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PII: S0040-4020(18)30528-3

DOI: 10.1016/j.tet.2018.05.013

Reference: TET 29520

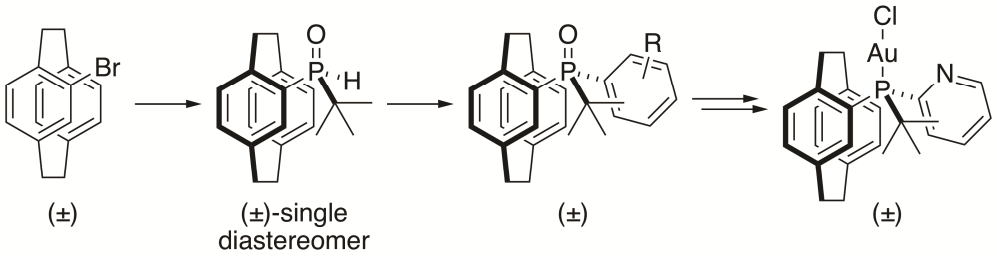
To appear in: *Tetrahedron*

Received Date: 27 February 2018

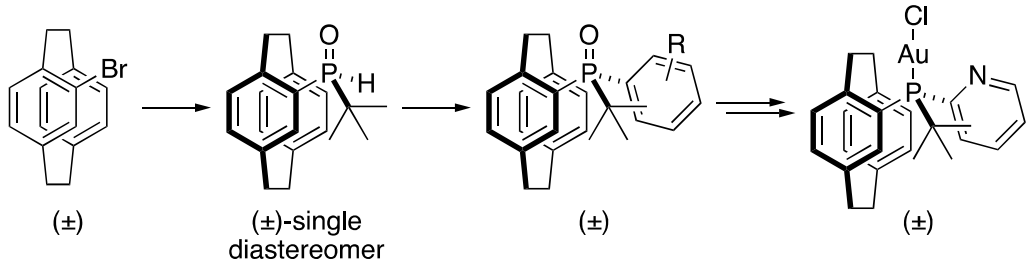
Revised Date: 2 May 2018

Accepted Date: 3 May 2018

Please cite this article as: Mungalpara MN, Wang J, Coles MP, Plieger PG, Rowlands GJ, The synthesis of a [2.2]paracyclophane-derived secondary phosphine oxide and a study of its reactivity, *Tetrahedron* (2018), doi: 10.1016/j.tet.2018.05.013.



(±) (±)-single diastereomer (±) (±)



(±) (±)-single diastereomer (±) (±)

The Synthesis of a [2.2]Paracyclophane-Derived Secondary Phosphine Oxide and a Study of its Reactivity

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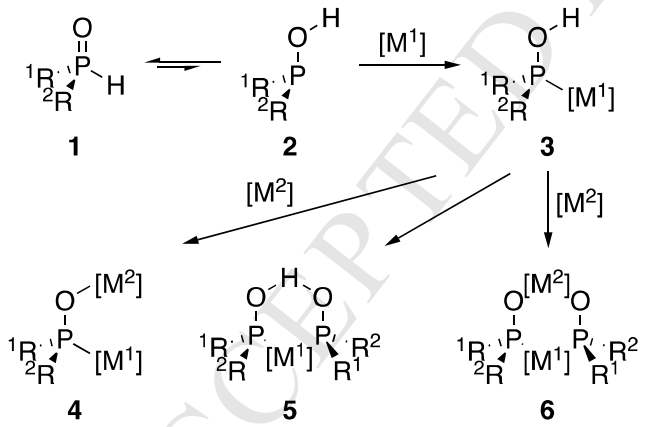
Abstract

A planar chiral secondary phosphine oxide based on [2.2]paracyclophane was synthesised and its chemistry investigated; it was shown to be a competent pre-ligand in palladium(0)-mediated reactions, and displayed promising activity in gold(I)-catalysed cyclisations. The secondary phosphine oxide could be transformed into a collection of P-stereogenic tertiary phosphine oxides. These are rare examples of the planar chirality of [2.2]paracyclophane being combined with a P-stereogenic centre. Unfortunately, epimerisation of the phosphorus stereocentre during reduction limits the use of this chemistry.

Introduction

Trivalent phosphine compounds are vital to modern synthesis acting as the quintessential ligand in a variety of metal-catalysed reactions,[1] and, to a lesser extent, as organocatalysts.[2] Even if we only consider chiral phosphines there are a staggering number of phosphorus(III) compounds, and yet there is still a demand for even more phosphines in order to sate the ever-increasing need for improved reactivity, improved selectivity, and/or more robust catalysts.

One of the major drawbacks with many phosphorus(III) compounds is their sensitivity to oxidation. Protection as borane adducts,[3] or phosphonium salts[4,3c] offers a solution to this problem. Another possibility is the use of secondary phosphine oxides (SPOs). These are frequently air-stable pentavalent phosphorus species **1** that exist in equilibrium with the trivalent phosphinous acid **2** as shown in Scheme 1.[5] The equilibrium strongly favours the P(V) species **1** until a transition metal is added then the equilibrium is driven towards formation of the P(III) complex **3**. SPOs offer a variety of binding modes making them appealing pre-ligands; they can mimic trialkylphosphines and behave as monodentate ligands **3**. Alternatively, they can form bimetallic species (**4** and **6**) by coordinating late-transition metals through the 'soft' phosphorus atom and early-transition metals through the 'hard' oxygen atoms[5-6] or they can 'self-assemble' into bidentate ligands through a hydrogen-bond bridge **5** or as a bimetallic bidentate complex **6**.



Scheme 1. Secondary phosphine oxides (SPOs) and their complexes.

A considerable body of work has been reported detailing the synthesis and application of SPOs in catalysis.[5] Notable applications of achiral SPOs have been the C–H activation and direct arylation of oxazolines,[7] and their use in gold-catalysed cyclopropanations.[8] Most chiral SPOs have not been resolved or applied to asymmetric transformations.[9] The earliest

example of a chiral SPO in an asymmetric transformation involved the reduction of an imine;[10] and this was followed by a limited number of other reductions,[11] additions to allenes,[12] and a bimetallic hydrocarbamoylation.[6]

[2.2]Paracyclophane offers an intriguing scaffold for the formation of chiral ligands.[13] Unlike ferrocene, it only requires a single substituent on one of the aromatic rings to create planar chirality. Its rigid structure restricts conformational freedom resulting in well-defined structures. This has led to the development of a number of useful [2.2]paracyclophane-based phosphine ligands, notably the isomeric diphosphines, PhanePhos[14] (*pseudo-ortho* or 4,12-disubstituted) and GemPhos[15] (*pseudo-gem* 4,13-disubstituted).

While many [2.2]paracyclophane-based phosphines have been reported,[16a-d,13g,16e] there is one glaring omission; there has, to the best of our knowledge, been no systematic research on P-stereogenic [2.2]paracyclophane derivatives. There is a single reference to a P-stereogenic [2.2]paracyclophane derivative in a 2007 patent.[17]

We have studied a range of planar chiral monophosphines,[13g] the majority of these separated the [2.2]paracyclophane from the phosphine with a heteroaromatic ring such as imidazole,[18] triazole,[16b] or indole.[16c] We have also studied the direct attachment of the phosphine to [2.2]paracyclophane.[19,13g,16d] The monodentate phosphines showed too much conformational freedom to induce high enantioselectivities, while the bidentate ligand[16d] was taxing to synthesise in high yield. We wanted a simpler route to bidentate planar chiral ligands. We saw an opportunity in SPO chemistry to prepare enantiomerically enriched bidentate ligands by the self-assembly of two SPOs. We anticipated that a menthol-derived H-phosphinate [20] would fix the P-stereocentre allowing installation of the SPO moiety with simultaneous resolution of the planar chirality of [2.2]paracyclophane. This would mimic our earlier successful sulfoxide chemistry.[21] On coordination with the appropriate metal, we then

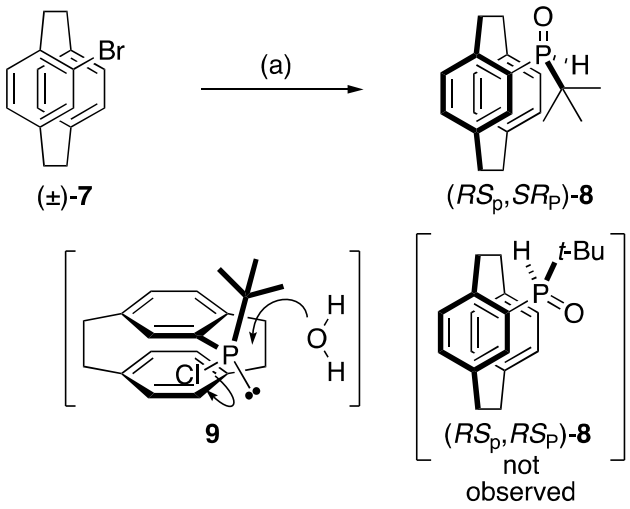
hoped that two planar chiral SPOs would interact through either hydrogen bonding or a bridging metal to give the desired bidentate complex analogous to **5** or **6**.

Such a route would also enable the synthesis of new planar chiral phosphines by P-arylation of the SPO. The resulting tertiary phosphine would allow the first systematic study of P-stereogenic [2.2]paracyclophane derivatives. In this paper we outline the synthesis and reactivity of a planar chiral SPO, highlighting the potential of this chemistry and delineating current limitations.

Results and Discussion

The chemistry started smoothly, addition of 4-lithio[2.2]paracyclophane, generated by halogen-metal exchange of **7**, to *tert*-butyldichlorophosphine followed by hydrolysis gave the desired *tert*-butyl secondary phosphine oxide **8** as essentially one diastereomer (> 95:5 d.r.) (Scheme 2). The ^{1}H NMR spectrum indicates that the *unlike* (RS_p,SR_P) diastereomer was formed.[*] The downfield shift of a proton at C2 is characteristic of the anisotropic influence of the proximal oxygen of the SPO. The same observation was made in the analogous sulfoxide chemistry.[21d,21e,21a] The stereochemistry was confirmed by single X-ray crystallography (Figure 1).[22]

[*] For compounds possessing both a stereogenic plane and a stereogenic centre we use a nomenclature where S_p (lowercase p) refers to the planar chirality as defined from the C1 pilot atom (a good description of defining the stereochemistry of [2.2]paracyclophane can be found in the Gibson review[13b]) and S_P (uppercase P) refers to the phosphorus stereochemistry. We have used Cahn-Ingold-Prelog labelling for racemates (*RS*,*SR* = *R**,*S**).[23]



Scheme 2. Synthesis of [2.2]paracyclophane-based SPO. *Reagents and conditions* (a) i. *n*-BuLi; ii. *t*-BuPCl$_2$; iii. H_2O, 30 - 55%, > 95:5 dr.

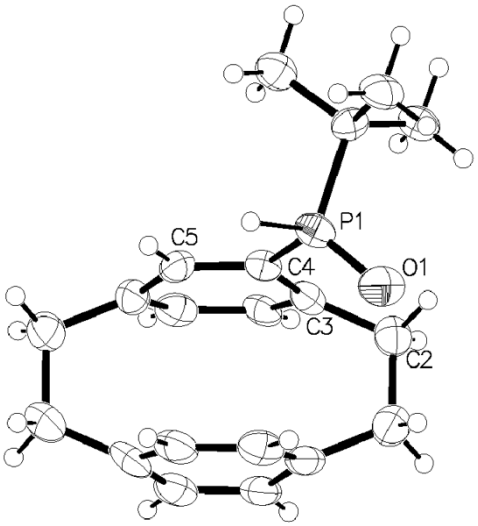


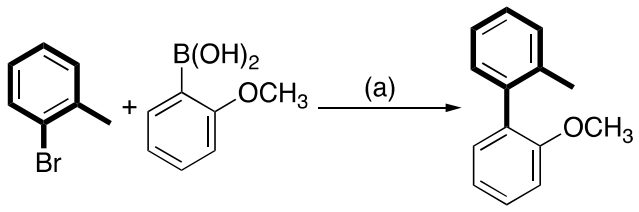
Figure 1. X-ray of secondary phosphine oxide (RS_p,SR_P)-**8**. Ellipsoids are drawn at a 50% probability level.[22]

The origin of the diastereoselectivity is unclear. Arguably, (RS_p,SR_P)-**8** is the more sterically congested diastereomer as the oxygen is forced into close proximity with the ethylene bridge. In our earlier sulfoxide chemistry, oxidation of 4-*tert*-butylsulfanyl[2.2]paracyclophane always furnished the *like* (RS_p,RS_S) diastereomer[21e] and we

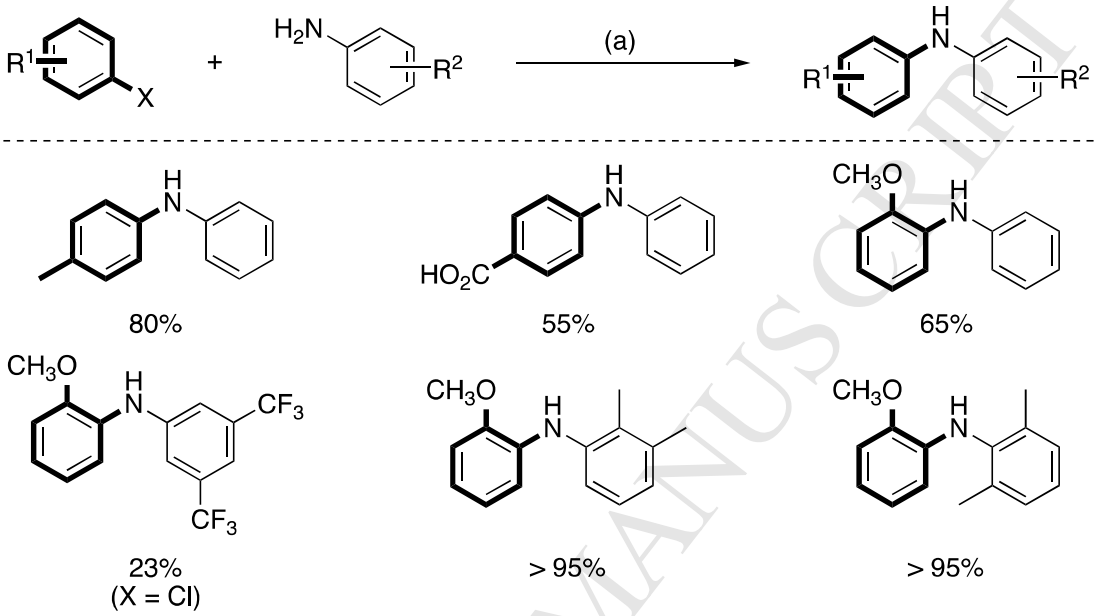
suggested that the lone pair facing C5 was more accessible. Based on this observation, it is plausible that addition to *tert*-butyldichlorophosphine results in formation of a single diastereomer of chlorophosphine (**9**) with the chlorine atom orientated towards the *ortho* proton. Hydrolysis then occurs with inversion of the stereochemistry to give the more congested phosphine oxide (Scheme 2).

The synthesis of other [2.2]paracyclophane-based SPOs proved impossible. A comprehensive array of reactions were attempted[24a-c,11f,20d,24d,20c,24e-g] but all to no avail. We were able to prepare alkyl [2.2]paracyclophane-H-phosphinates but could not displace the alkoxy substituent.[9f] It is unclear why these reactions failed; our experience with [2.2]paracyclophane suggests that the bulk, and the high basicity of this scaffold can impede seemingly simple transformations.

Fortunately, the chemistry of the planar chiral SPO (RS_p,SR_P)-**8** was more rewarding. It proved to be a competent pre-ligand in a number of metal-catalysed transformations. A catalyst formed from SPO **8** promoted Suzuki-Miyaura couplings, such as that of 2-bromotoluene and 2-methoxyphenylboronic acid (Scheme 3), but it should be noted that simpler SPO ligands, such as POPd [(*t*-$Bu_2P(O)H)_2PdCl_2$],[25] or analogous ligands such as (*tert*-butylphosphinyl)ferrocene,[9e] give better yields. The Buchwald_Hartwig arylation of various anilines were more promising (Scheme 4).[25b,26] Electron rich and electron poor aryl bromides and chlorides could be coupled to various anilines including sterically demanding examples.

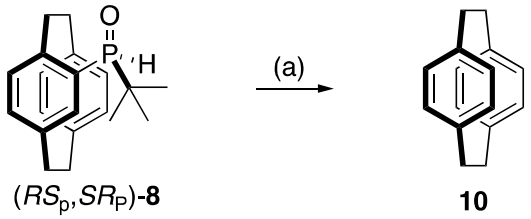


Scheme 3. Suzuki-Miyaura coupling catalysed by Pd(0) and SPO-**8**. *Reagents and Conditions* (a) $Pd(OAc)_2$ (1 mol%), **8** (1 mol%), NaO*t*-Bu (200 mol%), EtOH, 80 °C, 64% (gc yield).



Scheme 4. Buchwald-Hartwig coupling of aryl bromides (unless otherwise noted) and anilines catalysed by SPO-**8**. *Reagents and Conditions* (a) $[Pd_2(dba)_3]$ (2.5 mol%), **8** (10 mol%), NaO*t*-Bu (150 mol%), toluene, 105 °C, (isolated yields).

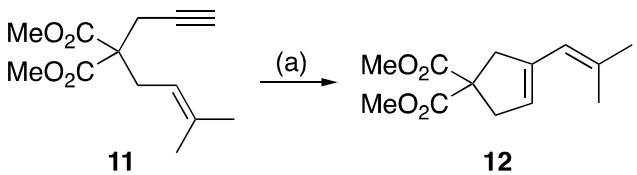
In an effort to gain greater insight into the palladium-mediated reactions we tried to prepare a Pd(II) complex of SPO-**8**. While we were unable to isolate a pure complex, presumably due to the racemic SPO furnishing a mixture of diastereomers along with potential geometric isomers, we made one pertinent observation; treating SPO-**8** with $Pd(OAc)_2$ in various solvents at room temperature, or higher, resulted in the clean decomposition of the SPO into [2.2]paracyclophane **10** (Scheme 5).



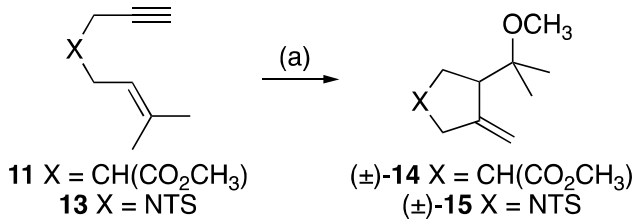
Scheme 5. Protodephosphinylation of SPO-**8**. *Reagents and conditions* (a) $Pd(OAc)_2$, toluene at 50 °C or CH_2Cl_2 or $CDCl_3$ at rt, > 95%.

Pd-mediated cleavage of C–P bonds is unusual but not unheard of. There have been reports of triarylphosphines acting as sources of the aryl moiety in cross coupling reactions[27] and such reactions have been performed with sub-stoichiometric quantities of $Pd(OAc)_2$.[28] Recently analogous methodology was used to prepare a *P*,*N*-[2.2]paracyclophane derivative.[16e] While there have been no reports of palladium insertion into the C–P bond of a secondary phosphine oxide, Pfaltz has reported the insertion of iridium into such a bond,[29] while it has also been shown that palladium will insert into the C–P bond of arylphosphonic acids.[30] It is clear that the combination of the *tert*-butyl secondary phosphine oxide and [2.2]paracyclophane activates the C–P bond. This may prove an interesting method to functionalise paracyclophane if the SPOs can be synthesized in enantiomerically pure form.

Concerned with the instability of SPO **8** in Pd-catalysed reactions, we turned our attention to Au-mediated cyclisations. At the outset of this research there had been only a single report of an Au(I)-SPO complex being used in catalysis.[8] Formation of the gold complex, as judged by ^1H and ^{31}P NMR, was readily achieved by treating the SPO with chloro(dimethyl sulfide)gold(I) in dichloromethane at room temperature.



Scheme 6. Cycloisomerisation of **11**. *Regents and conditions* (a) **8**-AuCl (2 mol%), $AgSbF_6$ (2 mol%), CH_2Cl_2, rt, 10 hrs, 73%.



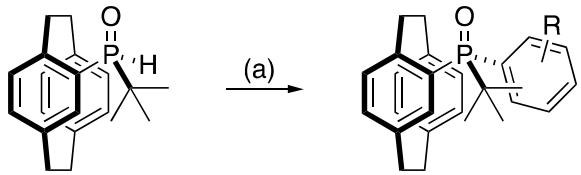
Scheme 7. Methoxycyclisation of enynes. *Reagents and conditions* (a) **8**-AuCl (2 mol%), $AgSbF_6$ (2 mol%), CH_2Cl_2, rt, 12 hrs, **14** = 72%; **15** = 97%.

Three cyclisations were examined, the cycloisomerisation of the dimethyl malonate-derived enyne **11** (Scheme 6) and the methoxycyclisation of **11** and the sulfonamide analogue **13** (Scheme 7). The reactions proceeded smoothly to give the excepted products, the diene **12** or the ethers **14** and **15**, in good yield. Comparing our results with those for the published SPO catalyst there is little difference; this result shows promise for future studies should we be able to resolve the racemate.

C–P bond formation by the arylation of P–H bonds is a powerful method for the formation of phosphines, phosphinates, and other other phosphorus containing species.[31]. The arylation of the SPO (RS_p,SR_P)-**8** would provide a general route to P-stereogenic [2.2]paracyclophane-derived phosphines. This is an unstudied area of [2.2]paracyclophane chemistry with only a single example reported in a patent.[17] Such a target is attractive as it might permit the tuning of steric properties on a planar chiral phosphine derivative.

Based on Bloomfield's methodology,[31a] we investigated the Pd-mediated arylation of SPO **8**. Optimisation led to conditions that permitted a variety of electron rich and electron poor aryl iodides to be coupled to the SPO to give the tertiary phosphine oxides **16a-e** in good yield (Scheme 8). Unlike Bloomfield's original couplings, the reaction required

elevated temperatures, suggesting that the sterically demanding nature of the [2.2]paracyclophane SPO impedes reaction.



(*RS*$_p$,*SR*$_P$)-**8**

16a R = H; 78 - 85%
16b R = 4-CH_3; 86 - 87%
16c R = 4-OCH_3; 42 - 80%
16d R = 4-CN; 64 - 66%
16e R = 2-pyridyl; 71%

Scheme 8 – (a) Ar–I (150 mol%), $Pd(OAc)_2$ (2 mol%), dppf (2.2 mol%), Cs_2CO_3 (130 mol%), 1,4-dioxane:DCE (9:1), 100 °C.

In each case, the new tertiary phosphine oxides were formed as a single diastereomer as judged by ^{1}H NMR spectroscopy. As before, the characteristic downfield shift of one of the H2 protons indicates that the *unlike* diastereomer is favoured as we would expect (except in the 2-pyridyl example where the *like* diastereomer is formed due to a change in priorities according the Cahn-Ingold-Prelog guidelines). This was later confirmed by X-ray crystallography (Figure 2).[22]

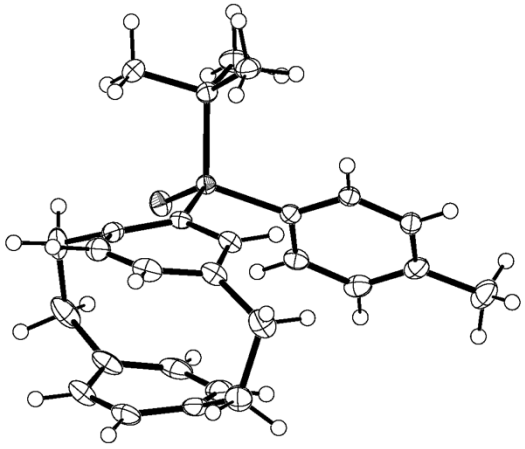
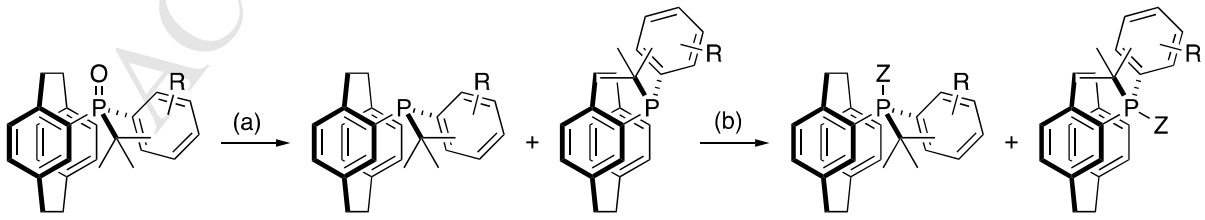


Figure 2. X-ray structure of tertiary phosphine oxide **16b**. Ellipsoids are drawn at a 50% probability level.[22]

The disadvantage of this route to chiral phosphines is that it requires reduction of a phosphine oxide. This is always a challenging reaction[32] but past precedent suggested it would be possible; a number of [2.2]paracyclophane phosphine oxides have been reduced.[14a,15b,33] Our confidence was misplaced. We attempted a comprehensive cross section of reduction methodologies but with no success.[34] The only conditions that furnished any of the desired compound was prolonged heating at 145 °C with excess trichlorosilane or use of phenylsilane for excessive reaction times (Scheme 9). Reduction of a single diastereomer of tertiary phosphine oxide gave two major compounds as revealed by ^{1}H NMR spectroscopy of the crude reaction mixture. The phosphines are unstable and this has made identification challenging. They could be 'protected' as the phosphonium salt by reaction with tetrafluoroboric acid or by complexation with chloro(tetrahydrothiophene)gold(I) or chloro(dimethyl sulfide)gold(I) to give, in each case, two inseparable products. Spectroscopic evidence shows that reduction and complexation was possible for all derivatives but **17a**, **17c** or **17d** could not be isolated as pure samples. Crude NMR have been included in the supplementary data.



(±)-**16**

(±)-**17a** R = H*
(±)-**17b** R = 4-CH_3; 60:40 dr
(±)-**17c** R = 4-OCH_3; 58:42 dr
(±)-**17d** R = 4-CN*
(±)-**17e** R = 2-pyridyl; 100:0

(±)-**17a·AuCl** R = H; 55:45 dr**
(±)-**17b·H** R = 4-CH_3; 69%; 57:43 dr
(±)-**17b·AuCl** R = 4-CH_3; 16; 62:38 dr
(±)-**17c·AuCl** R = 4-OCH_3; 61:39 dr**
(±)-**17d·AuCl** R = 4-CN**
(±)-**17e·H** R = 2-pyridyl; 100:0 dr**
(±)-**17e·AuCl** R = 2-pyridyl; 23%; 100:0 dr

Scheme 9. Reduction of phosphine oxides. *Reagents and conditions* (a) Cl_3SiH (28 eq.), xylene, 145 °C, 24 hrs or neat $PhSiH_3$, 140 °C for 3-5 days; crude reaction mixtures used without purification in step (b). (b) HBF_4 (15 eq.), H_2O, CH_2Cl_2 or Au(dms)Cl (1.0 eq.), CH_2Cl_2 or Au(tht)Cl (1.2 eq.), CH_3CN. *Overlapping peaks in the ^1H NMR spectrum prevented the diastereomeric ratio of **17a/17d** being determined. **__17a__, **17c**, **17d** could be reduced and complexes formed but it proved impossible to remove all impurities.

We believe that the reduction occurs with epimerisation at the phosphorus stereocentre to generate two diastereomeric phosphines. We have ruled out epimerisation of the planar chirality by conducting the reduction at 110 °C. This yields the same products in the same ratio but at a temperature unlikely to cause homolytic scission of the [2.2]paracyclophane ethylene bridge.

Curiously, the pyridine derivative **16e** gives a single diastereomer on reduction. Inspection of the ^1H NMR of the gold complex suggests that reduction occurs with retention of stereochemistry at phosphorus; there are two downfield signals that can be assigned to the ethylene bridge. This was later confirmed by X-ray crystallography (Figure 3).[22] It is unclear why the pyridine alters the stereochemical course of the reduction. It is possible that a pyridine-silane adduct delivers the hydride in an intramolecular fashion causing stereoselective reduction. Ideally, we would prepare a regioisomeric pyridine tertiary phosphine oxide and see if clean reduction is still observed.

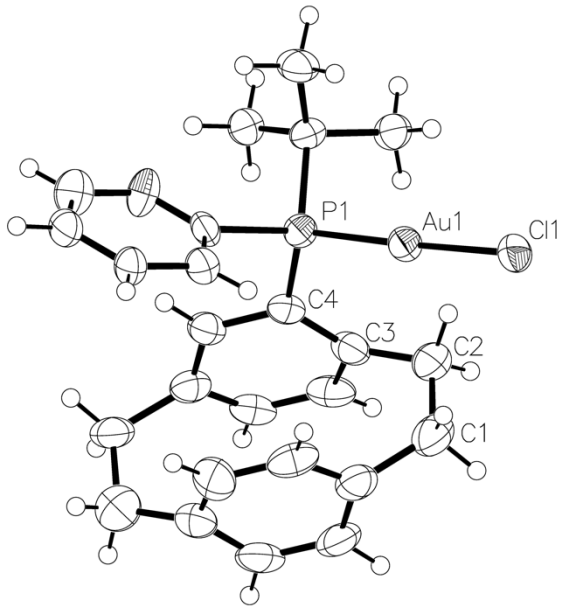


Figure 3. X-ray of the gold complex of phosphine **17e•AuCl**. Ellipsoids are drawn at a 50% probability level.[22]

Conclusion

This project set out to investigate the synthetic utility of [2.2]paracyclophane-derived secondary phosphine oxides. It is clear that the unusual properties of [2.2]paracyclophane has adversely affected the chemistry. The *tert*-butyl secondary phosphine oxide is readily prepared as a single diastereomer. It is a capable pre-ligand, facilitating both Suzuki-Miyaura cross coupling reactions and Buchwald-Hartwig aminations. More promising is its complexation with gold, which results in the formation of a complex capable of catalysing cycloisomerisations and methoxycyclisations.

It was noted that $Pd(OAc)_2$ inserts into the $C_{[2.2]paracyclophane}$–P bond causing protodephosphinylation. Should it be possible to prepare enantiomerically enriched [2.2]paracyclophane SPOs, this could offer a new route to planar chiral motifs.

The [2.2]paracyclophane SPO was readily transformed into a variety of tertiary phosphine oxides. These molecules are promising candidates for ligand synthesis as they are

both planar chiral and chiral at phosphorus. During the reduction of the phosphine oxide epimerisation of all but the pyridine derivative was observed leading to the isolation of a mixture of diastereomers.

Planar chiral SPOs show potential in asymmetric catalysis, but more research is required before they can fulfil their potential.

Experimental

All starting compounds and solvents were used as received from commercial sources without further purification unless otherwise noted. All reactions were performed in oven-dried glassware under an atmosphere of argon or nitrogen unless otherwise stated. Column chromatography was carried out on silica gel (grade 60, mesh size 230-400, Scharlau). Visualisation techniques employed included using ultraviolet light (254 nm), potassium permanganate, ethanolic phosphomolybdic acid or ninhydrin when applicable. NMR spectra were recorded at room temperature on Bruker-400 and Bruker-500 Avance instruments, with the use of the residual solvent proton as an internal standard ($CHCl_3$ = 7.26 ppm). Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. Mass spectra and high-resolution mass spectrometry were performed at Massey University, using a ThermoScientific Q Exactive Focus Hybrid Quadrupole-Orbitrap Mass Spectrometer.

(*SR*$_P$, *RS*$_p$)-*tert*-butyl([2.2]paracyclophan-4-yl)phosphine oxide (8)

A solution of *n*-BuLi (1.2 M in hexanes; 18.3 ml, 21.9 mmol, 1.05 eq.) was added dropwise over 30 min. to a solution of (±)-4-bromo[2.2]paracyclophane (6.0 g, 20.9 mmol, 1.0 eq.) in THF (60 ml), at -78 °C. The resulting yellow solution was stirred at -78 °C for 40 min. *tert*-Butyldichlorophosphine (1M in Et_2O; 21.9 ml, 21.9 mmol, 1.05 eq.) was added dropwise over 20 min. The solution was warmed to room temperature overnight. H_2O (75 ml)

was added to the reaction mixture and the resulting organic phases were separated. The aqueous phase was extracted with EtOAc (3 × 50 ml), the combined organics dried ($MgSO_4$) and concentrated under reduced pressure to yield a yellow residue. Purified by column chromatography on silica gel (EtOAc:Hex 6:4) followed by recrystallization (CH_2Cl_2:Pentane 2:8) to give white crystals of **8** (3.3 g, 55%).

R_f (4:6 Hex:EtOAc) 0.40.

mp: 142 – 144 °C

IR ν_{max} 2959, 2930, 2865, 1700, 1594, 1499, 1473, 1431, 1410, 1392, 1358, 1263, 1129, 1094, 1069, 1022, 994, 925, 900 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.42 (1H, d, $J_{P\text{-}H}$ = 398.1 Hz), 6.92 (1H, d, J = 7.7 Hz), 6.67 (1H, d, J = 8.1 Hz), 6.61-6.58 (2H, m, H-7), 6.53-6.52 (2H, m), 6.45 (1H, d, J = 8.1 Hz), 3.94 (1H, t, J = 11.5 Hz), 3.45 (1H, td, J = 12.1, 4.6 Hz), 3.22-3.18 (2H, m), 3.13-2.99 (4H, m), 1.00 (9H, d, J = 16.3 Hz).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 173.7, 145.3, 140.02, 139.6 (d, $J_{P\text{-}C}$ = 54.1 Hz), 135.5 (d, $J_{P\text{-}C}$ = 71.3 Hz), 134.2 (d, $J_{P\text{-}C}$ = 133.8 Hz), 133.2 (d, $J_{P\text{-}C}$ = 105.2 Hz), 132.2, 126.3 (d, $J_{P\text{-}C}$ = 375.7 Hz) 39.53, 36.2, 35.2, 32.6 (d, $J_{P\text{-}C}$ = 273.0 Hz), 23.5.

^{31}P NMR ($CDCl_3$, 200 MHz) δ 57.81.

HRMS-EI: *m/z* found: $[M]^+$, 312.1747. $C_{25}H_{25}OP$ requires $[M]^+$ 312.1643.

(*RS*$_P$,*RS*$_p$)-chloro(*tert*-butyl([2.2]paracyclophan-4-yl)phosphinous acid)gold(I) 8•AuCl

To a solution of secondary phosphine oxide **8** (30 mg, 0.01 mmol, 1eq.) in CH_2Cl_2 (5 mL) was added chloro(dimethyl sulfide)gold(I) (28 mg, 0.01 mmol, 1eq.). The mixture was stirred at room temperature overnight in the absence of light. The crude mixture was concentrated

under reduced pressure to give a greyish solid of the gold complex. Due to the instability of the complex only limited data could be collected.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.33 (1H, dd, J = 20.1, 1.7 Hz), 6.96 (2H, d, J = 7.7 Hz), 6.65 (2H, d, J = 8.0 Hz), 6.55 (2H, dd, J = 7.7, 3.2 Hz), 6.52 (1H, dd, J = 7.8, 1.7 Hz), 4.01 (1H, t, 11.2 Hz), 3.29-3.21 (2H, m), 3.22-3.16 (2H, m), 3.15-3.11 (1H, m), 3.10-3.02 (2H, m), 1.00 (9H, d, J = 17.3 Hz).

^{31}P NMR ($CDCl_3$, 200 MHz) δ 125.63.

(±)-Dimethyl 3-(2-methylprop-1-en-1-yl)cyclopent-3-ene-1,1-dicarboxylate 12[35]

To a solution of **8•AuCl** (3 mg, 0.007 mmol, 0.02 eq.) in CH_2Cl_2 (2 ml) was added $AgSbF_6$ (4 mg, 0.007 mmol, 0.02 eq.) and suspension stirred for 10 min. During this time AgCl precipitates as a white solid. A solution of 1,6-enyne **11** (90 mg, 0.37 mmol, 1eq.) in CH_2Cl_2 (5.5 ml). The mixture was stirred at room temperature and was monitored by TLC. After 10 hrs, the mixture was filtered through a short pad of silica (CH_2Cl_2, 10 ml) and concentrated under reduced pressure. Subsequent purification by column chromatography on silica gel (EtOAc:Hex 0.2:9.8) afforded product **12** as colourless oil (66 mg, 73%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.75 (1H, s), 5.41 (1H, s), 3.76 (6H, s), 3.22 (2H, s), 3.07 (2H, s), 1.84 (3H s), 1.80 (3H, s). Data comparable to that reported in the literature.[36]

(±)-Dimethyl 3-(2-methoxypropan-2-yl)-4-methylenecyclopentane-1,1-dicarboxylate 14

To a solution of **8•AuCl** (3 mg, 0.008 mmol, 0.02 eq.) in CH_2Cl_2 (2 ml) was added $AgSbF_6$ (5 mg, 0.008 mmol, 0.02 eq.) and suspension stirred for 10 min. During this time AgCl precipitates as a white solid. A solution of 1,6 enyne **11** (100 mg, 0.41 mmol, 1.0 eq.) in CH_3OH (8.3 ml) was added. The mixture was stirred at room temperature and was monitored by TLC. After 12 hrs, the mixture was filtered through a short pad of silica

(CH_2Cl_2, 10 ml) and concentrated under reduced pressure. Subsequent purification by column chromatography on silica gel (EtOAc:Hex 0.2:9.8) afforded product **14** as colorless oil (81 mg, 72%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.04 (1H, bs), 4.98 (1H, bs), 3.73 (3H, s), 3.72 (3H, s), 3.19 (3H, s), 2.94-2.83 (3H, m), 2.55 (1H, ddd, J = 13.5, 9.4, 1.7 Hz), 2.00 (2H, dd, J = 13.5, 9.4 Hz), 1.18 (3H, s), 1.12 (3H, s). Data comparable to that reported in the literature.[37]

(±)-3-(2-methoxypropan-2-yl)-4-methylene-1-tosylpyrrolidine 15

To a solution of **8•AuCl** (3 mg, 0.005 mmol, 0.02 eq.) in CH_2Cl_2 (2 ml) was added $AgSbF_6$ (2 mg, 0.005 mmol, 0.02 eq.) and suspension stirred for 10 min. During this time AgCl precipitates as a white solid. A solution of 1,6-enyne **13** (75 mg, 0.27 mmol, 1eq.) in CH_3OH (3.4 ml) was added. The mixture was stirred at room temperature and was monitored by TLC. After 12 hrs, the mixture was filtered through a short pad of silica (CH_2Cl_2, 10 ml) and concentrated under reduced pressure. Subsequent purification by column chromatography on silica gel (EtOAc:Hex 0.1:9.9) afforded product **15** as a white solid (81 mg, 97%); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.74 (2H, d, J = 6.1 Hz), 7.35 (2H, d, J = 7.9 Hz), 5.04 (2H, m), 3.80 (2H, m), 3.43 (1H, dd, J = 9.9, 4.2 Hz), 3.32-3.29 (1H, m), 2.74 (3H, s), 2.45 (3H, s), 1.14 (3H, s), 1.14 (3H, s), 1.03 (3H, s). Data comparable to that reported in the literature.[8]

General procedure for *P*-arylation

To a flame dried 25 ml round bottom flask was added $Pd(OAc)_2$ (2 mol%), dppf (2.2 mol%), Cs_2CO_3 (1.3 eq.). The reaction vessel was degassed and dioxane (2 ml) added. The resulting suspension was stirred under a flow of argon for 10 min. A solution of SPO **8** (1.0 eq.) and aryl iodide (1.5 equiv.) in dioxane:DCE (7:1) (8 ml) was added by syringe. The

reaction mixture was heated at 100 °C until the starting material had been completely consumed as judged by TLC (24 hrs). The mixture was cooled to room temperature, passed through celite pad and purified by column chromatography on silica gel (EtOAc:Hex 4:6) to obtain the appropriate tertiary phosphine oxide.

(RS_P,RS_p)-*tert*-Butyl([2.2]paracyclophan-4-yl)(phenyl)phosphine oxide 16a

$Pd(OAc)_2$ (1 mg, 0.004 mmol, 0.02 eq.), dppf (2 mg 0.004 mmol, 0.022 eq.), Cs_2CO_3 (81 mg, 0.25 mmol, 1.3 eq.), **8** (60 mg, 0.19 mmol, 1 eq.), phenylbromide (0.03 ml, 47.53 mg, 0.30 mmol, 1.5 eq.) to give a yellow solid of **16a** (45 mg, 61%).

mp: 166 – 168 °C.

IR: ν_{max} 2924, 2856, 1586, 1497, 1474, 1433, 1409, 1393, 1365, 1263, 1209, 1165, 1153, 1129, 1100, 1074, 1066, 1020, 996, 941, 916, 902 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ 8.20-8.16 (2H, m), 7.69-7.61 (3H, m), 6.68 (1H, dd, J = 7.8, 1.7 Hz), 6.60-6.58 (3H, m), 6.56 (1H, dd, J = 7.8, 1.5 Hz), 6.47 (1H, dd, J = 7.8, 1.8 Hz), 5.76 (1H, dd, J = 7.8, 1.8 Hz), 4.49 (1H, t, J = 10.9 Hz), 3.50 (1H, td, J = 8.3, 5.6 Hz), 3.13-3.06 (2H, m), 3.02-2.96 (2H, m), 2.94- 2.90 (1H, m), 2.82-2.76 (1H, m), 1.07 (9H , d, J = 16.1 Hz).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 146.6 (d, J_{P-C} = 27.4 Hz), 140.4, 138.7, 138.6 (d, J_{P-C} = 47.7 Hz), 136.7 (d, J_{P-C} = 47.8 Hz), 136.2 (d, J_{P-C} = 47.7 Hz), 135.9 (d, J_{P-C} = 11.5 Hz), 134.0, 133.0 (d, J_{P-C} = 27.9 Hz), 132.2 (d, J_{P-C} = 40.5 Hz), 131.8, 131.3 (d, J_{P-C} = 10.1 Hz), 131.1, 128.3, 127.3, 126.6, 36.8, 36.2, 35.2 (d, J_{P-C} = 25.5 Hz), 35.0, 34.6, 25.1.

^{31}P NMR ($CDCl_3$, 200 MHz) δ 41.93.

HRMS-EI: *m/z* found: $[M+H]^+$, 389.2024. $C_{26}H_{30}OP$ requires 389.2034; $[M+Na]^+$ 411.1846 $C_{26}H_{29}NaOP$ requires 411.1854.

(RS_P,RS_p)-*tert*-Butyl([2.2]paracyclophan-4-yl)(*p*-tolyl)phosphine oxide 16b

$Pd(OAc)_2$ (1 mg, 0.004 mmol, 0.02 eq.), dppf (2 mg, 0.004 mmol, 0.02 eq.), Cs_2CO_3 (81 mg, 0.25 mmol, 1.3 eq.), **8** (60 mg, 0.191 mmol), 4-iodotoulene (49.24 mg, 0.287 mmol, 1.5 eq.) in dioxane:DCE (7:1) (8 ml), to give a white solid of **16b** (52 mg, 68%).

R_f (7:3 Hex:EtOAc) 0.50.

mp: 216 – 218 °C

IR: ν_{max} 2925, 2851, 1725, 1598, 1500, 1466, 1433, 1394, 1365, 1293, 1259, 1205, 1162, 1150, 1111, 1066, 1013, 942, 919, 906, 906, 813, 799, 720 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ 8.05 (2H, t, J = 8.5 Hz), 7.46 (2H, d, J = 8.0 Hz), 6.68 (1H, d, J = 5.7 Hz), 6.59 (3H, m), 6.56 (1H, dd, J = 7.8, 1.7 Hz), 6.46 (1H, dd, J = 7.7, 1.8 Hz), 5.79 (1H, dd, J = 7.7, 1.8 Hz), 4.48 (1H, t, J = 10.8 Hz), 3.50 (1H, td, J = 10.7, 5.4 Hz), 3.12-3.07 (2H, m), 3.01- 2.91 (3H, m), 2.85-2.78 (1H, m), 2.54 (3H, s), 1.04 (9H, d, J = 16.9 Hz).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 138.6 (d, J_{P-C} = 47.9 Hz), 136.7 (d, J_{P-C} = 47.5 Hz), 136.2 (d, J_{P-C} = 48.8 Hz), 135.9 (d, J_{P-C} = 12.7 Hz), 135.9, 134.0, 133.0 (d, J_{P-C} = 29.4 Hz), 132.2 (t, J_{P-C} = 37.60 Hz), 129.0 (d, J_{P-C} = 42.05 Hz), 128.6, 127.5, 126.7, 36.8, 36.2, 35.2, 35.0, 25.1, 21.6.

^{31}P NMR ($CDCl_3$, 200 MHz) δ 42.19.

HRMS-EI: *m/z* found: $[M+H]^+$, 403.2178. $C_{27}H_{32}OP$ requires 403.2191; $[M+Na]^+$ 425.2003. $C_{27}H_{31}NaOP$ requires 425.2010.

(RS_P,RS_p)-*tert*-Butyl(4-methoxyphenyl)([2.2]paracyclophan-4-yl)phosphine oxide 16c

$Pd(OAc)_2$ (1 mg, 0.004 mmol, 0.02 eq.), dppf (2 mg, 0.004 mmol, 0.022 eq.), Cs_2CO_3 (81 mg, 0.25 mmol, 1.3 eq.), **8** (60 mg, 0.19 mmol, 1 eq.), 4-iodoanisole (67 mg, 0.29 mmol, 1.5 eq.) in dioxane:DCE (7:1) (8 ml) to give a yellow solid of **16c** (48 mg, 60 %).

R_f (7:3 Hex:EtOAc) 0.50.

mp: 137 – 139 °C.

IR: ν_{max} 2925, 2851, 1725, 1598, 1500, 1466, 1433, 1394, 1365, 1293, 1259, 1205, 1162, 1150, 1111, 1066, 1013, 942, 919, 906, 906, 813, 799, 720 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ 8.09 (2H, t, J = 8.7 Hz), 7.18 (2H, d, J = 7.2 Hz), 6.66 (1H, d, J = 13.2 Hz), 6.60-6.54 (4H, m), 6.47 (1H, d, J = 7.5 Hz), 5.81 (1H, d, J = 7.4 Hz), 4.45 (1H, d, J = 11.4 Hz), 3.98 (3H, s), 3.50 (1H, dd, J = 11.8, 5.3 Hz), 3.10 (2H, t, J = 4.4 Hz), 3.01-2.89 (3H, m), 2.84-2.78 (1H, m), 1.04 (9H, d, J = 14.8 Hz).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 162.0 (d, J_{P-C} = 10.3 Hz), 146.4 (d, J_{P-C} = 28.8 Hz), 140.5, 138.7, 138.6 (d, J_{P-C} = 48.1 Hz), 136.7 (d, J_{P-C} = 47.7 Hz), 136.3 (d, J_{P-C} = 48.6 Hz), 135.9, 134.7 (d, J_{P-C} = 32.9 Hz), 134.0, 132.2 (d, J_{P-C} = 40.1 Hz), 132.1, 127.5, 126.8, 122.5, 121.7, 113.9 (d, J_{P-C} = 44.9 Hz), 64.1, 55.3, 36.8, 36.2, 35.2 (d, J_{P-C} = 27.5 Hz), 35.2, 35.0, 25.1.

^{31}P NMR ($CDCl_3$, 200 MHz) δ 42.37.

HRMS-EI: *m/z* found: $[M+H]^+$, 419.2132. $C_{27}H_{32}O_2P$ requires 419.2140; $[M+Na]^+$ 441.1952 $C_{27}H_{31}NaO_2P$ requires 441.1959.

(*RS*$_P$,*RS*$_p$)-*tert*-Butyl(4-cyanophenyl)([2.2]paracyclophan-4-yl)phosphine oxide 16d

$Pd(OAc)_2$ (1 mg, 0.004 mmol, 0.02 eq.), dppf (2 mg, 0.004 mmol, 0.022 eq.), Cs_2CO_3 (81 mg, 0.25 mmol, 1.3 eq.), **8** (60 mg, 0.19 mmol, 1 eq.), 4-iodobenzonitrile (66 mg, 0.29 mmol) in dioxane:DCE (7:1) (8 ml), to give a white solid of **16d** (50 mg, 64%).

mp: 118 – 120 °C.

IR: ν_{max} 3430, 2960, 2926, 2855, 2230, 1669, 1500, 1476, 1465, 1394, 1367, 1263, 1200, 1156, 1130, 1091, 1065, 1017, 942, 915 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ 8.31 (2H, t, J = 5.7 Hz), 7.95 (2H, d, J = 8.2 Hz), 6.62 (2H, s), 6.56 (1H, dd, J = 7.7, 1.6 Hz), 6.53-6.47 (3H, m), 5.74 (1H, dd, J = 1.8, 7.8 Hz), 4.40 (1H,

t, *J* = 11.2 Hz), 3.46 (1H, td, *J* = 10.9, 5.4 Hz), 3.13-3.05 (2H, m), 3.00-2.96 (1H, m), 2.98-2.90 (2H, m), 2.81-2.75 (1H, m), 1.05 (9H, d, *J* = 15.2 Hz).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 146.7 (d, $J_{P\text{-}C}$ = 26.7 Hz), 140.3, 139.0 (d, $J_{P\text{-}C}$ = 48.1 Hz), 138.6, 137.1 (d, $J_{P\text{-}C}$ = 47.2 Hz), 136.5, 135.9 (d, $J_{P\text{-}C}$ = 47.9 Hz), 133.7, 133.6 (d, $J_{P\text{-}C}$ = 25.4 Hz), 132.3 (d, $J_{P\text{-}C}$ = 58.1 Hz), 132.0, 131.7 (d, $J_{P\text{-}C}$ = 38.1 Hz), 118.1, 115.2, 36.7, 36.2,35.0, 25.0.

^{31}P NMR ($CDCl_3$, 200 MHz) δ 41.75.

HRMS-EI: *m/z* found: $[M+H]^+$, 414.1979. $C_{27}H_{29}NOP$ requires $[M+H]^+$ 414.1989. *m/z* found: $[M+Na]^+$, 436.1800. $C_{27}H_{28}NNaOP$ requires $[M+Na]^+$ 436.1806.

(*SR*$_P$,*RS*$_p$)-*tert*-Butyl([2.2]paracyclophan-4-yl)(pyridine-2-yl)phosphine oxide 16e

$Pd(OAc)_2$ (1 mg, 0.004 mmol, 0.02 eq.), dppf (2 mg, 0.004 mmol, 0.022 eq.), Cs_2CO_3 (81 mg, 0.25 mmol, 1.3 eq.), **8** (60 mg, 0.19 mmol, 1 eq.), 2-iodopyridine (59 mg, 0.29 mmol, 1.5 eq.) in dioxane:DCE (7:1) (8 ml), brown solid of **16e** (43 mg, 58%).

mp: 136 – 137 °C.

IR: ν_{max} 3042, 2953, 2928, 2852, 1726, 1573, 1564, 1500, 1473, 1450, 1431, 1420, 1391, 1364, 1262, 1177, 1152, 1134, 1081, 1064, 1045, 1021, 991, 945, 918, 882 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.93 (1H, d, *J* = 3.9 Hz), 8.64 (1H, t, *J* = 6.5 Hz), 8.03 (1H, tdd, *J* = 7.7, 3.1, 1.7 Hz), 7.53-7.50 (1H, m), 7.34 (1H, d, *J* = 12.4 Hz), 6.60-6.54 (3H, m), 6.45 (1H, d, *J* = 7.8 Hz), 6.37 (1H, d, *J* = 7.8 Hz), 4.52 (1H, t, *J* = 10.8 Hz), 3.44 (1H, td, *J* = 10.5, 5.9 Hz), 3.16-3.08 (2H, m), 2.96-2.85 (4H, m), 1.06 (9H, d, *J* = 15.1 Hz).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 149.0 (d, $J_{P\text{-}C}$ = 65.5 Hz), 146.4 (d, $J_{P\text{-}C}$ = 24.9 Hz), 140.5, 138.9, 138.3 (d, $J_{P\text{-}C}$ = 47.2 Hz), 136.7 (d, $J_{P\text{-}C}$ = 41.8 Hz), 136.4 (d, $J_{P\text{-}C}$ = 47.2 Hz), 138.3 (d, $J_{P\text{-}C}$ = 41.8 Hz), 136.2 (d, $J_{P\text{-}C}$ = 47.9 Hz), 135.8 (d, $J_{P\text{-}C}$ = 13.2 Hz), 133.4, 132.6, 132.3,

131.9, 130.0 (d, J_{P-C} = 65.8 Hz), 124.7 (d, J_{P-C} = 12.1 Hz), 35.2 (d, J_{P-C} = 48.1 Hz), 34.9, 34.4, 24.4.

^{31}P NMR ($CDCl_3$, 200 MHz) δ 36.12.

HRMS-EI: *m/z* found: $[M+H]^+$, 390.1978. $C_{25}H_{29}NOP$ requires 390.1987; $[M+Na]^+$ 412.1798 $C_{25}H_{28}NaOP$ requires 412.1806.

(*RS*$_P$,*RS*$_p$)-*tert*-Butyl([2.2]paracyclophan-4-yl)(*p*-tolyl)phosphine and (*SR*$_P$,*RS*$_p$)-*tert*-butyl([2.2]paracyclophan-4-yl)(*p*-tolyl)phosphine 17b

Trichlorosilane (0.73 ml, 7.30 mmol, 28 eq.) was added to a stirred suspension of **16b** (105 mg, 0.26 mmol, 1.0 eq.) in *p*-xylene (2 ml) and heated to 140 °C in a pressure tube for 20 hrs. The reaction mixture was cooled to 0 °C and carefully quenched by the addition of 30% aqueous NaOH (10 ml) (Care: exothermic reaction). The aqueous layer was extracted with EtOAc (3 x15 ml), dried ($MgSO_4$) and the solvent was remove under reduced pressure. The crude material (80 mg, approximately 80% yield) as a 60:40 diastereomeric mixture was used without further purification.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.76 (2H, t, *J* = 7.9 Hz), 7.21 (2H, d, *J* = 7.6 Hz), 7.10 (1H, d, *J* = 7.7 Hz), 7.03-6.99 (3H, m), 6.93 (1H, d, *J* = 7.8 Hz), 6.73 (1H, d, *J* = 6.4 Hz), 6.51 (1H, d, *J* = 7.7 Hz, 1H), 6.46-6.43 (3H, m), 6.39-6.33 (5H, m), 6.23-6.20 (1H, m), 5.67 (1H, d, *J* = 7.8 Hz), 4.12-4.07 (1H, m), 3.35-3.30 (2H, m), 3.19-3.14 (1H, m), 3.11-3.05 (2H, m), 3.00-2.91 (3H, m), 2.90-2.84 (3H, m), 2.82-2.77 (2H, m), 2.76 (2H, m), 2.39 (3H, s), 2.21 (3H, s), 1.15 (6H, d, *J* = 12.2 Hz), 0.90 (9H, d, *J* = 12.5 Hz).

^{31}P NMR ($CDCl_3$, 200 MHz) δ 16.21, 8.40.

(RS_P,RS_p)-*tert*-Butyl([2.2]paracyclophan-4-yl)(*p*-tolyl)phosphinium tetrafluoroborate and (SR_P,RS_p)-*tert*-butyl([2.2]paracyclophan-4-yl)(*p*-tolyl)phosphinium tetrafluoroborate 17b•H

17b (80 mg, 0.21 mmol, 1.0 eq.), $HBF_4.OEt_2$ (54% solution in Et_2O; 0.52 ml, 3.22 mmol, 15.0 eq.) and CH_2Cl_2 (7 ml) were combined at 0 °C. After 2 hrs, the reaction mixture was warmed to 22 °C and aqueous tetrafluoroboric acid (5 ml) was added. The reaction mixture was allowed to stir for more 2 hrs. The aqueous phase was separated with EtOAc (3 x15 ml), dried ($MgSO_4$) and the solvent was removed under reduced pressure. The crude product **17b•H** was obtained as a 57:43 mixture of diastereomers as a fluffy white powder (55 mg, 69%).

IR: ν_{max} 2956, 2851, 1598, 1467, 1407, 1317, 1180, 1031, 919, 857, 809, 719 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ 8.68 (1H, s), 8.55 (1H, s), 8.22-8.18 (2H, m), 7.78-7.74 (1H, m), 7.68 (2H, s), 7.45-7.44 (1H, m), 7.40 (1H, d, *J* = 14.8 Hz, 1H), 7.00 (1H, d, *J* = 12.8 Hz, 1H), 6.87-6.79 (3H, m), 6.68-6.65 (1H, m), 6.62-6.60 (2H, m), 6.55-6.47 (2H, m), 5.96 (1H, d, *J* = 7.6 Hz, 1H), 5.78 (1H, d, *J* = 7.3 Hz, 1H), 3.92 (1H, t, *J* = 11.4 Hz), 3.53-3.49 (1H, m), 3.41-3.37 (1H, m), 3.30-3.25 (3H, m), 3.22 (2H, d, *J* = 10.2 Hz), 3.17 (2H, d, *J* = 9.2 Hz), 3.06-3.00 (4H, m), 2.59 (3H, s), 2.48 (2H, s), 1.59 (6H, d, *J* = 18.0 Hz), 1.31 (9H, d, *J* = 16.1 Hz).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 146.7, 146.5 (d, *J* = 30.6 Hz), 146.2, 145.6, 141.9, 141.5 (d, *J* = 46.1 Hz), 140.0, 139.6, 139.5, 139.1 (d, *J* = 60.0 Hz), 138.8, 137.9 (d, *J* = 45.5 Hz), 137.3 (d, *J* = 47.0 Hz), 136.0 (d, *J* = 32.5 Hz), 134.6 (d, *J* = 37.0 Hz), 134.4 (d, *J* = 41.2 Hz), 133.0 (d, *J* = 34.1 Hz), 132.8, 132.6 (d, *J* = 42.7 Hz), 132.2, 131.9, 131.7 (d, *J* = 50.2 Hz), 131.05 (d, *J* = 51.1 Hz), 35.51, 35.2 (d, *J* = 21.2 Hz), 35.1, 34.6, 33.5, 33.1, 29.7, 26.1, 25.2, 22.01 (d, *J* = 65.5 Hz).

^{31}P NMR ($CDCl_3$, 200 MHz) δ 18.5, 11.6.

(SR_P,RS_p)-Chloro[(*tert*-butyl([2.2]paracyclophan-4-yl)(*p*-tolyl)phosphine]gold(I) and (RS_P,RS_p)-chloro[(*tert*-butyl([2.2]paracyclophan-4-yl)(*p*-tolyl)phosphine]gold(I)

17b•AuCl

To a flame dried two necked 25 ml RBF was added **17b** (80 mg, 0.20 mmol, 1.0 eq.) and chloro(tetrahydrothiophene)gold(I) (66.3 mg, 0.20 mmol, 1.0 eq.) in dry CH_3CN (5 ml). The mixture was heated to refluxed for 2 hrs. The crude mixture was concentrated under reduced pressure. The resulting yellow solid was dissolved in CH_2Cl_2 (1 ml) before pentane (10 ml) was added to precipitate the desired complex as a yellow solid, which was isolated by decantation to obtain desired complex as a mixture of diastereomers (62:38 dr) (20 mg, 16% yield).

IR: ν_{max} 2961, 2920, 1710, 1600, 1498, 1460, 1394, 1261, 1090, 805, 713 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ 8.05-8.01 (2H, m), 7.66 (1H, d, J = 7.7 Hz), 7.44 (2H, d, J = 6.4 Hz), 7.38-7.34 (1H, m), 7.16-7.15 (1H, m), 7.10-7.09 (1H, m), 7.04-6.98 (2H, m), 6.65-6.60 (3H, m), 6.58-6.54 (3H, m), 6.42-6.37 (1H, m), 6.34 (1H, d, J = 12.8 Hz, 1H), 5.91 (1H, dd, J = 7.8, 1.5 Hz), 4.81-4.76 (1H, m), 4.28-4.17 (1H, m), 3.86-3.71 (2H, m), 3.23-3.09 (5H, m), 3.14-3.03 (6H, m), 2.98-2.95 (3H, m), 2.89 (1H, d, J = 7.2 Hz), 2.78-2.73 (2H, m), 2.54 (3H, s), 2.38 (2H, s), 1.36 (6H, d, J = 16.4 Hz), 1.17 (9H, d, J = 16.8 Hz).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 144.1 (d, J_{P-C} = 48.2 Hz), 142.9, 139.2 (d, J_{P-C} = 33.3 Hz), 139.0, 136.9 (d, J_{P-C} = 36.8 Hz), 136.7, 136.6, 136.4, 136.1, 135.6 (d, J_{P-C} = 50.9 Hz), 133.0 (d, J_{P-C} = 35.1 Hz), 132.6, 132.3 (d, J_{P-C} = 40.5 Hz), 132.0, 129.9 (d, J_{P-C} = 46.4 Hz), 129.0 (d, J_{P-C} = 47.3 Hz), 42.1, 36.6, 36.5 (d, J_{P-C} = 22.8 Hz), 36.2, 35.6, 35.1, 30.0, 34.9, 30.1, 28.3 (d, J_{P-C} = 23.6 Hz), 21.5 (d, J_{P-C} = 79.7 Hz), 1.0.

^{31}P NMR ($CDCl_3$, 200 MHz) δ 47.8, 46.7.

HRMS-EI: *m/z* found: $[M + Na]^+$ 641.1402 $C_{27}H_{31}ClNaP$ requires 641.1415.

(SR_P,RS_p)-Chloro[*tert*-butyl([2.2]paracyclophan-4-yl)(pyridin-2-yl)phosphine]gold(I)

17e•AuCl

To a solution of **17e** (40 mg, 0.10 mmol, 1.0 eq.) in dry CH_2Cl_2 (3 ml) was added chloro(dimethyl sulfide)gold(I) (31.57 mg, 0.10 mmol, 1.0 eq.). The mixture was stirred at room temperature in the absence of light. The crude mixture was concentrated after 2 hrs under reduced pressure. The resulting grey solid was dissolved in CH_2Cl_2 (1 ml) and pentane (10 ml) was added to precipitate the desired complex as a white solid, which was isolated by decantation. The solid was dissolved in CH_2Cl_2 (1 ml) and pentane was slowly added to get a biphasic solution. Slow crystallization furnished crystals of the desired complex (15 mg, 23%).

mp: 223 - 224 °C

IR: ν_{max} 2958, 2920, 1568, 1446, 1413, 1359, 1258, 1134, 1093, 805, 716 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.90 (1H, d, J = 4.1 Hz), 8.69-8.65 (1H, m), 8.00-7.99 (1H, m), 7.57-7.53 (1H, m), 6.82 (1H, d, J = 7.8 Hz), 6.62 (1H, dd, J = 7.8, 1.9 Hz), 6.59-6.58 (1H, m), 6.54 (1H, dd, J = 7.8, 1.8 Hz), 6.49 (1H, d, J = 12.1 Hz), 5.80 (1H, dd, J = 7.8, 1.8 Hz), 4.89-4.82 (1H, m), 3.84-3.75 (1H, m), 3.22-3.16 (2H, m), 3.11-3.03 (1H, m), 2.99-2.90 (2H, m), 2.76-2.71 (1H,m), 1.21 (9H, d, J = 17.4 Hz).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 150.3 (d, J = 50.6 Hz), 144.2 (d, J = 49.5 Hz), 139.8 (d, J = 34.8 Hz), 139.3, 139.1, 137.2 (d, J = 11.3 Hz), 136.8, 136.7 (d, J = 16.7 Hz), 136.58, 136.51 (d, J = 11.7 Hz), 134.8, 134.6, 133.0, 132.7, 132.4, 132.0, 125.4 (d, J = 8.9 Hz), 124.0, 36.6, 36.5 (d, J = 31.2 Hz), 36.3, 35.7, 35.0 (d, J = 21.7 Hz), 34.1, 27.4 (d, J = 21.6 Hz), 22.3, 14.0.

^{31}P NMR ($CDCl_3$, 200 MHz) δ 40.6.

HRMS-EI: *m/z* found: $[M + Na]^+$ 628.1193 $C_{25}H_{28}AuClNNaP$ requires 628.1211.

Acknowledgements

The authors thank Massey University for financial support and the Institute of Fundamental Sciences (Massey University) for a Graduate Assistant (MNM) position.

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