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Copper(I) Complexes of *P*-Stereogenic Josiphos and Related Ligands

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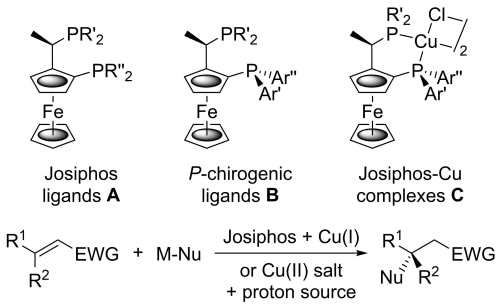
Starting from (*R*)-Ugi's amine, diastereoselective lithiation followed by Ar'PCl_2 and then Ar''MgBr led to the generation, as single diastereoisomers, of (R,S_p,S_{phos}) [Ar' = Ph, Ar'' = *o*-Tol] and (R,S_p,R_{phos}) [Ar' = *o*-Tol, Ar'' = Ph] PPFA ligand derivatives. Amine substitution of both with $HPCy_2$ gave *P*-stereogenic Josiphos ligands, and then addition of CuCl, the corresponding copper(I) complexes. The latter were also generated by using borane P and N protecting groups and *in situ* Cu(I) complexation, avoiding the isolation of air-sensitive phosphine intermediates. This protection methodology was also applied to the synthesis of Josiphos/CuCl complexes derived from PCl_3. In addition, related bulky cobalt-sandwich complex-based derivatives were also obtained. Preliminary investigation revealed isolated CuCl complexes as competent catalyst precursors for enantioselective conjugate addition reactions.

Introduction

Although many ligands have been developed for application in asymmetric synthesis, relatively few have found widespread use. Of these so-called 'privileged' ligands,[1] one of the most successful class are the ferrocene-based Josiphos ligands **A**.[2] Numerous derivatives are known, obtained by varying the identity of R′ and R″, and many are commercially available. This has aided the incorporation of **A** into many ligand screening exercises, often leading to a successful outcome.[3] In particular, *in situ* generated Josiphos-copper complexes have been applied successfully to enantioselective conjugative C–C,[4] C–H,[5] and C–B[6] bond-forming reactions of activated alkenes (Scheme 1). In addition to e.e. optimisation by varying the steric and electronic properties of the R′ and R″ substituents, there is the possibility of creating an additional phosphorus-based stereogenic centre, such that one of the two resulting diastereomeric ligands **B** may lead to higher enantioslectivity.[7] We chose to explore this aspect of ligand-optimisation by first synthesising a series of readily isolated and air-stable copper(I) chloride complexes **C** (Ar′ ≠ Ar'' and Ar′ = Ar'').



Scheme 1. Ligands and copper catalysts for asymmetric conjugate addition.

Results and Discussion

For the initial synthesis of *P*-stereogenic Josiphos derivatives we adapted the diastereoslective methodology reported previously by Chen,[8,9] and applied by ourselves for the synthesis of *P*-stereogenic Phosferrox derivatives.[10] As in our previous report, our aim was to control the introduction of phenyl and *o*-tolyl groups to create the phosphorus-based stereogenic centre. These aryl groups are differentiated by a methyl substituent, with this positioned *ortho* so that it influences the environment about a coordinated metal, but ideally not to the extent that this relatively small group changes the nature of ligand coordination. Accordingly, (*R*)-*N*,*N*-dimethyl-1-ferrocenylethylamine **1**[11] (Ugi's amine) was lithiated at 0 °C with *s*-butyl lithium followed by the addition of dichlorophenylphosphine. After warming to room temperature and re-cooling to −78 °C (*o*-tolyl)magnesium bromide was added, leading after chromatography and recrystallisation, to the isolation of (R,S_p,S_{phos})-**2** as a single diastereoisomer (Scheme 2). Use of the same procedure, but with dichloro(*o*-tolyl)phosphine and phenylmagnesium bromide, gave (R,S_p,R_{phos})-**3**, again as a single diastereoisomer. The configuration of these new PPFA ligand analogues was confirmed by X-ray crystallographic analysis (Figure 1 and Figure 2).[12] Separate reaction of both diastereoisomers with acetic anhydride at room temperature was followed by reaction with dicyclohexylphosphine, again at room temperature (*vide infra*), to give *P*-stereogenic Josiphos ligand derivatives (R,S_p,S_{phos})-**4** and (R,S_p,R_{phos})-**5** as single diastereoisomers. These

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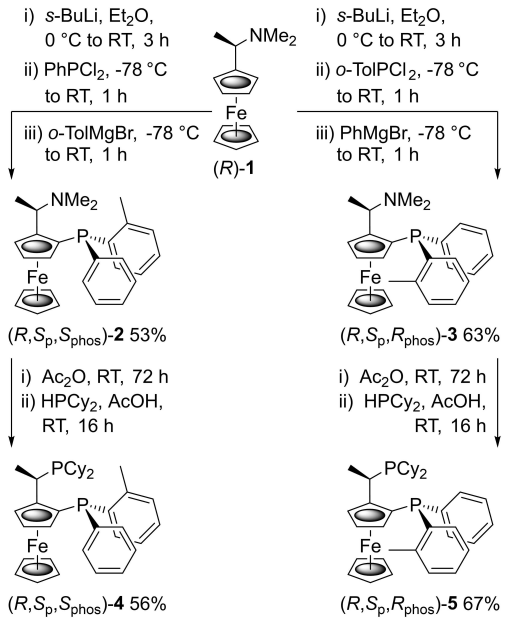


Scheme 2. Synthesis of *P*-stereogenic PPFA ligands (R,S_p,S_{phos})-**2** and (R,S_p,R_{phos})-**3** and Josiphos ligands (R,S_p,S_{phos})-**4** and (R,S_p,R_{phos})-**5**.

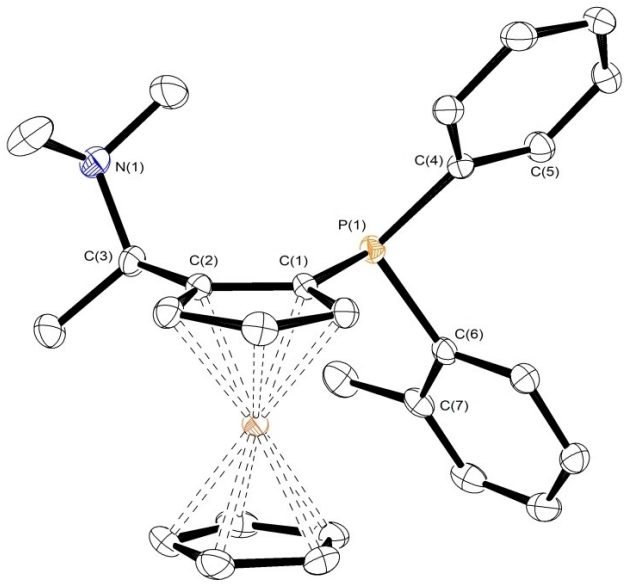


Figure 1. Representation of the X-ray crystal structure of (R,S_p,S_{phos})-**2** (hydrogen atoms omitted for clarity). Thermal ellipsoids are drawn at the 50% probability level. Principal bond lengths [Å] include: C(2)–C(3) 1.519(3), C(1)–P(1) 1.822(2), P(1)–C(4) 1.839(2), P(1)–C(6) 1.838(2). Principal torsion angles [°] include: C(1)–C(2)–C(3)–N(1) −98.4(3), C(2)–C(1)–P(1)–C(4) 130.27(19), C(2)–C(1)–P(1)–C(6) −124.57(19), C(1)–P(1)–C(4)–C(5) 160.79(17), C(1)–P(1)–C(6)–C(7) 106.00(17). Absolute structure parameter = −0.013(6).

stereospecific substitution reactions proceed with retention of configuration *via* an intermediate α-ferrocenyl carbenium ion.[13]

The configuration of the products (R,S_p,S_{phos})-**2** and (R,S_p,R_{phos})-**3** are consistent with the known lithiation diastereoselectivity of amine (*R*)-**1**,[11] and subsequent addition of R′PCl_2 followed by R″MgX for the creation of the phosphorus-based

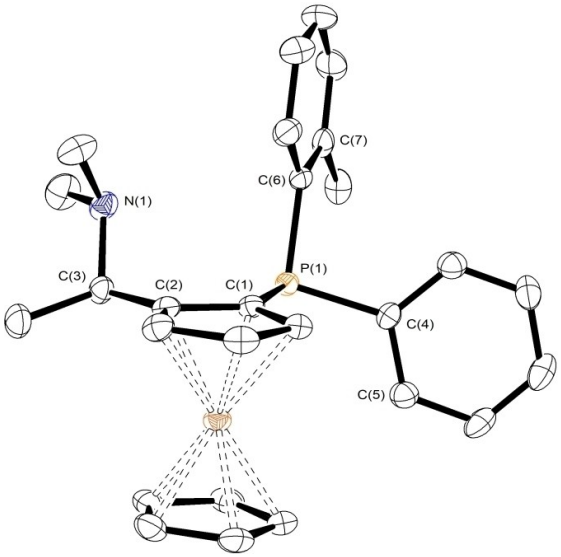
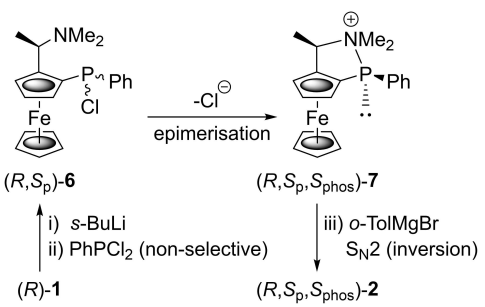


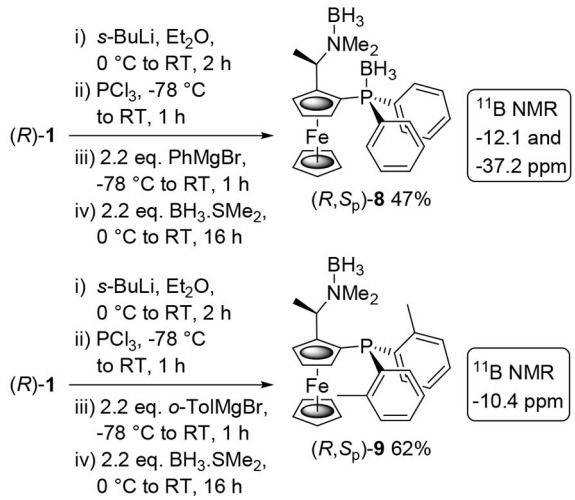
Figure 2. Representation of the X-ray crystal structure of (R,S_p,R_{phos})-**3** (hydrogen atoms omitted for clarity). Thermal ellipsoids are drawn at the 50% probability level. Principal bond lengths [Å] include: C(2)–C(3) 1.507(5), C(1)–P(1) 1.813(3), P(1)–C(4) 1.843(3), P(1)–C(6) 1.837(3). Principal torsion angles [°] include: C(1)–C(2)–C(3)–N(1) −69.6(4), C(2)–C(1)–P(1)–C(4) −166.9(3), C(2)–C(1)–P(1)–C(6) 90.5(3), C(1)–P(1)–C(4)–C(5) 78.0(3), C(1)–P-P(1)–C(6)–C(7) −176.9(3). Absolute structure parameter = −0.017(10).

stereogenic centre.[8] For the latter it was suggested that the reaction proceeds *via* an N–P bond containing intermediate such as (R,S_p,S_{phos})-**7** in which the phenyl group is oriented away from ferrocene (Scheme 3). Subsequent addition of the Grignard reagent (in this case *o*-TolMgBr) results in substitution (S_N2) to give (R,S_p,S_{phos})-**2**. Whilst the origin of the stereoselection in this process could arise from the reaction of lithiated (*R*)-**1** with prochiral $PhPCl_2$, an alternative explanation is that this gives (R,S_p)-**6** with little or no control at phosphorus, followed by loss of the second chloride leaving group and epimerisation of the resulting cyclic intermediate. This is consistent with the complete control of this process by the element of planar chirality, as observed also on the application of this chemistry to lithiated (S,S_p) and (S,R_p) ferrocenyloxazolines.[10]



Scheme 3. Planar chiral stereocontrol in the synthesis of *P*-stereogenic diastereoisomer (R,S_p,S_{phos})-**2**.

Although successful, an issue with the procedure outlined in Scheme 2 is the air sensitivity of the ferrocenylphosphine species, such that oxidation to the corresponding phosphine oxides occurs readily. We, therefore, investigated the use of a borane protecting group to prevent this during ligand synthesis, and in addition, aimed to avoid isolation of the deprotected ligand by complexing *in situ* with copper(I) chloride. The viability of this approach was investigated first by adding phosphorus trichloride to lithiated Ugi's amine, followed by greater than two equivalents each of phenylmagnesium bromide and then borane-dimethylsulfide. This gave doubly protected (R,S_p)-**8**, as revealed by the two (broad) ^{11}B NMR signals at −12.2 and −37.2 ppm (Scheme 4). Using the same protocol, but with *o*-tolylmagnesium bromide, gave singly protected (R,S_p)-**9** for which, in addition to there being a single ^{11}B NMR signal (−10.4 ppm), the ^{31}P NMR signal (18.2 ppm) differs significantly from that observed for (R,S_p)-**8** (9.9 ppm). The absence of phosphorus protection was confirmed by X-ray crystallographic analysis (Figure 3). This use of phosphorus trichloride in three substitution reactions with organolithium/Grignard reagents provides a simple alternative method to the use of preformed Ar_2PCl or $ArPCl_2$ reagents (*vide infra*).



Scheme 4. Investigation into the use of borane protection in ligand synthesis.

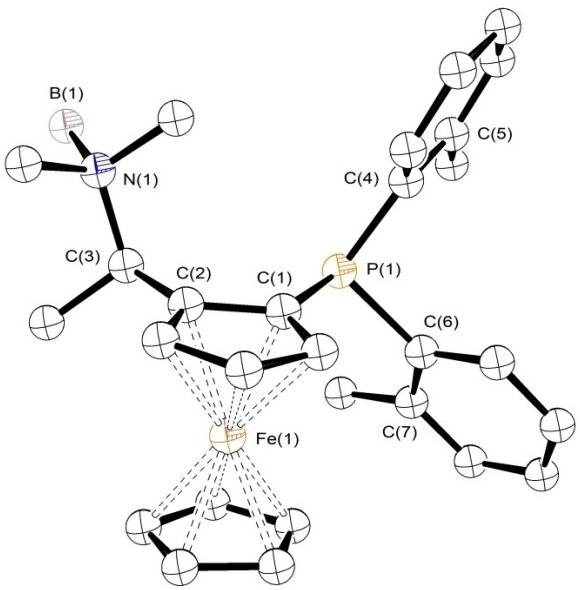
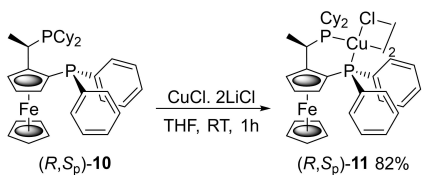


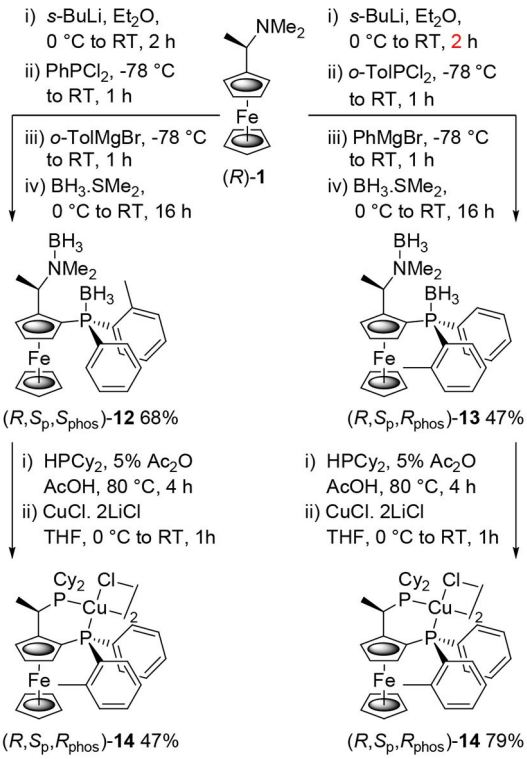
Figure 3. Representation of the X-ray crystal structure of (R,S_p)-**9** (hydrogen atoms omitted for clarity). Thermal ellipsoids are drawn at the 50% probability level. Principal bond lengths [Å] include: C(2)–C(3) 1.510(4), C(1)–P(1) 1.820(3), P(1)–C(4) 1.841(4), P(1)–C(6) 1.845(3). Principal torsion angles [°] include: C(1)–C(2)–C(3)–N(1) −100.1(3), C(2)–C(1)–P(1)–C(4) 113.7(3), C(2)–C(1)–P(1)–C(6) −141.2(3), C(1)–P(1)–C(4)–C(5) −176.3(3), C(1)–P(1)–C(6)–C(7) 110.1(3). Absolute structure parameter = −0.014(6).

Isolated copper complexes of Josiphos ligands are known,[15] generated from the addition of the ligand to a copper(I) halide salt dissolved in a polar solvent. On a mmol scale, and as an alternative to weighing out small quantities of air-sensitive copper(I) chloride, it was convenient to use commercially available copper(I) chloride – bis(lithium chloride) complex in THF, as illustrated by the complexation of the parent Josiphos ligand (R,S_p)-**10** to give air-stable and readily chromatographed complex (R,S_p)-**11** (Scheme 5). In the solid-state and as a solution in dichloromethane this complex is dimeric, but it is monomeric in strongly a coordinating solvent such as acetonitrile.[15b]

Putting together these components of *P*-stereogenic phosphine generation, protection, and complexation, the direct synthesis of new copper-Josiphos complexes was attempted (Scheme 6). Addition of BH_3.SMe_2 after the initial sequence of lithiation, phosphorus introduction, and Grignard substitution, resulted in the isolation of (R,S_p,S_{phos})-**12** and (R,S_p,R_{phos})-**13** as doubly protected P,N-ligands. Both were isolated readily as single diastereoisomers, and the identity and configuration of both were confirmed by X-ray crystallographic analysis (Figure 4 and Figure 5).[12] Subsequent treatment of (R,S_p,S_{phos})-**12** with dicyclohexylphosphine in 5% acetic anhydride/acetic acid at 80 °C followed, after workup, by copper(I) chloride – bis(lithium chloride) addition, resulted in an air-stable complex isolated by column chromatography as a single diastereoisomer. Significantly, the same product was obtained from (R,S_p,R_{phos})-**13**, revealing epimerisation of the phosphorus-based stereogenic centre for one of the diastereoisomers under the conditions required for deprotection and nitrogen substitution. Deprotection of borane-protected *P*-stereogenic phosphines is known to proceed with retention of configuration.[16] The identity of the copper-complex formed from both sequences as (R,S_p,R_{phos})-**14** was revealed by the separate formation of this from complexation of (R,S_p,R_{phos})-**5** with copper(I) chloride (Scheme 7). Com-



Scheme 5. Synthesis of copper chloride complex (R,S_p)-**11**.



Scheme 6. Application of borane-protection and *in-situ* complexation for the synthesis of *P*-stereogenic Josiphos-copper derivative (R,S_p,R_{phos})-**14**.

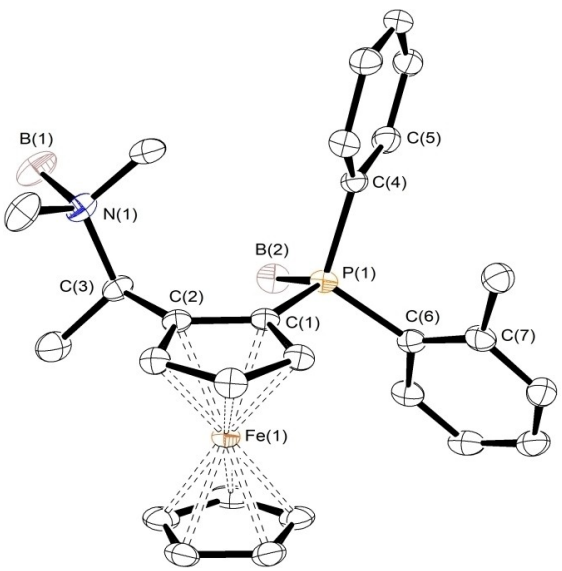


Figure 4. Representation of the X-ray crystal structure of (R,S_p,S_{phos})-**12** (hydrogen atoms omitted for clarity). Thermal ellipsoids are drawn at the 50% probability level. Principal bond lengths [Å] include: C(2)–C(3) 1.514(3), C(1)–P(1) 1.806(2), P(1)–C(4) 1.819(2), P(1)–C(6) 1.828(2). Principal torsion angles [°] include: C(1)–C(2)–C(3)–N(1) −101.4(3), C(2)–C(1)–P(1)–C(4) 96.9(2), C(2)–C(1)–P(1)–C(6) −148.3(2), C(1)–P(1)–C(4)–C(5) −169.19(17), C(1)–P(1)–C(6)–C(7) −75.7(2). Absolute structure parameter = −0.006(6).

plexation of (R,S_p,S_{phos})-**4** gave (R,S_p,S_{phos})-**15**, confirming that this was not formed using the borane-based protocol.

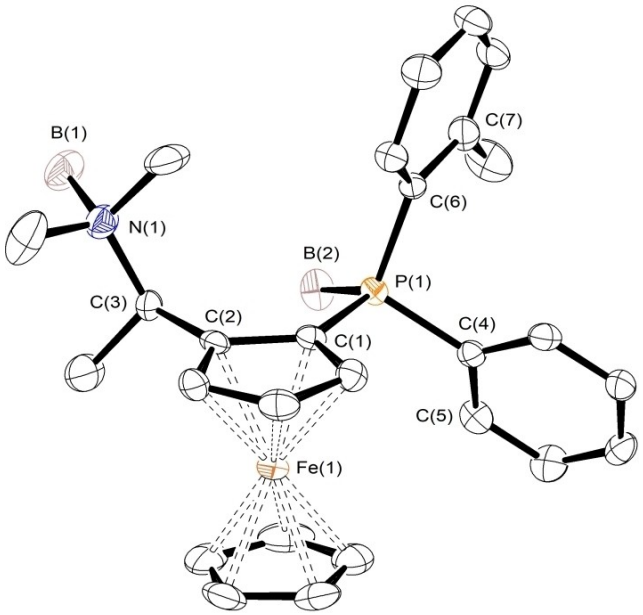
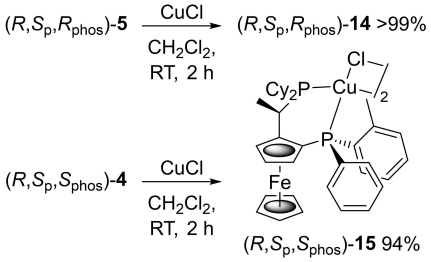
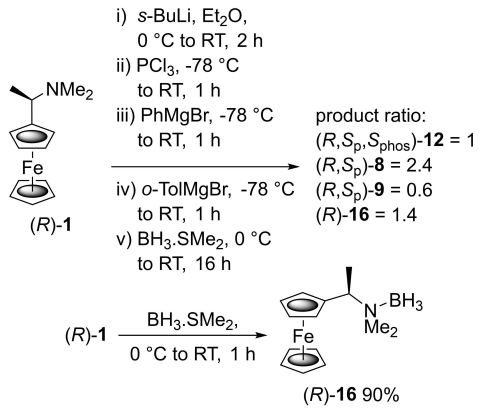


Figure 5. Representation of the X-ray crystal structure of (R,S_p,R_{phos})-**13** (hydrogen atoms omitted for clarity). Thermal ellipsoids are drawn at the 50% probability level. Principal bond lengths [Å] include: C(2)–C(3) 1.520(4), C(1)–P(1) 1.810(3), P(1)–C(4) 1.815(3), P(1)–C(6) 1.836(3). Principal torsion angles [°] include: C(1)–C(2)–C(3)–N(1) −105.7(4), C(2)–C(1)–P(1)–C(4) −150.1(3), C(2)–C(1)–P(1)–C(6) 102.3(3), C(1)–P(1)–C(4)–C(5) 98.7(3), C(1)–P(1)–C(6)–C(7) 178.7(3). Absolute structure parameter = 0.020(9).

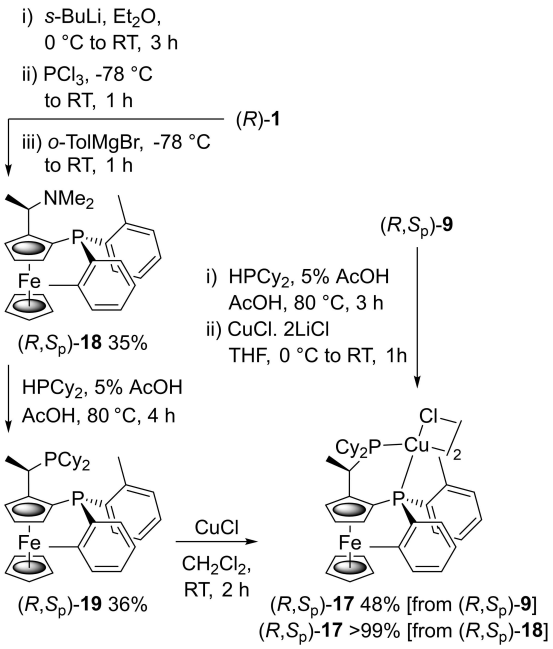


Scheme 7. Synthesis by ligand complexation of Josiphos-copper derivatives (R,S_p,R_{phos})-**14** and (R,S_p,S_{phos})-**15**.

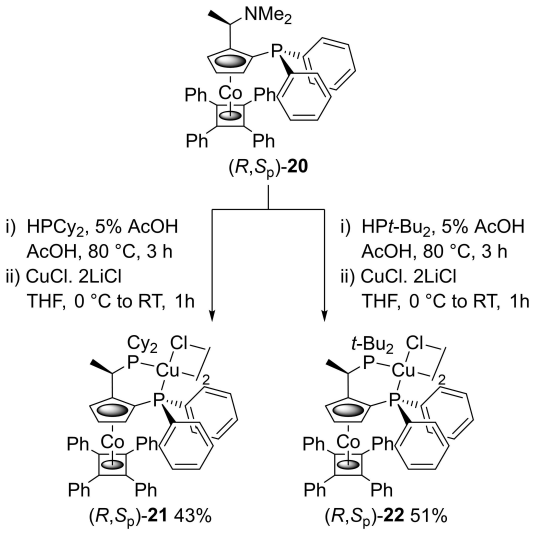
The successful synthesis of (R,S_p)-**8** and (R,S_p)-**9** from phosphorus trichloride prompted the use of this reagent for the synthesis of related *P*-stereogenic derivatives. Accordingly, following the lithiation of (*R*)-**1**, sequential addition of phosphorus trichloride, phenylmagnesium bromide, (*o*-tolyl) magnesium bromide, and borane-dimethylsulfide resulted in the formation of (R,S_p,S_{phos})-**12**, but also in significant quantities of the diphenyl and di(*o*-toly) derivatives (R,S_p)-**8** and (R,S_p)-**9**, as identified by NMR spectroscopy (Scheme 8). An additional compound formed was identified by independent synthesis as (*R*)-**16**, the borane adduct of the starting amine. Reversing the sequence of Grignard reagent addition, *i.e.* adding (*o*-tolyl) magnesium bromide and then phenylmagnesium bromide, resulted in a 1:2.4:1.2:1.1 ratio of (R,S_p,R_{phos})-**13**, (R,S_p)-**8**, (R,S_p)-**9** and (*R*)-**16**. Although this method is not suitable for the clean synthesis of the *P*-stereogenic derivatives, it is significant that



Scheme 8. Investigation into the use of PCl_3 for the synthesis of *P*-stereogenic protected ligand-precursor (R,S_p,S_{phos})-**12**.



Scheme 9. Synthesis of (R,S_p)-**17** by use of PCl_3 and from protected intermediate (R,S_p)-**9**.



Scheme 10. Synthesis of bulky cobalt sandwich complex-based Rossiphos-copper complexes (R,S_p)-**21** and (R,S_p)-**22**.

only one isomer was obtained in each case. This supports the earlier supposition that *P*-stereogenic stereocontrol does not arise from the selective substitution of prochiral $ArPCl_2$ reagents, and is instead a result of intermediate epimerisation (Scheme 3).

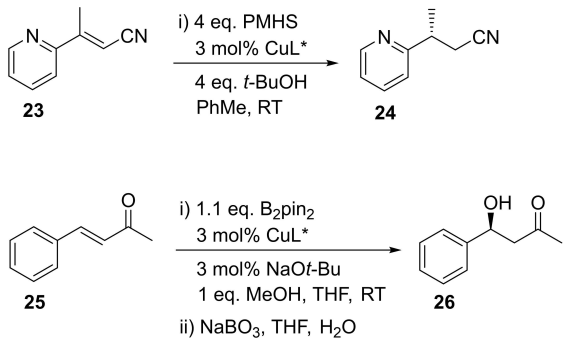
Epimerisation on heating *P*-stereogenic ferrocenylphosphines has been noted previously, with the diastereoisomer of S_p*,S_{phos}* relative configuration being significantly less stable than its S_p*,R_{phos}* epimer.[8,10] Further to the formation of only (R,S_p,R_{phos})-**14** using the methodology outlined in Scheme 6, diastereomerically pure samples of (R,S_p,S_{phos})-**2** and (R,S_p,R_{phos})-**3** were heated at 80 °C in hexane for 24 h in the presence of silica.[10] No change was observed for (R,S_p,R_{phos})-**3**. In contrast, the other sample gave a 3.8 : 1 ratio of (R,S_p,R_{phos})-**3**: (R,S_p,S_{phos})-**2**, confirming the greater stability of the S_p*,R_{phos}* diastereoisomer. This outcome is consistent with epimerisation to (R,S_p,R_{phos})-**5** under the conditions of its formation, prior to copper complexation to give (R,S_p,R_{phos})-**14**.

The utility of the *in situ* complexation methodology was further illustrated with the synthesis of (R,S_p)-**17** from (R,S_p)-**9**, a reaction sequence requiring, in this instance, the removal of a single borane protecting group (Scheme 9). Unprotected P–N and P–P ligands, (R,S_p)-**18** and (R,S_p)-**19** respectively, were also synthesised from PCl_3, although phosphine oxidation was again an issue resulting in a low yield of the latter. Subsequent complexation with copper(I) chloride resulted in the quantitative formation of (R,S_p)-**17**.

Finally, in the context of ligand synthesis, the utility of stereospecific phosphine introduction and *in situ* complexation was further illustrated starting with bulky cobalt-sandwich complex (R,S_p)-**20** (PPCA).[17] This was transformed into new air-stable Rossiphos[17] copper-complexes (R,S_p)-**21** and (R,S_p)-**22** that were readily purified by column chromatography (Scheme 10).

For application in conjugate addition reactions, most diphosphine/copper complexes are generated *in situ* from a variety of Cu(I) and Cu(II) salts.[4–6,18] The validity of generating and isolating the copper(I) chloride complexes described above is contingent upon these being suitable as catalyst precursors for such reactions. In an initial investigation of this issue two reactions were examined; the reduction of unsaturated nitrile **23** to give **24**,[18a] and the β-borylation of unsaturated ketone **25** to give, after oxidation, β-hydroxyketone **26** (Scheme 11).[18b] Using the parent Josiphos ligand (R,S_p)-**10**, an e.e. value of *ca.* 65 % has been reported for both reactions, giving scope for a significant improvement in enantioselectivity.

Repetition of the conditions reported for the reduction of **23** using $Cu(OAc)_2$ resulted in an improvement of the literature e.e. value of 65 % to 91 %, albeit with poor conversion (Table 1, entries 1 and 2). Use of CuCl for *in situ* catalyst generation



Scheme 11. Representative copper-catalysed asymmetric conjugate-addition reactions.

Table 1. Copper-catalysed asymmetric conjugate-addition reactions of **23** and **25**.[a]

Entry	Substrate	Cu source[b]	Time [h]	Conversion [%]	e.e. [%]
1[c]	**23**	$Cu(OAc)_2$	8.5	96	65
2	**23**	$Cu(OAc)_2$	24	25[d]	91[e]
3	**23**	CuCl	120	100[d]	95[e]
4	**23**	(R,S_p)-**11**	24	97[d]	95[e]
5	**23**	(R,S_p,R_{phos})-**14**	72	19[d]	27[e]
6	**23**	(R,S_p,S_{phos})-**15**[f]	1	100[d]	57[e]
7[g]	**25**	CuCl	24	100	68
8	**25**	CuCl	18	87[d]	70[h]
9	**25**	(R,S_p)-**11**	96	94[d]	71[h]
10	**25**	(R,S_p,R_{phos})-**14**	1.5	98[d]	≈0[h]
11	**25**	(R,S_p,S_{phos})-**15**[f]	144	80[d]	≈0[h]

[a] Using conditions outlined in Scheme 11. [b] With (R,S_p)-**10** [(R,S_p)-Josiphos] for *in situ* generated catalysts unless otherwise stated. [c] Lit. value.[18a] [d] Determined by ^{1}H NMR spectroscopy. [e] Of (*R*)-**24** as determined by HPLC.[f] Generated *in situ* from CuCl and (R,S_p,S_{phos})-**4**. [g] Lit. value.[18b] [h] Of (*S*)-**26** as determined by HPLC.

further improved the e.e. to 95% (entry 3), and this was maintained, together with a significantly shorter reaction time, on employing preformed (R,S_p)-**11** (entry 4). Use of the *P*-stereogenic Josiphos ligands as either a preformed complex (entry 5), or generated *in situ* (entry 6), resulted in a large reduction in e.e. For β-borylation of **25** followed by oxidation, repetition of the conditions reported with CuCl resulted in a similar selectivity (*ca.* 70% e.e, entries 7 and 8). This was also the case with (R,S_p)-**11**, although in this instance a longer reaction time was required to achieve high conversion (entry 9). Essentially racemic product was obtained on application of the *P*-stereogenic Josiphos ligands (entries 10 and 11). The reaction time required for β-borylation of **25** was significantly reduced with the catalyst derived from (R,S_p,R_{phos})-**5**. In contrast, the reaction time for reduction of **23** was significantly reduced with the catalyst derived from (R,S_p,S_{phos})-**4**. Thus for these two reactions, the difference between the ligand diastereoisomers is more apparent as catalyst activity rather than catalyst enantioselectivity. This may be the result of a different, perhaps monodentate, coordination mode in the catalyst for one or both *P*-stereogenic ligand diastereoisomers containing the additional *ortho*-methyl substituent.[19]

Conclusion

Methodology for the synthesis of *P*-stereogenic ferrocene ligands was applied successfully to PPFA (P–N ligands) derivatives containing phenyl and *o*-tolyl phosphorus substituents. Subsequent transformation into the corresponding Josiphos derivatives (P–P ligands) was also successful. Modification of this methodology by use of a borane protecting group avoided complications arising from phosphine oxidation, and this was further assisted, following deprotection, by direct coordination to copper, and isolation/purification of the resulting air-stable complexes. Further adaptation of this methodology gave a new Josiphos derivative from the use of lithiated Ugi's amine, PCl_3, and two equivalents of aryl Grignard, although this approach was only partially successful for the synthesis of *P*-stereogenic ligands by sequential use of two different aryl Grignard compounds. The *P*-stereogenic ligands/complexes are configurationally stable at room temperature, but epimerisation can occur on heating (S_p*,S*$_{phos}$ to S_p*,R*$_{phos}$). The copper chloride complex of the parent Josiphos ligand is suitable as a catalyst precursor, as illustrated by the comparable e.e. values to those obtained from *in situ* generated complexes (up to 95% e.e.) for representative conjugate reduction and β-borylation reactions. For these, lower enantioselectivities were obtained with the *P*-stereogenic derivatives, but marked increases in catalyst activity were observed. Further application of these copper-chloride complexes in asymmetric catalysis is under investigation.

Experimental Section

Preparation of (R,S_p,R_{phos})-13. (*R*)-**1** (0.200 g, 0.78 mmol) added to a flame dried Schlenk tube and dissolved in diethyl ether (6 mL). The solution was cooled to 0 °C and *sec*-butyllithium (1.4 M in Hexanes) (0.61 ml, 0.86 mmol) added slowly. The reaction was allowed to warm to room temperature and stirred for 2 h. Upon cooling to −78 °C, dichloro *ortho*-tolylphosphine (0.165 g, 0.86 mmol) was added and the reaction allowed to stir at room temperature for 1 h. The reaction was re-cooled to −78 °C and phenylmagnesium bromide (1.0 M in THF) (0.86 mL, 0.86 mmol) was added and the reaction allowed to warm to room temperature and stirred for an additional hour. The reaction was cooled to 0 °C and borane dimethyl sulfide complex (2.0 M in THF) (0.86 mL, 1.71 mmol) was added and the reaction allowed to stir overnight at room temperature. The reaction was quenched with saturated sodium carbonate solution, extracted with dichloromethane, dried ($MgSO_4$) and the solvent removed *in vacuo*. Purification by column chromatography (SiO_2, 50/50 CH_2Cl_2/hexane) yielded an orange solid (0.18 g, 47%): R_f 0.30 (50/50 CH_2Cl_2/hexane); Mp 209–211 °C; $[\alpha]_D^{26\,°C} = -184$ (c = 0.24, chloroform); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83–7.76 (2H, m, Ph*H*), 7.56–7.51 (1H, m, Ph*H*), 7.51–7.46 (2H, m, Ph*H*), 7.34–7.27 (2H, m, Ar*H*), 7.16–7.12 (1H, m, Ar*H*), 7.10 (2H, t, J = 7.6 Hz, Ar*H*), 5.12 (1H, dd, J = 3.3, 2.5 Hz, Cp*H*), 4.82 (1H, q, J = 6.6 Hz, C*H*), 4.63 (1H, t, J = 2.6 Hz, Cp*H*), 4.24–4.21 (1H, m, Cp*H*), 4.01 (5H, s, Cp*H*), 2.38 (3H, s, NCH_3), 2.22 (3H, s, $ArCH_3$), 2.10 (3H, s, NCH_3), 1.94 (3H, d, J = 6.8 Hz, $CHCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.8 (d, J = 12.8 Hz, Ar*C*), 134.0 (d, J = 5.7 Hz, Ar*C*), 133.5 (d, J = 9.4 Hz, Ph*C*), 132.2 (d, J = 9.2 Hz, Ar*C*), 131.4 (d, J = 2.0 Hz, Ar*C*), 131.3 (d, J = 2.3 Hz, Ph*C*), 130.7 (d, J = 59.9 Hz, Ph*C*), 129.1 (d, J = 52.9 Hz, Ar*C*), 128.5 (d, J = 10.1 Hz, Ph*C*), 125.0 (d, J = 8.4 Hz, Ar*C*), 93.6 (d, J = 16.6 Hz, Cp*C*), 73.6 (d, J = 8.0 Hz, Cp*C*), 73.2 (d, J = 2.5 Hz, Cp*C*), 71.4 (C_5H_5), 71.3 (d, J = 5.9 Hz, Cp*C*), 69.5 (d, J = 61.9 Hz, Cp*C*), 62.8 ($CHCH_3$), 53.5 (NCH_3),

50.3 (NCH_3), 22.6 (d, J = 4.4 Hz, ArCH_3), 20.8 ($CHCH_3$); ^{31}P NMR (202 MHz, $CDCl_3$) δ 14.53 (*P*ArPh); ^{11}B NMR (160 MHz, $CDCl_3$) δ −12.26 (*B*H_3–NMe_2), −35.09 (*B*H_3–PArPh). IR (film) $\tilde{\nu}$ = 3058, 3007, 2956, 2345 (B–H), 2278, 1471, 738; MS (EI) *m/z* calcd for $C_{27}H_{36}B_2FeNP$ $[M]^+$ 483.2; found 483.2. [HRMS of the borane complex was not obtained due to the loss of BH_3, HRMS (ASAP) [M-2BH_3 + H]$^+$ $C_{37}H_{46}FeP_2 + H^+$, Calc. 609.2503, Obs. 609.2503].

Preparation of (R,S_p,R_{phos})-14 from (R,S_p,R_{phos})-13. A flame dried Schlenk tube (fitted with a glass stopper) containing glacial acetic acid (3 mL) and acetic anhydride (0.15 mL) was degassed by the freeze-pump-thaw method (x3) and the atmosphere replaced with argon. Then (R,S_p,R_{phos})-**13** (0.040 g, 0.08 mmol) was added and the sample degassed once more. After freezing for a 5th and final time the stopper was replaced by a septum and the atmosphere flushed with argon. Dicyclohexylphosphine (0.08 mL, 0.41 mmol) was then added *via* syringe. The septum was again replaced by a glass stopper and the vessel evacuated once more and allowed to thaw under an atmosphere of argon. After stirring at room temperature for 5 mins, the Schlenk tube was introduced to an oil bath pre-heated to 80 °C and stirred for 3 hours. The reaction was allowed to cool to room temperature and then cooled to 0 °C before adding copper(I) chloride bis(lithium chloride) complex (1 M in THF) (0.62 mL, 0.62 mmol) and stirred at room temperature for 1 hour. The reaction was re-cooled to 0 °C, quenched with saturated sodium hydrogen carbonate solution (30 mL), and the resulting yellow precipitate collected by filtration. The solids were washed with water followed by hexane and then dissolved in dichloromethane. This was washed with water, dried ($MgSO_4$) and the solvent removed *in vacuo*. Purification by column chromatography (SiO_2, 5% Et_2O/CH_2Cl_2) yielded an orange solid (0.046 g, 79%): R_f 0.11 (10% EtOAc/hexane); Mp 148–149 °C; $[\alpha]_D^{26\,°C} = -186$ (c = 0.64, $CHCl_3$); ^{1}H NMR (500 MHz, $CHCl_3$) δ 7.93–7.86 (4H, m, Ph*H*), 7.47–7.41 (6H, m, Ph*H*), 7.23–7.17 (2H, m, Ar*H*), 7.11–7.06 (6H, m, Ar*H*), 4.52 (2H, brs, Cp*H*), 4.45 (2H, brs, Cp*H*), 4.13 (2H, brs, Cp*H*), 3.90 (10H, s, Cp*H*), 3.50–3.42 (2H, m, C*H*), 2.25 (6H, s, ArCH_3), 2.04–0.64 (44H, m, PCy_2), 1.45 (6H, t, J = 7.7 Hz, CHCH_3); ^{13}C NMR (125 MHz, $CHCl_3$) δ 142.0 (d, J = 18.1 Hz, Ar*C*), 134.6 (d, J = 17.1 Hz, Ph*C*), 134.2 (dd, J = 25.5, 11.7 Hz, Ph*C*), 133.6 (d, J = 26.4 Hz, Ar*C*), 132.0 (d, J = 4.1 Hz, Ar*C*), 131.2 (d, J = 6.6 Hz, Ar*C*), 130.3 (Ph*C*), 129.3 (Ar*C*), 128.7 (d, J = 10.3 Hz, Ph*C*), 125.3 (d, J = 4.8 Hz, Ar*C*), 95.4 (d, J = 21.2 Hz, Cp*C*), 73.8 (Cp*C*), 72.5–72.3 (m, Cp*C*), 71.2 (d, J = 32.8 Hz, Cp*C*), 70.5 (C_5H_5), 70.1 (d, J = 3.2 Hz, Cp*C*), 34.2–25.6 (m, Cy*C*), 30.7 (d, J = 10.4 Hz, *C*HCH_3), 22.5 (d, J = 15.5 Hz, ArCH_3), 17.7 ($CHCH_3$); ^{31}P NMR (202 MHz, $CHCl_3$) δ 6.28 (d, J = 203.5 Hz, *P*Cy_2), −27.43 (d, J = 203.6 Hz, *P*ArPh). IR (film) $\tilde{\nu}$ = 3055, 2926, 2849, 2222, 1449, 918, 731; HRMS (EI) *m/z* calcd for $C_{37}H_{46}ClCuFeP_2$ 704.1450 $[M]^+$; found 704.1452.

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Conflict of Interest

The authors declare no conflict of interest.

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