Planar-chiral imidazole-based phosphine ligands derived from [2.2]paracyclophane†

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Two planar chiral heteroaryl monophosphines have been synthesised and studied. The phosphines are readily prepared from 4-imidazole[2.2]paracyclophane by selective deprotonation and reaction with the appropriate dialkylchlorophosphines. The planar chiral imidazole was constructed in four steps from readily available [2.2]paracyclophane. The 2-phosphino-*N*-[2.2]paracyclophanes were active in the Suzuki–Miyaura coupling of aryl bromides and chlorides. Coordination studies indicate *P*,*N*-chelation in the solid-state. These studies lay the foundations for asymmetric couplings.

Introduction

Bulky, electron-rich phosphines have been successfully used to stabilise active palladium species for cross-coupling reactions.[1] To date, much of the work has concentrated on biaryl monophosphines (*e.g.* **1**; Fig. 1),[2] for which it has been postulated that a secondary interaction with the lower arene ring results in a pseudo-bidentate coordination of the ligand.[3] An alternative ligand class that promotes high reactivity is the 2-phosphino-*N*-aryl imidazoles (*e.g.* **2**).[4-7] Structurally characterised examples of isolated palladium(II) compounds incorporating **2** show unusual four-membered metallacycles generated through *P*,*N*-chelation of the ligand.[5,7,8]

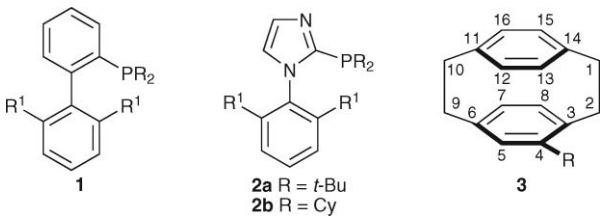


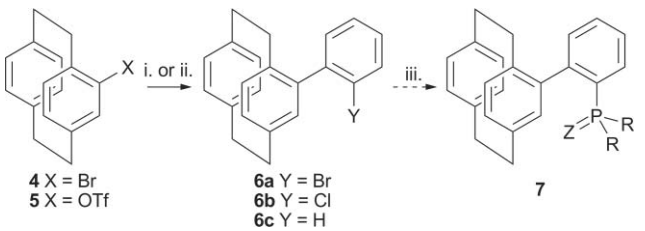
Fig. 1 Various monophosphine ligands and [2.2]paracyclophane numbering.

The singular structure of [2.2]paracyclophane (**3**, R = H) bestows unique electronic and steric properties on its derivatives, making them excellent scaffolds for a range of applications.[9,10] Many derivatives exhibit planar chirality and have found use as chiral ligands for enantioselective catalysis.[11] Of these chiral compounds, the most successful is 4,12-bis(diphenylphosphino)[2.2]paracyclophane (PhanePhos), a commercially available diphosphine that is employed in catalytic asymmetric reductions.[12] A number of other mono- and diphosphines derived from [2.2]paracyclophane have also been reported.[13]

Building upon chemistry previously developed within our laboratory,[10,14,15] we have synthesised a new class of planar-chiral imidazole-based phosphine ligands. We present preliminary results of their behaviour in the Suzuki–Miyaura reaction and the structural characterisation of a representative Pd(II) compound that confirms bidentate coordination at the metal.

Results and discussion

Due to the success of Buchwald's biaryl monophosphines **1**, the initial target was an analogue of JohnPhos (**1**; R = *t*-Bu; R^1 = H), in which the lower arene ring has been replaced by [2.2]paracyclophane (*e.g.* **7**; Z = lone pair; Scheme 1). To this end, 4-(2-bromophenyl)[2.2]paracyclophane **6a** (Y = Br) was prepared from 4-bromo[2.2]paracyclophane **4** by Roche's methodology.[16] The low yield was a result of unproductive consumption of 1,2-dibromobenzene under the reaction conditions. The chloride **6b** (X = Cl) was prepared by Suzuki–Miyaura aryl coupling of [2.2]paracyclophan-4-yl triflate **5** and 2-chlorophenylboronic acid. Unfortunately, it proved impossible to substitute either halide **6a/b** for a phosphine moiety; conversion to the organolithium species or Grignard reagent resulted in the recovery of 4-phenyl[2.2]paracyclophane **6c** whilst attempts at palladium-mediated C–P bond formation[17] gave either unreacted starting material or **6c**. Aryl coupling of



Scheme 1 Attempted synthesis of phosphine **7**. Reagents and conditions: i. (a) *t*-BuLi (2.05 eq.), $B(OMe)_3$ (2.5 eq.), THF; (b) $Pd(PPh_3)_4$ (0.06 eq.), $1,2\text{-}Br_2C_6H_4$ (1.3 eq.), K_2CO_3 (2.7 eq.), tol/H_2O, reflux, 13% (**6a**; Y = Br); ii. Pd_2dba_3 (0.03 eq.), SPhos (0.06 eq.), $2\text{-}ClC_6H_4B(OH)_2$ (2 eq.), K_3PO_4 (3 eq.), toluene, reflux, 55% (**6b**; Y = Cl); iii. Failed with combinations of *n*-BuLi, *t*-BuLi, Mg, Bu_2*i*PrMgLi, R_2PCl, $R_2P(O)Cl$ and $Pd(OAc)_2$, DiPPF, *t*-BuOK, $HPCy_2$.

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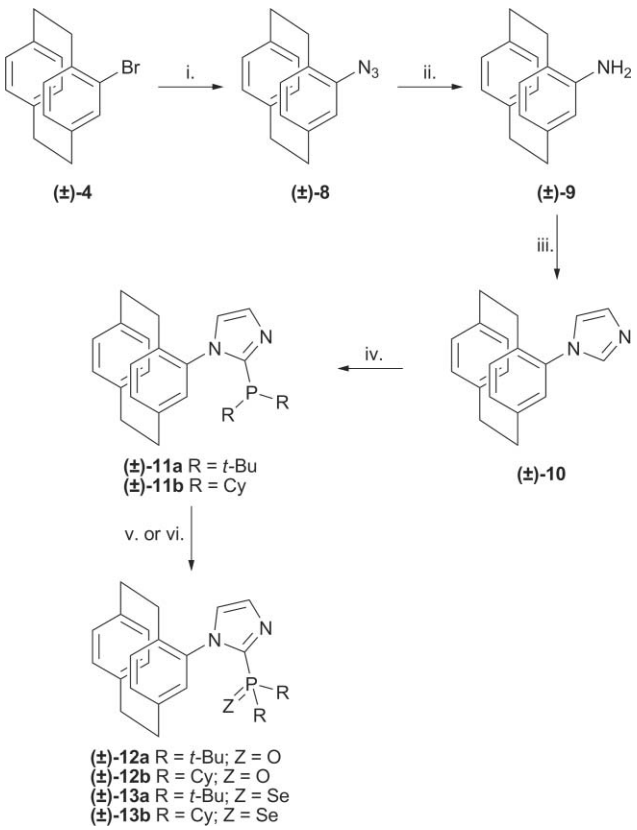
(2-bromophenyl)dicyclohexylphosphine oxide with **4** employing either Roche's conditions or a Negishi coupling also failed to yield the desired compound. Whilst the latter couplings failed due to the steric bulk of [2.2]paracyclophane, the failure of **6a/b** in simple anion chemistry is less understandable.

Experience within our group indicated that formation of a planar chiral analogue of **2** would be more achievable.[18] Racemic 4-amino[2.2]paracyclophane (±)-**9** was prepared in 2 steps from 4-bromo[2.2]paracyclophane (±)-**4** (Scheme 2). First, lithium–halogen exchange followed by reaction with tosyl azide gave (±)-**8**, which was then reduced with $NaBH_4$ under phase transfer conditions to give (±)-**9**. Whilst it is possible to reduce the crude 4-azo[2.2]paracyclophane (±)-**8**, higher, and more reproducible yields are obtained when (±)-**8** is purified prior to reduction.[15] The optimal conditions for the conversion of (±)-**9** into imidazole (±)-**10** were found to be treatment with paraformaldehyde, ammonium chloride, glyoxal and catalytic phosphoric acid in THF/dioxane at reflux.[19] All other conditions gave low yields with polymeric material predominating. It is important to basify (pH = 8–11) the reaction mixture prior to extraction of (±)-**10** as the protonated imidazole shows surprisingly high water solubility. Selective functionalisation of the imidazole ring was achieved by deprotonation with *n*-butyllithium in THF/TMEDA,



Scheme 2 Synthesis of 2-phosphino-*N*-[2.2]paracyclophane imidazoles. Reagents and conditions: i. (a) *n*-BuLi (1.05 eq.), THF, −78 °C; (b) TsN_3 (1.05 eq.), −78 °C to rt, 60%; ii. $NaBH_4$ (11 eq.), *n*-Bu_4NI (1 eq.), THF–H_2O, rt, 97%; iii. $(CH_2O)_n$ (2.5 eq.), NH_4Cl (2.5 eq.), $C_2H_2O_2$ (2.5 eq.), H_3PO_4 (2 drops), dioxane/H_2O, reflux, 63%; iv. (a) *n*-BuLi (1.05 eq.), TMEDA (1.05 eq.), THF, −78 °C; (b) $ClPR_2$ (1.05 eq.), −78 °C to rt, 49% (R = *t*-Bu), 44% (R = Cy); v. H_2O_2 (xs), $CDCl_3$, rt, 89% (R = *t*-Bu), 100% (R = Cy); vi. Se, $CDCl_3$, 50 °C.

followed by reaction with chlorophosphines R_2PCl (R = *t*-Bu, Cy) to afford (±)-**11a** and (±)-**11b** in moderate yields. Extensive attempts to improve the yields by varying temperature, solvent and co-solvent were unsuccessful. Compounds (±)-**11** are air-stable crystalline solids that can be handled and stored in air but slowly oxidise in solution. The phosphine oxides (±)-**12** were prepared by oxidation with hydrogen peroxide. Non-racemic monophosphines ((***R***$_p$)-**11**) were prepared from enantiomerically enriched amine (***R***$_p$)-**4**, formed *via* either classic resolution[20] or by our own sulfoxide-based methodology.[15] Yields were, of course, comparable to the racemic system. All the subsequent studies were performed on racemic (±)-**11a/b**.

The ^{1}H NMR spectrum of **11a** reveals the effect of planar chirality with the diastereotopic *tert*-butyl groups exhibiting very different chemical shifts (0.79 and 1.35 ppm). Both molecules show characteristic high field resonances for the *ortho* (H5) hydrogen of the paracyclophane ring (6.32 ppm for **11a** and 6.36 for **11b**) and the *syn* C1 and C2 hydrogens (2.89–2.84 and 2.77–2.71 ppm for **11a** and 2.77–2.72 for **11b**). The electronic and steric environment of the phosphorus appears similar to the achiral phosphines **2**; ^{31}P NMR of **11a** = 8.74 ppm and **11b** = −20.8 ppm compared to values of 10.2 ppm and −23.3 ppm reported for **2a** and **2b** (R^1 = *i*Pr) respectively.[4] There is an inverse relationship between the magnitude of the ^{77}Se–^{31}P coupling constant and the σ-basicity.[21] To ascertain the relative σ-basicity of **11a** and **11b** they were converted to the corresponding phosphine selenides **13a** and **13b** on an NMR scale using elemental selenium.‡ The $^1J_{SeP}$ coupling constants (**13a** 730 Hz; **13b** 753 Hz) suggest lower σ-basicity than in compounds **2**, for which corresponding values of 726 Hz and 732 Hz were reported for **2a** and **2b** (R^1 = *i*Pr), respectively.[4]

X-Ray diffraction data (Tables 1 and 2) confirm **11a** and **11b** as the triorganophosphines, with pyramidal phosphorus atoms and C–P–C angles in the range 100.34(11)–111.47(13) and 98.63(19)–103.66(18), respectively (Fig. 2). The bonds to the phosphino and [2.2]paracyclophane substituents are approximately coplanar with the imidazole ring [P–C17–N1–C4 torsion angles (α): **11a**, 5.22(33)°; **11b**, 0.36(58)°], with bond lengths consistent with other 2-phosphino-*N*-substituted imidazoles.[5,22] The C2 bridgehead methylene group prevents the imidazole ring and the substituted "top" deck of the [2.2]paracyclophane from adopting a coplanar arrangement [angle between C_3N_2- and C_6-least squares planes (β): **11a**, 56.91(8)°; **11b** 45.42(19)°], preventing effective π-conjugation between these two units.

The molecular structure of phosphine oxide **12a** has also been determined by X-ray diffraction (Fig. 2). We note that conversion to the P(v) analogue has negligible effect on the bond lengths compared with phosphine **11a** (Table 2), and the overall conformation of the molecule remains very similar [$\alpha = -1.09(33)°$ and $\beta = 51.80(08)°$, Fig. 3]. This suggests a stable arrangement of the paracyclophane, imidazole and phosphine substituents in the solid-state for **11a**.

We investigated the potential of (±)-**11a** and (±)-**11b** in the palladium mediated coupling of 4-bromotoluene and 4-chlorotoluene with phenylboronic acid (Table 3). In both cases, the di-*tert*-butyl derivative **11a** gave better results, with yields of 90% and 53% for

‡ Reactions performed on an NMR scale and compounds not purified. Selected analytical data: **13a** ^{31}P NMR (202 MHz, $CDCl_3$): δ 62.2 (d, J 730). **13b** ^{31}P NMR (202 MHz, $CDCl_3$): δ 41.9 (d, J 753).

Table 1 Crystal structure and refinement data for **11a**, **11b**, **12a** and **14a**

	11a	**11b**	**12a**	**14a**
Formula	$C_{27}H_{35}N_2P$	$C_{31}H_{39}N_2P$	$C_{27}H_{35}N_2OP$, $0.5(C_6H_{12})$	$C_{27}H_{35}Cl_2N_2PPd$, CH_2Cl_2
Formula weight	418.54	470.61	476.62	680.77
T/K	173(2)	173(2)	173(2)	173(2)
Wavelength/Å	0.71073	0.71073	0.71073	0.71073
Crystal size/mm	$0.30 \times 0.05 \times 0.02$	$0.20 \times 0.05 \times 0.02$	$0.35 \times 0.10 \times 0.10$	$0.30 \times 0.20 \times 0.10$
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1$ (No. 4)
a/Å	8.4500(6)	10.7792(3)	9.1186(3)	7.7953(2)
b/Å	11.6495(9)	15.7625(8)	11.6152(3)	13.8315(3)
c/Å	12.9271(8)	15.3052(7)	13.9871(4)	13.0449(3)
α/°	109.719(4)	90	105.127(1)	90
β/°	90.305(5)	97.193(3)	105.574(2)	91.366(2)
γ/°	98.638(3)	90	102.542(2)	90
V/Å^3	1182.17(14)	2580.00(19)	1310.24(7)	1406.11(6)
Z	2	4	2	2
D_c/Mg m^{-3}	1.18	1.21	1.21	1.61
Absorption coefficient/mm^{-1}	0.13	0.13	0.13	1.12
θ range for data collection/°	3.54 to 25.93	3.48 to 26.00	3.61 to 26.02	3.41 to 26.07
Reflections collected	16 283	39 349	18 924	16 669
Independent reflections	4541 [$R_{int} = 0.091$]	5049 [$R_{int} = 0.230$]	5112 [$R_{int} = 0.043$]	5426 [$R_{int} = 0.044$]
Reflections with $I > 2\sigma(I)$	3240	2851	4188	5243
Data/restraints/parameters	4541/0/277	5049/0/307	5112/0/313	5426/3/320
Goodness-of-fit on F^2	1.039	1.111	1.045	1.045
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.060$	$R_1 = 0.095$	$R_1 = 0.054$	$R_1 = 0.038$
	$wR_2 = 0.122$	$wR_2 = 0.141$	$wR_2 = 0.143$	$wR_2 = 0.105$
R indices (all data)	$R_1 = 0.097$	$R_1 = 0.185$	$R_1 = 0.069$	$R_1 = 0.040$
	$wR_2 = 0.140$	$wR_2 = 0.168$	$wR_2 = 0.153$	$wR_2 = 0.107$
Largest diff. peak/hole/e Å^3	0.21 and –0.28	0.31 and –0.34	0.87 and –0.69	0.99 and –0.83

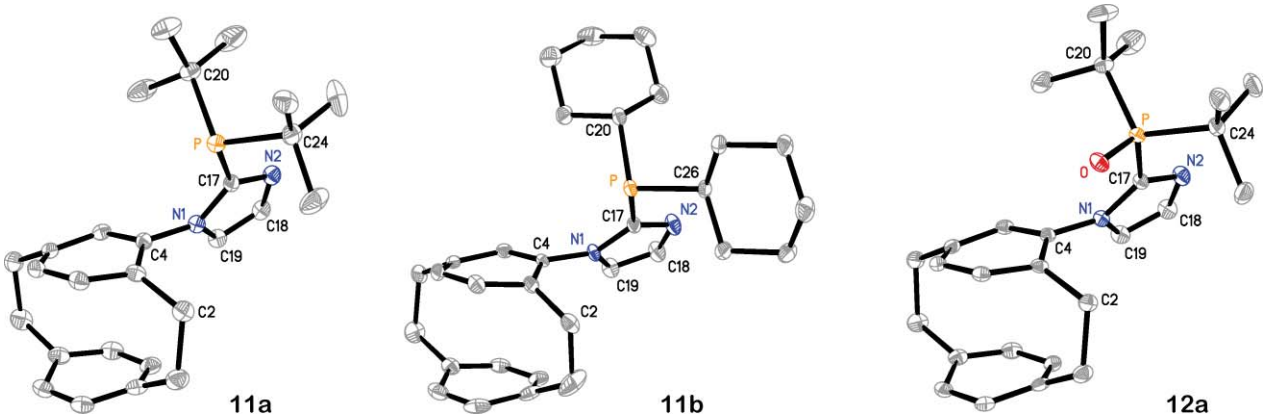


Fig. 2 Thermal elliposid (30%) plots of **11a**, **11b** and **12a** (hydrogen atoms omitted).

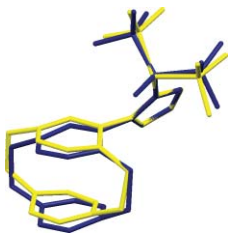


Fig. 3 Overlay of **11a** (yellow) and **12a** (blue) mapping the imidazole ring and phosphorus positions.

the bromide and chloride, respectively. The best conditions for the coupling of 4-bromotoluene employed a 1 : 1 mixture of THF and water (entry 10), whilst dioxane gave better results for the chloride. It should be noted that $Pd(OAc)_2$ catalyses the coupling of the bromide even in the absence of phosphine ligand. Interestingly, a lower ratio of palladium to ligand gave better results for the *tert*-butylphosphine **11a** (entries 5 *vs.* 6; entries 7 *vs.* 8) with the opposite trend noted for the dicyclohexylphosphine **11b** (entries 1 *vs.* 2; entries 3 *vs.* 4). Coupling of the aryl chloride benefited from an increased ratio of Pd : **11a/b**; the best results were achieved with either a 1 : 10 ratio of $Pd(OAc)_2$: **11a** (entry 16) although this could be lowered if an alternative source of Pd was employed (entry 20).

To examine ligand/metal interactions with these phosphines, the reaction between **11a** and $PdCl_2(COD)$ was performed. The product, **14a**, was isolated as pale pink crystals, which analysed as the monophosphine complex [$PdCl_2$(**11a**)](Fig. 4). Single crystal X-ray diffraction confirmed *P*,*N*-chelation of the ligand,[5,7,8] with a distorted square planar metal [angles in the range 70.68(11)–99.96(5)°] in which the bite angle of the ligand forms the smallest

Table 2 Selected bond lengths (Å) and angles (°) for **11a**, **11b** and **12a**

	11a	**11b**	**12a**
P–C17	1.828(2)	1.828(4)	1.825(2)
P–C20	1.893(3)	1.860(4)	1.857(2)
P–C24	1.883(3)	—	1.859(2)
P–C26	—	1.855(4)	—
P–O	—	—	1.4841(15)
N1–C17	1.386(3)	1.384(5)	1.381(3)
N2–C17	1.329(3)	1.327(5)	1.323(3)
N1–C4	1.435(3)	1.439(5)	1.438(3)
C17–P–C20	100.34(11)	100.55(19)	103.49(10)
C17–P–C24	102.69(12)	—	104.67(10)
C20–P–C24	111.47(13)	—	114.69(11)
C17–P–C26	—	98.63(19)	—
C20–P–C26	—	103.66(18)	—
O–P–C17	—	—	113.85(9)
O–P–C20	—	—	109.85(10)
O–P–C24	—	—	110.16(10)
C4–N1–C17	127.5(2)	127.8(3)	129.53(18)
C4–N1–C19	125.2(2)	125.1(3)	124.07(18)
C17–N1–C19	106.5(2)	106.9(3)	106.23(18)
C17–N2–C18	105.7(2)	105.8(3)	105.7(2)

Table 3 Summary of results from Suzuki–Miyaura coupling of 4-bromotoluene and 4-chlorotoluene employing **11a** or **11b** as a ligand source

	X	Ligand	Pd source	% Pd	Pd : ligand	Solvent	Yield[a]
1[b]	Br	**11b**	$Pd(OAc)_2$	0.01	1 : 2	Toluene	39
2[b]	Br	**11b**	$Pd(OAc)_2$	0.01	1 : 10	Toluene	63
3[b]	Br	**11b**	$Pd(OAc)_2$	0.1	1 : 2	Toluene	52
4[b]	Br	**11b**	$Pd(OAc)_2$	0.1	1 : 10	Toluene	67
5[b]	Br	**11a**	$Pd(OAc)_2$	0.01	1 : 2	Toluene	58
6[b]	Br	**11a**	$Pd(OAc)_2$	0.01	1 : 10	Toluene	41
7[b]	Br	**11a**	$Pd(OAc)_2$	0.1	1 : 2	Toluene	73
8[b]	Br	**11a**	$Pd(OAc)_2$	0.1	1 : 10	Toluene	59
9[c]	Br	—	$Pd(OAc)_2$	0.5	—	$THF–H_2O$	51
10[c]	Br	**11b**	$Pd(OAc)_2$	0.5	1 : 3	$THF–H_2O$	74
11[c]	Br	**11a**	$Pd(OAc)_2$	0.5	1 : 3	$THF–H_2O$	90
12[d]	Cl	—	$Pd(OAc)_2$	1.0	—	Toluene	2
13[d]	Cl	**11b**	$Pd(OAc)_2$	0.1	1 : 2	Toluene	4
14[d]	Cl	**11b**	$Pd(OAc)_2$	0.1	1 : 10	Toluene	13
15[d]	Cl	**11a**	$Pd(OAc)_2$	0.1	1 : 2	Toluene	33
16[d]	Cl	**11a**	$Pd(OAc)_2$	0.1	1 : 10	Toluene	49
17[e]	Cl	**11a**	$Pd(OAc)_2$	0.5	1 : 3	$THF–H_2O$	22
18[f]	Cl	**11a**	$Pd_2(dba)_3$	1.0	1 : 2	Toluene	10
19[g]	Cl	**11a**	$Pd_2(dba)_3$	1.0	1 : 2	Dioxane	15
20[h]	Cl	**11a**	$PdCl_2(PPh_3)_2$	1.0	1 : 4	Dioxane	53

[a] Average of 2 runs. [b] Conditions: K_3PO_4 (2 eq.), *p*-TolBr (1.0 eq.), $PhB(OH)_2$ (1.5 eq.), reflux. [c] K_3PO_4 (3 eq.), *p*-TolBr (1.0 eq.), $PhB(OH)_2$ (1.5 eq.), reflux. [d] K_3PO_4 (2 eq.), *p*-TolCl (1.0 eq.), $PhB(OH)_2$ (1.5 eq.), reflux. [e] K_3PO_4 (3 eq.), *p*-TolCl (1.0 eq.), $PhB(OH)_2$ (1.5 eq.), reflux. [f] K_3PO_4 (2 eq.), *p*-TolCl (1.0 eq.), $PhB(OH)_2$ (1.5 eq.), reflux. [g] K_3PO_4 (2 eq.), *p*-TolCl (1.0 eq.), $PhB(OH)_2$ (1.5 eq.), reflux. [h] K_3PO_4 (2 eq.), *p*-TolCl (1.0 eq.), $PhB(OH)_2$ (1.5 eq.), reflux.

angle. The main conformational difference in the phosphine upon complexation is a rotation about the P–C17 bond such that the lone pairs on P and N2 interact with the metal. As a consequence, *t*-Bu groups point towards the [2.2]paracyclophane substituent in **14a**, effectively crowding one side of the metal coordination sphere. In addition, the torsion between substituents of the imidazole is considerably larger [$\alpha = -19.84(89)°$] and the interplane angle β increases to 61.64(15)°.

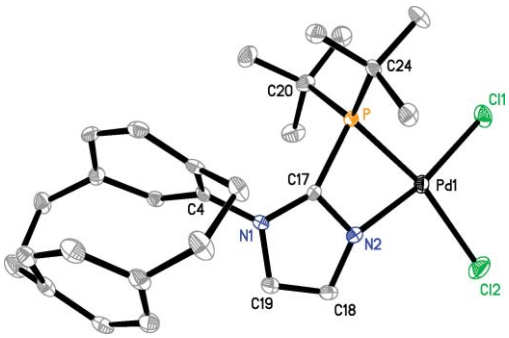


Fig. 4 Thermal elliposid (30%) plot of **14a** (dichloromethane solvate and hydrogen atoms omitted).

Conclusions

In conclusion, we have developed a route to planar chiral imidazole-based phosphine ligands, that chelate to metals with *P*,*N*-coordination. Palladium catalysts derived from these ligands promote the Suzuki–Miyaura reaction of aryl bromides and chlorides. Whilst the present results do not match the best ligands reported, they are promising. Further studies are currently being undertaken in order to optimise the reaction conditions for the coupling of more substituted aryl moieties and thus permit enantiomerically pure variants of **11a/b** to be screened in atroposelective coupling reactions. These results will be published in due course.

Experimental

General information

All reaction glassware was oven dried and reactions performed under an inert atmosphere of nitrogen or argon where applicable. Solvents were dried *via* the following methods: diethyl ether and THF were heated at reflux over fresh sodium wire in the presence of benzophenone indicator. Toluene was dried over 4 Å molecular sieves or by reflux over calcium chloride. Dioxane was stored over sodium wire and DMF was stored over 4 Å molecular sieves. NMR solvents were stored over molecular sieves and triethylamine and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine were freshly distilled over sodium hydroxide pellets. Solvents were purchased from Fisher or Acros. Palladium metal catalysts were purchased from Strem or Sigma-Aldrich. Other reagents were purchased from Avocado, Acros or Sigma-Aldrich.

Flash chromatography was performed using Fischer Davisil 60 silica gel and t.l.c was carried out using glass backed pre-coated silica plates (Merck 60 silica). Visualisation techniques employed included using ultraviolet light (254 nm), potassium permanganate, dinitropyridine, ethanolic phosphomolybdic acid or ninhydrin when applicable.

Optical rotation was recorded on a Perkin Elmer 241 polarimeter using the sodium lamp, emitting at 589 nm. All samples were measured in chloroform ($c = 1$) in a 10 cm cell and an average taken of 10 readings. Average temperature was 27 °C. Gas chromatography was carried out on a Perkin Elmer Autosystem XL using a Supelco MDN-5S, 30 m × 0.25 mm × 0.25 um column. The injector temperature was set to 200 °C and detector (flame ionization detector) set to 300 °C with a temperature

ramp of 15 °C min^{-1}. Data was recorded *via* PowerchromTM and transferred into MS excel for processing. Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected.

NMR spectroscopy was carried out on a Bruker 400 MHz, Bruker 300 MHz, Varian 500 MHz or Varian 400 Mhz. Frequencies used for measurements were 400 MHz and 500 MHz for proton; 75 MHz and 125 MHz for carbon; 161.7 MHz for phosphorus. All spectra were run in deuterated chloroform unless otherwise stated. Chemical shifts are in ppm and referenced to the NMR solvent. Coupling constants are given in Hz. Multiplicities are described as follows: *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, dd = double doublet, ddd = double double doublet, *m* = multiplet, br = broad. Infrared spectroscopy was carried out on a Perkin-Elmer 1600 Fourier Transform spectrometer as either thin film (DCM) or solid. Mass spectra and exact mass data were recorded by Dr Ali Abdul-Sada at University of Sussex or by the EPSRC national mass spectrometry service, Swansea.

4-(2-Bromophenyl)[2.2]paracyclophane 6a

To a solution of (±)-4-bromo[2.2]paracyclophane (4.1 g, 14.4 mmol, 1.0 eq.) in THF (144 mL) at −78 °C was added *tert*-butyllithium (1.7 M in pentane; 17.3 mL, 29.5 mmol, 2.05 eq.) dropwise over 5 min to produce a blood red solution. After 5 min $B(OMe)_3$ (4.1 mL, 36.0 mmol, 2.5 eq.) was added. The resulting yellow solution was warmed to room temperature over 6 h. $Pd(PPh_3)_4$ (1.0 g, 0.9 mmol, 6 mol%) and 1,2 dibromobenzene (2.2 mL, 18.7 mmol, 1.3 eq.) in toluene (100 mL) were added, followed by potassium carbonate (5.4 g, 38.3 mmol, 2.7 eq.) and water (3.0 mL). The reaction mixture was heated to reflux for 5 days. After cooling to room temperature, the reaction mixture was poured into water (150 mL) and extracted with Et_2O (3 × 100 mL). The combined organic layers were dried ($MgSO_4$) and concentrated. The crude material was purified by flash column chromatography (Et_2O–hexane gradient) to give 4-(2-bromophenyl)[2.2]paracyclophane as a white solid (0.62 g, 13%); R_f 0.7 (10 : 1 60/80 petroleum ether : Et_2O); m.p. = 144–146 °C; IR 3056, 2987, 2922, 2894, 1422, 1071, 1037, (Ar C–Br) and 896 cm^{-1}; δ_H ($CDCl_3$, 300 MHz) 7.72 (1H, d, *J* 7.0, H6′), 7.65 (1H, d, *J* 7.5, H3′), 7.53 (1H, t, *J* 7.5, H4′), 7.24 (1H, t, *J* 8.0, H5′), 6.70 (1H, d, *J* 7.5, H13), 6.65 (1H, d, *J* 8.0, H8), 6.61 (1H, d, *J* 8.0, H7), 6.53 (3H, d, *J* 7.5, H12, H15, H16), 6.45 (1H, s, H5), 3.18–3.10 (4H, m, H1, H2, H9, H10), 3.06–3.02 (1H, m, H10), 2.98–2.91 (1H, m, H2), 2.88–2.85 (2H, m, H1, H9); δ_C ($CDCl_3$, 125 MHz) 140.1 (C), 139.6 (C), 139.5 (C), 139.1 (C), 139.0 (C), 134.6 (CH), 133.6 (CH), 133.0 (CH), 132.3 (CH), 132.2 (CH), 131.4 (C), 129.5 (C), 129.5 (CH), 128.3 (CH), 35.7 (CH_2), 35.4 (CH_2), 35.3 (CH_2), 35.1 (CH_2); MS (EI+): *m*/*z* 364 $[M]^+$, 257, 208, 179, 104 (Found: $[M]^+$, 362.0662, $C_{22}H_{19}Br^{79}$ requires $[M]^+$, 362.0665).

4-(2-Chlorophenyl)[2.2]paracyclophane 6b

To a flask charged with tris(dibenzylideneacetone)dipalladium(0) (24.5 mg, 0.03 mmol, 3 mol%), SPhos (21.9 mg, 0.05 mmol, 6 mol%), boronic acid (278 mg, 1.78 mmol, 2.0 eq.) and tripotassium phosphate (0.57 g, 2.67 mmol, 3 eq.) was added a solution of [2.2]paracyclophan-4-yl triflate (300 mg, 0.89 mmol, 1.0 eq.) in toluene (6 mL). The reaction mixture was heated to reflux for 16 h. The reaction was cooled to room temperature then poured into H_2O (25 mL) and extracted with Et_2O (3 × 25 mL). The combined organic layers were dried ($MgSO_4$) and concentrated. The residue was purified *via* flash column chromatography (5 : 1 60/80 petroleum ether : Et_2O) and recrystallised from *n*-heptane/CH_2Cl_2 to give 4-(2-chlorophenyl)[2.2]paracyclophane as white crystals (170 mg, 55%); R_f 0.59 (5 : 1 60/80 petroleum ether/Et_2O); m.p. = 139–140 °C; IR 3054, 2986, 2932, 1421, 896 cm^{-1}; δ_H ($CDCl_3$, 300 MHz) 7.68 (1H, d, *J* 6.6, H6′), 7.46 (2H, t and d, *J* 8.1 and 7.8, H3′, H4′), 7.30 (1H, t, *J* 7.2, H5′), 6.69–6.46 (7H, m, H5, H7, H8, H12, H13, H15, H16), 3.13–2.89 (6H, m, H1, H2, 2 × H9, 2 × H10), 2.86–2.80 (2H, m, H1, H2); δ_C ($CDCl_3$, 75 MHz) 140.0 (C), 139.5 (C), 139.1 (C), 137.2 (C), 134.5 (CH), 133.9 (CH), 133.5 (CH), 133.3 (CH), 133.0 (CH), 132.3 (CH), 132.2 (CH), 131.4 (CH), 129.7 (CH), 129.5 (CH), 128.2 (CH), 127.0 (CH), 35.5 (CH_2), 35.2 (CH_2), 35.2 (CH_2), 34.0 (CH_2); MS (EI+): *m*/*z* 318 $[M]^+$, 208, 213, 181, 178, 104, 78 (Found: $[M + Na]^+$, 341.1074, $C_{22}H_{19}Cl^{35}Na$ requires $[M + Na]^+$, 341.1067).

(±)-4-Azo[2.2]paracyclophane (±)-8

n-Butyllithium (2.5 M in hexanes; 17.9 mL, 36.64 mmol, 1.05 eq.) was added dropwise to (±)-4-bromo[2.2]paracyclophane (10.0 g, 34.9 mmol, 1.0 eq.) in THF (160 mL) at −78 °C over 5 min, turning the solution blood red then yellow. After 1 h at −78 °C, *p*-tosylazide (7.33 g, 36.64 mmol, 1.05 eq.) in THF (40 mL, 0.92 M) was added dropwise turning the solution dark purple. The reaction mixture was then allowed to room temperature over 14 h. The reaction mixture was poured into sat. $NH_4Cl_{(aq)}$ (250 mL) and extracted with Et_2O (2 × 100 mL). The combined organic phase was dried ($MgSO_4$) and solvent removed. The crude solid was purified *via* flash chromatography on silica gel (DCM–hexane gradient) to isolate the product as pale brown solid (5.22 g, 60%); R_f 0.35 (60/80 petroleum ether); m.p = 84–86 °C; IR 2929, 2852 (C–H), 2104 (N=N=N), 1593, 1559 (C–N), 1493, 1410 (C–C alkane), 890, 861, 798, 719, 646 (aromatic C–H) cm^{-1}; δ_H ($CDCl_3$, 500 MHz) 6.89 (1H, d, *J* 8.0, H_{Ar}), 6.54 (1H, d, *J* 8.0, H_{Ar}), 6.47 (1H, d, *J* 8.0, H_{Ar}), 6.44–6.41 (3H, m, H_{Ar}), 5.98 (1H, s, H_{Ar}), 3.35 (1H, ddd, *J* 15.0, 9.0, 3.0, C*H*H), 3.38–3.02 (6H, m, CH_2), 2.69–2.63 (1H, m, CH*H*); δ_C ($CDCl_3$, 125 MHz) 142.0 (C), 139.8 (C), 139.0 (C), 138.9 (C), 135.6 (CH), 133.7 (CH), 133.0 (CH), 131.6 (CH), 133.1 (CH), 131.2 (C), 129.0 (CH), 128.8 (CH), 124.5 (CH), 35.7 (CH_2), 35.4 (CH_2), 34.0 (CH_2), 31.9 (CH_2); MS (EI+): *m*/*z* 249 $[M]^+$, 221, 206, 119, 104 (Found: $[M]^+$, 249.1259, $C_{16}H_{15}N_3$ requires $[M]^+$, 249.1260).

(±)-4-Amino[2.2]paracyclophane (±)-9

To a flask charged with tetrabutylammonium iodide (8.83 g, 23.89 mmol, 1.0 eq.) and sodium borohydride (9.89 g, 261.4 mmol, 11.0 eq.) was added 4-(±)-azo[2.2]paracyclophane (5.90 g, 23.7 mmol, 1.0 eq.) in THF (158 mL) followed by water (128 mL). The reaction mixture was left to stir at room temperature for 3 days. A further portion of sodium borohydride was added (5.29 g, 139.83 mmol, 5.85 eq.) and stirred at room temperature for a further 24 h. After this time, the reaction mixture was poured into water (250 mL) and extracted with Et_2O (3 × 250 mL). The combined organic phase was dried ($MgSO_4$) and solvent removed to give a light brown solid (5.17 g, 97%); R_f 0.45 (1 : 1 60/80

petroleum ether : Et_2O); m.p. = 222–224 °C (lit. value 239–241 °C); IR 3388 (NH), 2922, 2852 (C–H alkyl), 1614 (NH), 1498, 1425, 1286, 912, 864, 795, 718 cm^{-1}; δ_H ($CDCl_3$, 500 MHz) 7.17 (1H, d, *J* 7.5, H_{Ar}), 6.59 (1H, d, *J* 8.0, H_{Ar}), 6.40 (2H, d, *J* 8.0, H_{Ar}), 6.27 (1H, d, *J* 7.5, H_{Ar}), 6.13 (1H, d, *J* 7.5, H_{Ar}), 5.38 (1H, s, H_{Ar}), 3.47 (s, broad, NH_2), 3.15–2.96 (6H, m, CH_2), 2.86–2.80 (1H, m, C*H*H), 2.71–2.65 (1H, m, C*H*H); δ_C ($CDCl_3$, 125 MHz): 144.9 (C), 141.0 (C), 138.9 (C), 138.9 (C), 135.2 (CH), 133.4 (CH), 132.4 (CH), 131.4 (CH), 126.8 (CH), 124.5 (C), 122.8 (CH), 122.3 (CH), 35.4 (CH_2), 34.9 (CH_2), 33.0 (CH_2), 32.2 (CH_2). In agreement with literature.[20]

(R_p)-(−)-4-Amino[2.2]paracyclophane (R_p)-9[20]

(1*S*)-(+)-10-Camphor sulfonic acid (5.21 g, 22.41 mmol, 1.0 eq.) was placed under vacuum then flushed with nitrogen (×3). To this was added (±)-4-amino[2.2]paracyclophane (5.0 g, 22.42 mmol, 1.0 eq.) in EtOAc (163 mL) and the reaction mixture stirred at 4 °C for 2 days. The solid formed was filtered off over a high porosity scinter and placed in a clean round bottomed flask. The solid was re-dissolved in EtOAc (20 mL) then (1*S*)-(+)-10-camphor sulfonic acid (5.21 g, 22.41 mmol, 1.0 eq.) added. The reaction mixture was stirred at 4 °C for a further 2 days. After this time, the solid formed was filtered off over a high porosity scinter, washed with sodium hydroxide (0.1M; 200 mL + 150 mL). The collected solid was re-dissolved in the minimum amount of MeOH–DCM and dried ($MgSO_4$). The solid (1.11 g) was purified *via* flash chromatography (hexane–ethyl acetate, neutralized silica gel) to give a pale orange-brown solid (767.5 mg, 15.3%); $[\alpha]_D$= −72 (*c* = 0.078, $CHCl_3$) (lit. value −83.5);[20] all other data as above. The amine was also prepared as previously reported.[15]

(±)-4-Imidazole[2.2]paracyclophane (±)-10

(±)-4-Amino[2.2]paracyclophane (1.12 g, 5.03 mmol, 1.0 eq.), paraformaldehyde (388 mg, 12.81 mmol, 2.5 eq.) and NH_4Cl (672 mg, 12.58 mmol, 2.5 eq.) were suspended in dioxane (20 mL) and water (20 mL). To this was added glyoxal (1.80 mL, 12.58 mmol, 2.5 eq.) and 2 drops of phosphoric acid added. The reaction mixture heated to reflux for 18 h. After this time the dark green reaction mixture was cooled to room temperature and poured into sodium hydroxide (3.0 M; 30 mL). The aqueous phase was extracted with Et_2O (3 × 20 mL), combined, dried ($MgSO_4$) and solvent removed to give a brown powder. Purification *via* flash chromatography (50 : 50 ethyl acetate–hexane, neutralized silica gel) to yield a light brown powder (870.8 mg, 63.1%); R_f 0.02 (1 : 1 60/80 petroleum ether : Et_2O); m.p = 156–158 °C; IR 3369 (broad, =N), 3116, 3010, 2931, 2855, 2214, 1597, 1500, 1454, 1436, 1423, 907, 839, 822, 731, 663 cm^{-1}; δ_H ($CDCl_3$, 500 MHz) 7.74 (1H, s, H17), 7.26 (1H, s, H19), 7.20 (1H, s, H18), 6.66 (1H, d, *J* 8.0, H_{Ar}), 6.64–6.57 (4H, m, H_{Ar}), 6.51 (1H, d, *J* 8.0, H_{Ar}), 6.41 (1H, s, H_{Ar}), 3.23 (1H, t, *J* 9.0, C*H*H), 3.15 (3H, s, CH_2), 3.04 (1H, t, *J* 13.5, C*H*H), 2.94–2.88 (2H, m, C*H*H), 2.71 (1H, t, *J* 9.5, C*H*H); δ_C ($CDCl_3$, 125 MHz) 141.9 (CH), 139.4 (CH), 139.3 (C), 136.8 (C), 136.7 (CH), 136.5 (C), 133.4 (CH), 133.0 (CH), 132.9 (C), 132.7 (C), 132.7 (CH), 131.9 (CH), 129.9 (CH), 129.3 (CH), 127.0 (CH), 119.5 (C), 35.3 (CH_2), 34.9 (CH_2), 34.6 (CH_2), 32.5 (CH_2); MS (EI+): *m*/*z* 274 $[M]^+$, 169, 143, 104 (Found: $[M]^+$, 274.1465, $C_{19}H_{18}N_2$ requires $[M]^+$, 274.1465).

(R_p)-(−)-4-Imidazole[2.2]paracyclophane (R_p)-10

Carried out as above except employing enantiomerically enriched (R_p)-4-amino[2.2]paracyclophane as starting material to yield the product as a light brown powder (391.1 mg, 1.425 mmol, 44.3%); $[\alpha]_D$ = −39.6 (*c* = 0.2, $CHCl_3$); all data as above.

(±)-4-(1-Di-*tert*-butyl)imidazole[2.2]paracyclophane phosphine (±)-11a

n-Butyllithium (2.5 M in hexanes; 1.45 mL, 2.97 mmol, 1.05 eq) was added dropwise to (±)-4-imidazole[2.2]paracyclophane (0.81 g, 2.96 mmol, 1.0 eq.) in THF (15 mL) and TMEDA (0.47 mL, 3.10 mmol, 1.05 eq.) at −78 °C. After 1 h at −78 °C, chloro-di-*tert*-butylphosphine (0.54 g, 3.00 mmol, 1.01 eq.) in THF (1.5 mL) was added to the dark red solution and the reaction mixture allowed warmed to room temperature over 18 h. The reaction mixture was then poured into water (50 mL) and extracted with Et_2O (3 × 30 mL). The combined organic extracts were dried ($MgSO_4$) and solvent removed. The residue was purified *via* flash chromatography (50 : 50 Et_2O/hexanes) to yield the product as a white powder (0.61 g, 48.8%); R_f 0.70 (1 : 1 60/80 petroleum ether/Et_2O); m.p. = 160–162 °C; IR 2932, 2894, 2858, 2214, 1596, 1560, 1497, 1471, 1425, 1178, 1148, 1097 cm^{-1}; δ_H ($CDCl_3$, 500 MHz) 7.56 (1H, s, H18), 7.49 (1H, s, H19), 6.72 (2H, t, *J* 7.0, H15, H16), 6.67 (1H, d, *J* 8.5, H13), 6.58 (1H, d, *J* 8.0, H8), 6.54 (1H, d, *J* 8.0, H7), 6.46 (1H, d, *J* 8.0, H12), 6.32 (1H, s, H5), 3.14–2.96 (6H, m, CH_2), 2.89–2.84 (1H, m, C*H*H), 2.77–2.71 (1H, m, C*H*H), 1.35 (9H, d, *J* 12.5, *tert*-butyl), 0.79 (9H, d, *J* 12.0, *tert*-butyl); δ_C ($CDCl_3$, 125 MHz) 148.6 (C, d, J_{PC} 26), 140.0 (C), 139.9 (CH), 139.4 (CH), 136.8 (C), 136.1 (C), 136.1 (C), 135.7 (CH), 134.2 (CH), 133.5 (CH), 132.3 (CH), 130.2 (CH), 129.8 (CH), 129.3 (CH), 121.9 (C), 35.3 (CH_2), 34.9 (CH_2), 34.4 (C, d, J_{PC} 18.4), 32.7 (C, d, J_{PC} 17.5), 32.5 (CH_2, d, J_{PC} 6.8), 30.7 (CH_3, d, J_{PC} 24.8), 29.8 (CH_3, d, J_{PC} 13.6); δ_P ($CDCl_3$, 161.7 MHz) 8.74; MS (EI+): *m*/*z* 418 $[M]^+$, 361, 306, 201, 187 (Found: $[M]^+$, 418.2530, $C_{27}H_{35}N_2P$ requires $[M]^+$, 418.2532).

(R_p)-4-(1-Di-*tert*-butyl)imidazole[2.2]paracyclophane phosphine (R_p)-11a

Reaction performed as above except using enantiomerically enriched imidazole. All data as above; $[\alpha]_D$ = 88.2 (*c* = 0.9, $CHCl_3$).

(±)-4-(1-Dicyclohexyl)imidazole[2.2]paracyclophane phosphine (±)-11b

n-Butyllithium (2.5 M in hexanes; 0.58 mL, 1.19 mmol, 1.0 eq) was added dropwise to (±)-4-imidazole[2.2]paracyclophane (0.32 g, 1.19 mmol, 1.0 eq.) in THF (6.0 mL) and TMEDA (0.19 mL, 1.27 mmol, 1.05 eq.) at −78 °C. After 1 h at −78 °C, chlorodicyclohexylphosphine (0.29 g, 1.25 mmol, 1.05 eq.) in THF (1.0 mL) was added to the dark red solution and the reaction mixture warmed to room temperature over 3 days. The reaction mixture was then poured into water (25 mL) and extracted with Et_2O (3 × 20 mL). The combined organic extracts were dried ($MgSO_4$) and solvent removed. The residue was purified *via* flash chromatography (Et_2O) to yield the product as a white powder (0.25 g, 44.2%); R_f 0.89 (Et_2O); m.p. = 194–196 °C; IR 3369, 2927, 2851, 2205, 1596, 1560, 1497, 1447, 1428, 1179, 1146, 1098 cm^{-1};

δ_H ($CDCl_3$, 500 MHz) 7.51 (1H, s, H18), 7.46 (1H, s, H19), 6.70 (1H, d, *J* 8.0, H13), 6.68 (2H, dd, *J* 8.0, 8.0, H15, H16), 6.59 (1H, d, *J* 8.0, H8), 6.55 (1H, d, *J* 8.0, H7), 6.47 (1H, d, *J* 7.5, H12), 6.36 (1H, s, H5), 3.19–2.77 (7H, m, CH_2), 2.75–2.72 (1H, m, C*H*H), 2.55–2.53 (1H, m, P–C*H*), 1.85 (1H, d, *J* 12.0, P–C*H*), 1.75–1.71 (4H, m, Cy), 1.54–1.13 (11H, m, Cy), 1.04–0.94 (2H, m, Cy), 0.89–0.84 (1H, m, Cy), 0.78–0.70 (1H, m, Cy), 0.38–0.33 (1H, m, Cy); δ_C ($CDCl_3$, 125 MHz) 147.6 (C, d, *J* 20.0), 140.4 (CH), 140.0 (CH), 139.3 (C), 135.8 (C), 135.6 (C), 133.4 (CH), 132.4 (CH), 132.3 (CH), 130.7 (CH), 129.7 (C), 128.7 (CH), 122.0 (CH), 35.5 (CH, d, J_{PC} 13), 35.4 (CH_2), 35.1 (CH_2), 35.0 (CH_2), 32.6 (CH, d, J_{PC} 9.2), 32.0 (CH_2, d, *J* 5.6), 30.5 (CH_2, d, J_{PC} 5.3), 30.4 (CH_2, d, J_{PC} 7.4), 29.3 (CH_2, d, J_{PC} 16.0), 28.1 (CH_2), 27.0 (CH_2), 26.9 (CH_2), 26.8 (CH_2), 26.6 (CH_2), 26.2 (CH_2); δ_P ($CDCl_3$, 161.7 MHz) –20.8; MS (EI+) *m*/*z* 469 $[M]^+$, 361, 306, 201, 187 (Found: $[M]^+$, 470.2844, $C_{31}H_{39}N_2P$ requires $[M]^+$, 470.2845).

(R_p)-4-(1-Dicyclohexyl)imidazole[2.2]paracyclophane phosphine (R_p)-11b

Experiment performed as above. All data as above; $[\alpha]_D = 70.4$ ($c = 1$, $CHCl_3$).

(±)-4-(1-Di-*tert*-butyl)imidazole[2.2]paracyclophane phosphine oxide (±)-12a

Hydrogen peroxide (0.015 mL, excess, 37% in water) was added to (±)-4-(1-di-*tert*-butyl)imidazole[2.2]paracyclophane phosphine (10.0 mg, 0.02 mmol, 1.0 eq.) in $CDCl_3$ (1.0 mL) and shaken at room temperature for 10 min. DCM (5 mL) was added and the organic phase dried ($MgSO_4$), the solvent was then removed to give a white solid (9.3 mg, 0.021 mmol, 89.0%); m.p. 220–222 °C; IR 3252, 2928, 2855, 2325, 1597, 1563, 1474, 1428, 1365, 1299, 1170, 1120, 1081 cm^{-1}; δ_H ($CDCl_3$, 500 MHz) 7.60 (1H, t, *J* 1.5, H18), 7.43 (1H, t, *J* 1.5, H19), 6.73 (1H, dd, *J* 10.5, 1.5, H13), 6.67 (2H, br d, *J* 10.5, H15, H16), 6.55 (1H, d, *J* 10.0, H8), 6.52 (1H, dd, *J* 10.0, 2.5, H7), 6.42 (1H, dd, *J* 10.5, 2.5, H12), 6.32 (1H, d, *J* 2.0, H5), 3.15–2.97 (6H, m, CH_2), 2.90–2.82 (1H, m, C*H*H), 2.76–2.69 (1H, m, C*H*H), 1.42 (9H, d, *J* 18.0, *t*-Bu), 0.89 (9H, d, *J* 18.0, *t*-Bu); δ_C ($CDCl_3$, 125 MHz) 140.2 (C, d, J_{PC} 125.0), 140.1 (CH), 139.4 (CH), 138.9 (C), 138.0 (C), 135.4 (C), 135.1 (CH), 134.5 (CH), 133.6 (CH), 132.4 (CH), 132.0 (CH), 129.6 (C, d, J_{PC} 17.1), 129.4 (CH), 128.4 (CH), 123.8 (C, d, J_{PC} 2.5), 37.8 (C, d, J_{PC} 28.1), 37.2 (C, d, J_{PC} 27.3), 35.3 ($2 \times CH_2$), 34.8 (CH_2), 31.8 (CH_2), 27.0 (CH_3), 26.2 (CH_3); δ_P ($CDCl_3$, 161.7 MHz) 51.7; MS EI+) *m*/*z* 435.5 $[M]^+$ (Found: $[M]^+$, 435.2560, $C_{27}H_{35}N_2PO$ requires $[M]^+$, 435.2560).

(±)-4-(1-Dicyclohexyl)imidazole[2.2]paracyclophane phosphine oxide (±)-12b

Hydrogen peroxide (0.5 mL, excess, 37% in water) was added to (±)-4-(1-dicyclohexyl)imidazole[2.2]paracyclophane phosphine (16.0 mg, 0.03 mmol, 1.0 eq.) in $CDCl_3$ (1.6 mL) and shaken at room temperature for 10 min. DCM (5 mL) was added and the organic phase dried ($MgSO_4$). The solvent was then removed to give an oily pale yellow solid (25.2 mg, 100%); IR 2924, 2852, 1596, 1498, 1448, 1427, 1298, 1213, 1174, 1144, 1080 cm^{-1}; δ_H ($CDCl_3$, 500 MHz) 7.59 (1H, s, H18), 7.45 (1H, s, H19), 6.72 (1H, d, *J* 7.5, H13), 6.68 (2H, d, *J* 7.5, H15, H16), 6.57 (1H, d, *J* 7.5, H8), 6.54 (1H, d, *J* 8.0, H7), 6.44 (1H, d, *J* 8.0, H12), 6.37 (1H, s, H5), 3.15–2.92 (6H, m, CH_2), 2.90–2.85 (1H, m, C*H*H), 2.82–2.76 (1H, m, C*H*H), 2.45–2.36 (1H, m, C*H*), 1.94–1.84 (3H, m, Cy), 1.71–1.26 (13H, m, Cy), 1.02–0.87 (4H, m, Cy), 0.51–49 (1H, m, Cy); δ_C ($CDCl_3$, 125 MHz) 140.3 (C, d, J_{PC} 116.1), 140.1 (CH), 139.4 (CH), 139.3 (C), 138.0 (C), 135.4 (CH), 134.8 (C), 134.6 (CH), 133.6 (CH), 132.5 (CH), 132.0 (CH), 130.1 (C, d, J_{PC} 14.1), 129.4 (CH), 128.2 (CH), 124.0 (C, d, *J* 1.8), 42.6 (Cy), 38.2 (Cy), 37.6 (Cy), 36.0 (Cy), 35.4 (Cy), 35.3 (CH_2), 35.2 (CH_2), 34.9 (CH_2), 32.0 (CH_2), 29.7 (Cy), 26.3 (Cy, d, *J* 3.5), 26.2 (Cy, t, *J* 4.0), 26.1 (Cy, d, *J* 3.7), 25.9 (Cy), 25.7 (Cy), 25.2 (Cy, d, *J* 2.4), 24.6 (Cy, d, *J* 3.4), 24.3 (Cy, d, *J* 2.2); δ_P ($CDCl_3$, 161.7 MHz) 42.6; MS (EI+) *m*/*z* 487.5 $[M]^+$, 275.3 (Found: $[M]^+$, 487.2875, $C_{31}H_{39}N_2PO$ requires $[M]^+$, 487.2873).

(±)-4-Imidazolyl(17-di-*tert*-butylphosphino-*P*-*N*2-palladium(0)dichloride)-*N1*-[2.2]paracyclophane phosphine (±)-14a

(±)-4-*N*-Imidazolyl(17-di-*tert*-butylphosphine)[2.2]paracyclophane (50 mg, 0.119 mmol, 1.0 eq.) was dissolved in DCM (1.0 mL) and added to dichloro(1,5-cyclooctadiene)palladium(II) (34.0 mg, 0.119 mmol, 1.0 eq.), Et_2O added (0.5 mL) and the reaction mixture evaporated slowly to form orange crystals. δ_H (CD_2Cl_2, 500 MHz) 7.78 (1H, s, H18), 7.67 (1H, s, H19), 6.80 (1H, d, *J* 5.0, H13), 6.74 (2H, t, *J* 7.5, H7, H8), 6.69 (2H, d, *J* 10.0, H16), 6.66 (1H, d, *J* 8.3, H15), 6.55 (2H, br s, H5, H12), 3.20–2.98 (7H, m, CH_2), 2.63–2.56 (1H, m, H2), 1.50 (9H, d, *J* 20.0, *t*-Bu), 1.06 (9H, d, *J* 15.0, *t*-Bu); δ_C (CD_2Cl_2, 125.7 MHz) 148.8 (C, d, J_{PC} 26.3), 143.4 (C), 140.6 (C), 139.5 (C), 137.5 (CH), 137.1 (CH), 136.4 (C), 134.2 (CH), 133.3 (CH), 132.7 (CH), 130.4 (CH), 130.4 (CH), 129.2 (C, d, J_{PC} 7.5), 124.8 (CH), 117.7 (C), 38.9 (C, t, *J* 10.6), 35.9 (CH_2), 35.5 (CH_2), 35.1 (CH_2), 32.7 (CH_2), 31.6 (C), 30.0 (CH_3, d, *J* 5.0), 29.4 (CH_3, d, *J* 3.8); δ_P (CD_2Cl_2, 161.7 MHz) 41.7; Elemental analysis calcd. (%) for $C_{27}H_{35}Cl_2N_2PPd$: C 54.42, H 5.92, N 4.70; found: C 54.39, H 5.88, N 4.67.

X-Ray diffraction data

Crystals were covered in oil and suitable single crystals were selected under a microscope and mounted on a Kappa CCD diffractometer. The structures were refined with SHELXL-97.[23] Details of the crystal data, intensity collection and refinement are listed in Table 1. Selected bond lengths are presented in Table 2 (**11a**, **11b** and **12a**) and Table 4 (**14a**). Additional features of note are listed below:

Table 4 Selected bond lengths (Å) and angles (°) for **14a**

Pd1–N2	2.028(4)	Pd1–P	2.2671(11)
P–C17	1.824(5)	P–C20	1.856(4)
P–C24	1.855(5)	N1–C17	1.356(6)
N2–C17	1.342(6)	N1–C4	1.447(6)
P–Pd1–N2	70.68(11)	P–Pd1–Cl1	99.96(5)
N2–Pd1–Cl2	95.64(11)	Cl1–Pd1–Cl2	93.79(5)
C17–P–Pd1	81.86(14)	C20–P–Pd1	117.10(15)
C24–P–Pd1	114.87(15)	C17–P–C20	107.8(2)
C17–P–C24	111.7(2)	C20–P–C24	117.4(2)
C4–N1–C17	127.0(4)	C4–N1–C19	126.2(4)
C17–N1–C19	106.8(4)	C17–N2–Pd1	104.7(3)
C18–N2–Pd1	144.8(3)	C17–N2–C18	108.9(4)

14a. The dichloromethane solvate was restrained to have C–Cl distances initially set at 1.75 Å; the carbon atom was left isotropic.

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