J_{PC}$ = 35, ArCH$_2$), 46.2 (d, $^1J_{PC}$ = 35, ArCH$_2$), 31.2 (dd, $^1J_{PC}$ = 24, $^3J_{PC}$ = 3, *t*Bu{C}), 30.5 (dd, $^1J_{PC}$ = 27, $^3J_{PC}$ = 5, *t*Bu{C}), 30.2 (d, $^2J_{PC}$ = 10, CH$_2$), 29.9 (s, CH$_2$), 29.7 (d, $^2J_{PC}$ = 9, CH$_2$), 29.4 (s, CH$_2$), 29.3 (s, CH$_2$), 29.1 (s, CH$_2$), 28.8 (s, CH$_2$), 28.5 (s, CH$_2$), 28.3 (s, CH$_2$), 28.2 (s, CH$_2$), 27.9 (dd, $^1J_{PC}$ = 29, $^3J_{PC}$ = 4, PCH$_2$), 27.7 (s, CH$_2$), 27.3 (dd, $^1J_{PC}$ = 24, $^3J_{PC}$ = 3, PCH$_2$), 27.2 (s, CH$_2$), 26.2 (d, $^2J_{PC}$ = 4, *t*Bu{CH$_3$}), 26.1 (d, $^2J_{PC}$ = 4, *t*Bu{CH$_3$}).

^{31}P{^{1}H} NMR (162 MHz, toluene-d_8): δ 51.0 (d, $^2J_{PP}$ = 286, 1P), 45.8 (d, $^2J_{PP}$ = 286, 1P).

trans-[Ir(PCP-14)(H)$_2$(CO)] (*trans*-17a)

^{1}H NMR (400 MHz, toluene-d_0, CO, selected data): δ 1.01 (vt, $^2J_{PH}$ = 7.1, 18H, *t*Bu), −9.65 (t, $^2J_{PH}$ = 14.4, 2H, IrH).

^{31}P{^{1}H} NMR (162 MHz, toluene-d_0, CO): δ 54.1 (s).

[Ir(PCP-14)Cl$_2$(CO)] (19a)

^{1}H NMR (500 MHz, toluene-d_8): δ 6.94–7.00 (m, 3H, Ar), 3.64 (dvt, $^2J_{HH}$ = 15.8, J_{PH} = 5.0, 2H, ArCH$_2$), 3.05 (dvt, $^2J_{HH}$ = 15.8, J_{PH} = 3.8, 2H, ArCH$_2$), 2.91–3.01 (m, 2H, PCH$_2$), 1.81–1.97 (m, 2H, CH$_2$), 1.02–1.81 (m, 24H, CH$_2$), 1.13 (br, 18H, *t*Bu).

^{13}C{^{1}H} NMR (126 MHz, toluene-d_8): δ 175.7 (t, $^2J_{PC}$ = 5, CO), 155.3 (s, Ar{CIr}), 148.5 (vt, J_{PC} = 8, Ar{C}), 126.0 (s, Ar), 121.6 (vt, J_{PC} = 8, Ar), 38.9 (vt, J_{PC} = 17, ArCH$_2$), 34.3 (vt, $^1J_{PC}$ =

13, *t*Bu{C}), 30.8 (vt, J_{PC} = 5, CH_2), 29.2 (s, CH_2), 29.1 (s, CH_2), 29.0 (s, CH_2), 28.6 (s, CH_2), 27.5 (s, *t*Bu{CH_3}), 26.4 (s, CH_2), 20.6 (vt, J_{PC} = 13, PCH_2).

$^{31}P\{^1H\}$ NMR (162 MHz, toluene-d_8): δ 33.8 (s).

IR (toluene): ν(CO) 2034 cm^{-1}.

Anal. Calcd for $C_{31}H_{53}Cl_2IrOP_2$ (766.83 g mol^{-1}): C, 48.56; H, 6.97; found: C, 48.66; H, 6.92.

Synthesis of iridium complexes of POCOP-14

A solution of POCOP-14′ (69.1 mg, 144 μmol) and $[Ir(COD)Cl]_2$ (53.1 mg, 79.1 μmol) in toluene (5 mL) within a reaction flask fitted with a J Young's value was freeze–pump–thaw-degassed and placed under dihydrogen (1 atm), sealed, and heated at 100 °C for 3 days. The solution was cooled to RT and cannula transferred under dihydrogen into a reaction flask fitted with a J Young's value and charged with KO*t*Bu (19.4 mg, 173 μmol). The flask was then sealed and heated at 120 °C for 2 h to generate **16b**, which was characterised *in situ*. The solution was freeze–pump–thaw degassed and placed under carbon monoxide (1 atm) resulting in immediate formation of *cis*-**17b**, which was characterised *in situ*. To this solution *tert*-butylethylene (93 μL, 0.72 mmol) was added and the reaction mixture heated under carbon monoxide (1 atm, sealed flask) at 120 °C for 18 h, resulting in partial conversion to *trans*-**17b** but ultimately affording $[Ir(POCOP\text{-}14)(CO)_2]$ (δ_{31P} 164.8, fwhm = 127 Hz). The solution was freeze–pump–thaw degassed and placed under argon to generate **18b**, filtered, and slowly added to a suspension of $PhICl_2$ (39.5 mg, 144 μmol) in toluene (2 mL) at −78 °C. The reaction mixture was allowed to warm to RT overnight, the volatiles removed *in vacuo*, and the resulting residue extracted with hexane to afford the crude product, which was purified by silica chromatography in air (20% CH_2Cl_2 in hexane, R_f = 0.28) to afford analytically pure **19b**. Yield: 107.9 mg (73%).

[Ir(POCOP-14)H_4] (16b). This complex is unstable to vacuum, ultimately resulting in irreversible decomposition. Attempts to prepare samples in toluene-d_8 resulted in extensive H/D exchange of hydride ligands, pincer backbone and some positions of the tetramethylene linker (see ESI†). T_1 values were determined following rapid freeze–pump–thaw-degassing and placing under argon.

^{1}H NMR (500 MHz, toluene-d_0, H_2, selected data): δ 6.67 (d, $^3J_{HH}$ = 7.9, 2H, Ar), 1.07 (vt, J_{PH} = 7.5, 18H, *t*Bu), −8.26 (t, $^2J_{PH}$ = 9.9, 4H, IrH).

$^{31}P\{^1H\}$ NMR (162 MHz, toluene-d_0, H_2): δ 165.0 (s).

^{1}H NMR (600 MHz, toluene-d_0, Ar, selected data): δ −8.26 (t, $^2J_{PH}$ = 10.0, 4H, IrH, T_1 = 194 ± 4 ms).

^{1}H NMR (600 MHz, toluene-d_0, Ar, 200 K, selected data): δ −8.10 (br, 4H, IrH, T_1 = 242 ± 15 ms).

***cis*-[Ir(POCOP-14)$(H)_2$(CO)] (*cis*-17b).** This complex is most conveniently characterised *in situ* by placing a toluene-d_8 (0.5 mL) solution of analytically pure **18b** (6.0 mg, 8.6 μmol) under dihydrogen (1 atm) in a J Young's valve NMR tube.

^{1}H NMR (500 MHz, toluene-d_8): δ 6.86 (t, $^3J_{HH}$ = 7.9, 1H, Ar), 6.70 (d, $^3J_{HH}$ = 7.9, 1H, Ar), 6.70 (d, $^3J_{HH}$ = 7.9, 1H, Ar), 2.68–2.79 (m, 1H, PCH_2), 2.30–2.46 (m, 3H, CH_2), 1.85–1.97 (m, 1H, PCH_2), 1.12–1.70 (m, 23H, CH_2), 1.08 (d, $^2J_{PH}$ = 14.8, 9H, *t*Bu), 1.04 (d, $^2J_{PH}$ = 15.0, 9H, *t*Bu), −9.82 (app t, $^2J_{PH}$ = 9, 1H, IrH), −10.75 (dd, $^2J_{PH}$ = 21.8, $^2J_{PH}$ = 14.7, 1H, IrH).

$^{13}C\{^1H\}$ NMR (126 MHz, toluene-d_8): δ 180.6 (m, CO), 163.2 (dd, $^2J_{PC}$ = 6, J_{PC} = 4, Ar{C}), 162.8 (dd, $^2J_{PC}$ = 7, J_{PC} = 4, Ar{C}), 126.2 (s, Ar), 123.0 (app t, $^2J_{PC}$ = 6, Ar{CIr}), 104.8 (d, $^3J_{PC}$ = 12, Ar), 104.7 (d, $^3J_{PC}$ = 16, Ar), 37.2 (dd, $^1J_{PC}$ = 28, $^3J_{PC}$ = 7, *t*Bu{C}), 37.0 (dd, $^1J_{PC}$ = 27, $^3J_{PC}$ = 6, *t*Bu{C}), 34.6 (dd, $^1J_{PC}$ = 30, $^3J_{PC}$ = 5, PCH_2), 33.0 (dd, $^1J_{PC}$ = 27, $^3J_{PC}$ = 5, PCH_2), 30.3 (s, CH_2), 29.8 (s, CH_2), 29.7 (d, J_{PC} = 6, CH_2), 29.5 (s, CH_2), 29.16 (s, CH_2), 29.15 (s, CH_2), 28.9 (s, CH_2), 28.6 (s, CH_2), 28.5 (s, CH_2), 27.7 (d, J_{PC} = 6, CH_2), 25.7 (d, J_{PC} = 5, CH_2), 25.2 (app vt, J_{PC} = 5, *t*Bu{CH_3}), 25.1 (d, J_{PC} = 6, CH_2).

$^{31}P\{^1H\}$ NMR (162 MHz, toluene-d_8): δ 160.4 (d, $^2J_{PP}$ = 305, 1P), 154.6 (d, $^2J_{PP}$ = 305, 1P).

***trans*-[Ir(POCOP-14)$(H)_2$(CO)] (*trans*-17b)**

^{1}H NMR (400 MHz, toluene-d_0, CO, selected data): δ 1.10 (vt, J_{PH} = 7.6, 18H, *t*Bu), −9.76 (t, $^2J_{PH}$ = 16.5, 2H, IrH).

$^{31}P\{^1H\}$ NMR (162 MHz, toluene-d_0, CO): δ 167.3 (s).

[Ir(POCOP-14)Cl_2(CO)] (19b)

^{1}H NMR (500 MHz, toluene-d_8): δ 6.80 (t, $^3J_{HH}$ = 8.0, 1H, Ar), 6.64 (d, $^3J_{HH}$ = 8.0, 2H, Ar), 3.57 (app dp, $^2J_{HH}$ = 14.3, J = 7, 2H, PCH_2), 1.85–1.99 (m, 2H, CH_2), 1.72–1.83 (m, 2H, PCH_2), 1.26 (vt, J_{PH} = 7.7, 18H, *t*Bu), 1.11–1.71 (m, 22H, CH_2).

$^{13}C\{^1H\}$ NMR (126 MHz, toluene-d_8): δ 175.6 (t, $^2J_{PC}$ = 3, CO), 164.4 (vt, J_{PC} = 6, Ar{C}), 129 (obsc, Ar{CIr}), 128.9 (s, Ar), 106.8 (vt, J_{PC} = 6, Ar), 41.0 (vt, J_{PC} = 15, *t*Bu{C}), 30.3 (vt, J_{PC} = 6, $PCH_2\underline{C}H_2$), 29.5 (s, CH_2), 29.4 (s, CH_2), 29.1 (s, CH_2), 28.3 (s, CH_2), 26.5 (s, *t*Bu{CH_3}), 24.2 (vt, J_{PC} = 2, CH_2), 22.0 (vt, J_{PC} = 16, PCH_2).

$^{31}P\{^1H\}$ NMR (121 MHz, toluene-d_8): δ 144.4 (s).

IR (toluene): ν(CO) 2049 cm^{-1}.

Anal. Calcd for $C_{29}H_{49}Cl_2IrO_3P_2$ (770.77 g mol^{-1}): C, 45.19; H, 6.41; found: C, 44.95; H, 6.30.

General procedure for the preparation of Rh(I) carbonyls

To a solution of **15** (*ca.* 30 μmol) in THF (2 mL) at RT was added *i*PrMgCl·LiCl (1.3 M in THF, 3 equivalents). The resulting solution was stirred at RT for 1 h, excess MeOH added and then reduced to dryness *in vacuo*. The residue was extracted with pentane to afford the crude product on removal of volatiles, which was subsequently recrystallised by slow evaporation of $SiMe_4$.

[Rh(PCP-14)(CO)] (14a). The product was obtained following the general procedure using **15a** (20.0 mg, 29.5 μmol) and *i*PrMgCl·LiCl (68 μL, 89 μmol). Yield: 15.2 mg (85%).

^{1}H NMR (600 MHz, toluene-d_8): δ 7.06 (d, $^3J_{HH}$ = 7.3, 2H, Ar), 7.02 (t, $^3J_{HH}$ = 7.3, 1H, Ar) 3.19 (dvt, $^2J_{HH}$ = 16.3, J_{PH} = 3.4, 2H, $ArC\underline{H}_2$), 3.15 (dvt, $^2J_{HH}$ = 16.5, J_{PH} = 4.2, 2H, $ArC\underline{H}_2$), 2.10–2.01 (m, 2H, CH_2), 1.77–1.36 (m, 26H, CH_2), 1.00 (vt, J_{PH} = 6.6, 18H, *t*Bu).

$^{13}C\{^1H\}$ NMR (151 MHz, toluene-d_8): δ 201.5 (dvt, $^1J_{RhC}$ = 57, $^2J_{PC}$ = 12, CO), 179.4 (dt, $^1J_{PC}$ = 29, $^2J_{PC}$ = 7, Ar{CRh}), 152.2 (vt, J_{PC} = 12, Ar{C}), 125.7 (s, Ar), 120.5 (vt, J_{PC} = 9, Ar), 41.3 (vt, J_{PC} = 12, $Ar\underline{C}H_2$), 32.7 (vt, J_{PC} = 11, *t*Bu{C}), 30.5 (vt, J_{PC} = 4,

CH_2), 29.4 (s, CH_2), 29.2 (s, CH_2), 29.0 (s, CH_2), 28.52 (vt, J_{PC} = 4, *t*Bu{CH_3}), 28.47 (s, CH_2), 26.4 (vt, J_{PC} = 4, CH_2), 24.2 (vt, $^1J_{PC}$ = 9, PCH_2).

$^{31}P\{^1H\}$ NMR (243 MHz, toluene-d_8): δ 75.0 (d, $^1J_{RhP}$ = 146).

IR (toluene): ν(CO) 1939 cm^{-1}.

Anal. Calcd for $C_{31}H_{53}OP_2Rh$ (606.62 g mol^{-1}): C, 61.38; H, 8.81; found: C, 61.34; H, 8.74.

[Rh(POCOP-14)(CO)] (14b). The product was obtained following the general procedure using **15b** (20.0 mg, 29.3 μmol) and *i*PrMgCl·LiCl (68 μL, 89 μmol). Yield: 16.8 mg (94%).

^1H NMR (600 MHz, toluene-d_8): δ 6.91 (t, $^3J_{HH}$ = 7.9, 1H, Ar), 6.70 (d, $^3J_{HH}$ = 7.9, 2H, Ar), 2.00–2.06 (m, 4H, PCH_2), 1.73–1.85 (m, 4H, CH_2), 1.26–1.60 (m, 20H, CH_2), 1.15 (vt, J_{PH} = 7.2, 18H, *t*Bu).

$^{13}C\{^1H\}$ NMR (151 MHz, toluene-d_8): δ 201.2 (dt, $^1J_{RhC}$ = 60, $^2J_{PC}$ = 10, CO), 167.7 (vt, J_{PC} = 9, Ar{C}), 145.5 (dt, $^1J_{RhC}$ = 26, $^2J_{PC}$ = 10, Ar{CRh}), 128.8 (obsc, Ar), 104.8 (vt, J_{PC} = 7, Ar), 38.1 (vt, $^1J_{PC}$ = 12, *t*Bu{C}), 30.6 (br, CH_2), 29.4 (s, CH_2), 29.3 (s, CH_2), 29.24 (vt, J_{PC} = 9, PCH_2), 29.16 (s, CH_2), 28.8 (s, CH_2), 26.8 (vt, J_{PC} = 4, *t*Bu{CH_3}), 25.8 (vt, J_{PC} = 4, CH_2).

$^{31}P\{^1H\}$ NMR (243 MHz, toluene-d_8): δ 201.6 (d, $^1J_{RhP}$ = 156).

IR (toluene): ν(CO) 1958 cm^{-1}.

Anal. Calcd for $C_{29}H_{49}O_3P_2Rh$ (610.56 g mol^{-1}): C, 57.05; H, 8.09; found: C, 57.14; H, 8.07.

General procedure for the preparation of Ir(I) carbonyl complexes

A solution of **19** (*ca.* 20 μmol) in pentane (2 mL) was added to a flask charged with KC_8 (10 equivalents) and stirred at RT for 2 days. The solution was filtered, reduced to dryness *in vacuo*, and the analytically pure product obtained following recrystallisation.[16]

[Ir(PCP-14)(CO)] (18a). Following the general procedure using **19a** (17.2 mg, 22.4 μmol) and KC_8 (30.4 mg, 225 μmol), **18a** was obtained following recrystallisation by slow evaporation of neohexane. Yield: 13.1 mg (84%).

^1H NMR (500 MHz, toluene-d_8): δ 7.14 (d, $^3J_{HH}$ = 7.5, 2H, Ar), 7.02 (t, $^3J_{HH}$ = 7.5, 1H, Ar), 3.35 (dvt, $^2J_{HH}$ = 16.4, J_{PH} = 4.0, 2H, $ArC\underline{H}_2$), 3.09 (dvt, $^2J_{HH}$ = 16.4, J_{PH} = 3.8, 2H, $ArC\underline{H}_2$), 2.03–2.19 (m, 2H, CH_2), 1.90–1.78 (m, 2H, PCH_2), 1.76–1.34 (m, 24H, CH_2), 1.01 (vt, J_{PH} = 6.7, 18H, *t*Bu).

$^{13}C\{^1H\}$ NMR (126 MHz, toluene-d_8): δ 198.6 (t, $^2J_{PC}$ = 7, CO), 181.3 (t, $^2J_{PC}$ = 4, Ar{CIr}), 153.8 (vt, J_{PC} = 11, Ar{C}), 126.1 (s, Ar), 120.2 (vt, J_{PC} = 8, Ar), 41.7 (vt, J_{PC} = 15, $Ar\underline{C}H_2$), 33.5 (vt, J_{PC} = 14, *t*Bu{C}), 30.5 (vt, J_{PC} = 5, CH_2), 29.5 (s, CH_2), 29.3 (s, CH_2), 29.0 (s, CH_2), 28.5 (s, CH_2), 28.2 (vt, J_{PC} = 3, *t*Bu{CH_3}), 26.3 (vt, J_{PC} = 3, CH_2), 24.2 (vt, J_{PC} = 13, PCH_2).

$^{31}P\{^1H\}$ NMR (162 MHz, toluene-d_8): δ 68.1 (s).

IR (toluene): ν(CO) 1925 cm^{-1}.

Anal. Calcd for $C_{31}H_{53}IrOP_2$ (695.93 g mol^{-1}): C, 53.50; H, 7.68; found: C, 53.24; H, 7.76.

[Ir(POCOP-14)(CO)] (18b). Following the general procedure using **19b** (12.3 mg, 16.0 μmol) and KC_8 (21.6 mg, 160 μmol), **18b** was obtained following recrystallisation by slow evaporation of $SiMe_4$. Yield: 8.8 mg (79%).

^1H NMR (500 MHz, toluene-d_8): δ 6.87 (t, $^3J_{HH}$ = 7.9, 1H, Ar), 6.74 (d, $^3J_{HH}$ = 7.9, 2H, Ar), 2.03–2.19 (m, 4H, CH_2), 1.73–1.87 (m, 4H, CH_2), 1.23–1.66 (m, 20H, CH_2), 1.15 (vt, J_{PH} = 7.4, 18H, *t*Bu).

$^{13}C\{^1H\}$ NMR (126 MHz, toluene-d_8): δ 200.5 (t, $^2J_{PC}$ = 5, CO), 168.3 (vt, J_{PC} = 8, Ar{C}), 148.7 (t, $^2J_{PC}$ = 9, Ar{CIr}), 129.5 (s, Ar), 104.4 (vt, J_{PC} = 6, Ar), 39.5 (vt, J_{PC} = 16, *t*Bu{C}), 30.8 (vt, J_{PC} = 2, CH_2), 29.6 (vt, J_{PC} = 14, PCH_2), 29.4 (s, CH_2), 29.3 (s, CH_2), 29.2 (s, CH_2), 28.9 (s, CH_2), 26.7 (vt, J_{PC} = 3, *t*Bu{CH_3}), 26.0 (vt, J_{PC} = 3, CH_2).

$^{31}P\{^1H\}$ NMR (162 MHz, toluene-d_8): δ 186.7 (s).

IR (toluene): ν(CO) 1943 cm^{-1}.

Anal. Calcd for $C_{29}H_{49}IrO_3P_2$ (699.87 g mol^{-1}): C, 49.77; H, 7.06; found: C, 49.85; H 7.01.

Crystallographic details

Data were collected on a Rigaku Oxford Diffraction SuperNova AtlasS2 CCD diffractometer using graphite monochromated Mo Kα (λ = 0.71073 Å) or CuKα (λ = 1.54184 Å) radiation and an Oxford Cryosystems N-HeliX low temperature device [150(2) K]. Data were collected and reduced using CrysAlisPro and refined using SHELXL,[29] through the Olex2 interface.[30] Full details about the collection, solution, and refinement are documented in CIF format, which have been deposited with the Cambridge Crystallographic Data Centre under CCDC 1972811–1972820.†

Conflicts of interest

There are no conflicts to declare.

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References

1 (*a*) *Pincer Compounds: Chemistry and Applications*, ed. D. Morales-Morales, Elsevier, 2018, vol. 1; (*b*) S. Murugesan and K. Kirchner, *Dalton Trans.*, 2016, **45**, 416–439; (*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, in *Topics in Organometallic Chemistry*, ed. G. van Koten and R. A. Gossage, Springer, 2016; vol. 45; (*e*) M. Asay and D. Morales-Morales, *Dalton Trans.*, 2015, **44**, 17432–17447; (*f*) S. Werkmeister, J. Neumann, K. Junge and M. Beller, *Chem. – Eur. J.*, 2015, **21**, 12226–12250;

(*g*) *Pincer and Pincer-Type Complexes: Applications in Organic Synthesis and Catalysis*, ed. K. J. Szabó and O. F. Wendt, Wiley-VCH, 2014; (*h*) *Organometallic Pincer Chemistry*; ed. G. van Koten and D. Milstein, *Topics in Organometallic Chemistry*, Springer, 2013, vol. 40; (*i*) M. Albrecht and M. M. Lindner, *Dalton Trans.*, 2011, **40**, 8733–8744; (*j*) J. I. van der Vlugt and J. N. H. Reek, *Angew. Chem., Int. Ed.*, 2009, **48**, 8832–8846; (*k*) M. E. van der Boom and D. Milstein, *Chem. Rev.*, 2003, **103**, 1759–1792; (*l*) M. Albrecht and G. van Koten, *Angew. Chem., Int. Ed.*, 2001, **40**, 3750–3781.

2 C. J. Moulton and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1976, 1020–1024.

3 (*a*) A. Kumar, T. M. Bhatti and A. S. Goldman, *Chem. Rev.*, 2017, **117**, 12357–12384; (*b*) J. Choi, A. H. R. MacArthur, M. Brookhart and A. S. Goldman, *Chem. Rev.*, 2011, **111**, 1761–1779.

4 E. Peris and R. H. Crabtree, *Chem. Soc. Rev.*, 2018, **47**, 1959–1968.

5 (*a*) M. R. Gyton, B. Leforestier and A. B. Chaplin, *Organometallics*, 2018, **37**, 3963–3971; (*b*) C. M. Storey, M. R. Gyton, R. E. Andrew and A. B. Chaplin, *Angew. Chem., Int. Ed.*, 2018, **57**, 12003–11200; (*c*) S. L. Apps, R. E. Alflatt, B. Leforestier, C. M. Storey and A. B. Chaplin, *Polyhedron*, 2018, **143**, 57–61; (*d*) R. E. Andrew, C. M. Storey and A. B. Chaplin, *Dalton Trans.*, 2016, **45**, 8937–8944; (*e*) R. E. Andrew, D. W. Ferdani, C. A. Ohlin and A. B. Chaplin, *Organometallics*, 2015, **34**, 913–917; (*f*) R. E. Andrew and A. B. Chaplin, *Inorg. Chem.*, 2015, **54**, 312–322; (*g*) R. E. Andrew and A. B. Chaplin, *Dalton Trans.*, 2014, **43**, 1413–1423.

6 T. M. Hood, M. R. Gyton and A. B. Chaplin, *Dalton Trans.*, 2020, DOI: 10.1039/c9dt04474d.

7 (*a*) E. Salomó, S. Orgué, A. Riera and X. Verdaguer, *Synthesis*, 2016, **48**, 2659–2663; (*b*) S. Orgué, A. Flores-Gaspar, M. Biosca, O. Pàmies, M. Diéguez, A. Riera and X. Verdaguer, *Chem. Commun.*, 2015, **51**, 17548–17551; (*c*) T. León, A. Riera and X. Verdaguer, *J. Am. Chem. Soc.*, 2011, **133**, 5740–5743.

8 D. Mimeau, O. Delacroix and A.-C. Gaumont, *Chem. Commun.*, 2003, 2928–2929.

9 Z. Pakulski, O. M. Demchuk, R. Kwiatosz, P. W. Osiński, W. Świerczyńska and K. M. Pietrusiewicz, *Tetrahedron: Asymmetry*, 2003, **14**, 1459–1462.

10 K. Zhu, P. D. Achord, X. Zhang, K. Krogh-Jespersen and A. S. Goldman, *J. Am. Chem. Soc.*, 2004, **126**, 13044–13053.

11 (*a*) G. J. Kubas, *Metal Dihydrogen and σ-Bond Complexes*, Kluwer Academic Publishers, 2001; (*b*) R. H. Crabtree, *Chem. Rev.*, 2016, **116**, 8750–8769.

12 (*a*) M. Findlater, K. M. Schultz, W. H. Bernskoetter, A. Cartwright-Sykes, D. M. Heinekey and M. Brookhart, *Inorg. Chem.*, 2012, **51**, 4672–4678; (*b*) K.-W. Huang, J. H. Han, C. B. Musgrave and E. Fujita, *Organometallics*, 2007, **26**, 508–513.

13 It is interesting to note that the $PC\underline{H}_2$ resonances of the $M^{III}Cl_2(CO)$ derivatives are appreciably diastereotopic, giving rise to downfield 2H signals at *ca.* δ 3.0 (PCP-14) and 3.6 (POCOP-14) presumably as a consequence of diamagnetic anisotropy induced by close proximity to the chloride ligands. See for example: A. M. Camp, M. R. Kita, J. Grajeda, P. S. White, D. A. Dickie and A. J. M. Miller, *Inorg. Chem.*, 2017, **56**, 11141–11150.

14 For structures of [M(pincer)(CO)] (M = Rh, Ir; pincer = PCP-*t*Bu, POCOP-*t*Bu) see: (*a*) M. Montag, I. Efremenko, R. Cohen, L. J. W. Shimon, G. Leitus, Y. Diskin-Posner, Y. Ben-David, H. Salem, J. M. L. Martin and D. Milstein, *Chem. – Eur. J.*, 2010, **16**, 328–353; (*b*) S. A. Kuklin, A. M. Sheloumov, F. M. Dolgushin, M. G. Ezernitskaya, A. S. Peregudov, P. V. Petrovskii and A. A. Koridze, *Organometallics*, 2006, **25**, 5466–5476; (*c*) K.-W. Huang, D. C. Grills, J. H. Han, D. J. Szalda and E. Fujita, *Inorg. Chim. Acta*, 2008, **361**, 3327–3331; (*d*) D. Morales-Morales, R. Redón, Z. Wang, D. W. Lee, C. Yung, K. Magnuson and C. M. Jensen, *Can. J. Chem.*, 2001, **79**, 823–829.

15 T. J. Hebden, K. I. Goldberg, D. M. Heinekey, X. Zhang, T. J. Emge, A. S. Goldman and K. Krogh-Jespersen, *Inorg. Chem.*, 2010, **49**, 1733–1742.

16 Reduction of **19a/b** can also be achieved by reaction with *i*PrMgCl·LiCl (3 equiv.) in THF. Whilst **18a/b** are formed in quantitative spectroscopic yield within 4 h at RT, they decompose on treatment with protic solvents that are needed to quench the excess Grignard reagent.

17 For NHC and phosphine ligands see: (*a*) H. V. Huynh, *Chem. Rev.*, 2018, **118**, 9457–9492; (*b*) T. Dröge and F. Glorius, *Angew. Chem., Int. Ed.*, 2010, **49**, 6940–6952; (*c*) R. A. Kelly III, H. Clavier, S. Giudice, N. M. Scott, E. D. Stevens, J. Bordner, I. Samardjiev, C. D. Hoff, L. Cavallo and S. P. Nolan, *Organometallics*, 2008, **27**, 202–210; (*d*) C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313–348; (*e*) C. A. Tolman, *J. Am. Chem. Soc.*, 1970, **92**, 2953–2956.

18 (*a*) G. L. Parker, S. Lau, B. Leforestier and A. B. Chaplin, *Eur. J. Inorg. Chem.*, 2019, 3791–3798; (*b*) L. Maser, C. Schneider, L. Vondung, L. Alig and R. Langer, *J. Am. Chem. Soc.*, 2019, **141**, 7596–7760; (*c*) J. J. Davidson, J. C. DeMott, C. Douvris, C. M. Fafard, N. Bhuvanesh, 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.

19 T. R. Hoye, B. M. Eklov and M. Voloshin, *Org. Lett.*, 2004, **6**, 2567–2570.

20 Y. Chen, T. P. Clark, B. A. Jazdzewski, S. B. Klamo and T. T. Wenzel, *Polyhedron*, 2014, **84**, 32–36.

21 M. S. Carle, G. K. Shimokura and G. K. Murphy, *Eur. J. Org. Chem.*, 2016, 3930–3933.

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

23 A. van der Ent, A. L. Onderdelinden and R. A. Schunn, *Inorg. Synth.*, 1990, **28**, 90–92.

24 J. L. Herde, J. C. Lambert, C. V. Senoff and M. A. Cushing, *Inorg. Synth.*, 1974, **15**, 18–20.

25 (*a*) S. Nemeh, C. Jensen, E. Binamira-Soriaga and W. C. Kaska, *Organometallics*, 1983, **2**, 1442–1447; (*b*) I. Göttker-Schnetmann, P. S. White and M. Brookhart,

Organometallics, 2004, **23**, 1766–1776; (*c*) A. V. Polezhaev, S. A. Kuklin, D. M. Ivanov, P. V. Petrovskii, F. M. Dolgushin, M. G. Ezernitskaya and A. A. Koridze, *Russ. Chem. Bull.*, 2009, **58**, 1847–1854.

26 G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176–2179.

27 C. R. Hilliard, N. Bhuvanesh, J. A. Gladysz and J. Blümel, *Dalton Trans.*, 2012, **41**, 1742–1754.

28 Data for a mixture of the *cis*- and *trans*-diastereoisomers.

29 G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3–8.

30 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.