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A crystalline chiral phosphide for the synthesis of the first P-stereogenic P(III) fluoride: a stable ligand for the Rh-catalyzed asymmetric arylation of isatins

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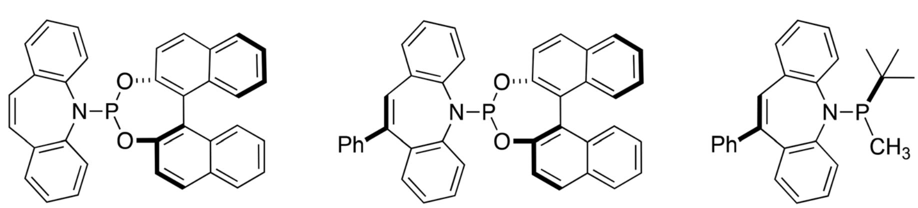
Stable P-stereogenic P(III) fluorides of the type $*PR^1R^2F$ have long resisted isolation, despite their great potential as ligands in asymmetric catalysis. We report the synthesis of a crystalline, chiral lithium alkene-phosphide that undergoes rapid, enantiospecific fluorination with *N*-fluorobenzenesulfonimide with retention of configuration to yield the corresponding fluorophosphinamide–alkene hybrid ligand in >99% ee. The ligand is configurationally stable up to 100 °C and forms a Rh(I) complex that catalyzes the base- and water-free asymmetric arylation of isatins to biologically important 3-hydroxyoxindoles with up to 99.5% ee.

Introduction

Despite the fact that Burg and Brendel 66 years ago reported the synthesis of the first organo-fluorophosphine, namely $(CF_3)_2PF$,[1] the use of P(III) fluorides as ligands in coordination chemistry is, apart from PF_3,[2] scarcely described.[3] Applications in catalysis are even rarer,[4] and asymmetric versions have not yet been reported, due to the lack of effective synthetic methods towards optically pure fluorophosphines. Chiral phosphines are the ligands of choice for many transition-metal-catalyzed asymmetric reactions in industry and academia.[5] Of special interest are P-stereogenic phosphines, which place chirality in proximity of the metal center. This concept gained industrial maturity with Monsanto's L-Dopa process in the late 1970's, for which Knowles was awarded the Nobel prize.[6] However, the synthesis of enantiopure P-stereogenic compounds is notoriously difficult[7] and a topic of high relevance to asymmetric catalysis.[8] In particular, the stereoselective installation of a P–F bond in P-stereogenic phosphine ligands has remained elusive so far and is of prime interest because it would allow to introduce strong steric and electronic differentiation on the P-donor and considerably widen the diversity of chiral ligand design.[9] Even though the P–F bond is polar and possesses a significant strength of 545 kJ mol^{-1},[10] applications of fluorophosphines in catalysis have been hampered by their high propensity towards redox disproportionation.[4]

In a recent evolution of the 'privileged ligand' **1**[11] we found the planar chirality in the diastereomers (p*S*,*R*)-**2** and (p*R*,*R*)-**2** to completely overwhelm the axial chirality of the potent binol auxiliary in the enantioselective Hayashi-Miyaura reaction.[12] Some years ago, we explored the possibility to introduce the promising P-chiral *tert*-butylmethylphosphine function[13] to such systems by isolating the stereochemically stable ligand *rac*-**3**.[14] Having taken inspiration from the seminal reports on P-stereogenic P(III)-fluorides by Wild,[15] Pringle,[4b] Puckette,[4e] and others,[16] we disclose here a perfectly stereoselective P–F bond forming protocol that allowed us to isolate the first enantiopure P-stereogenic P(III) fluoride, its Rh(I) complex, and use in catalytic asymmetric C–C bond formation.



(*R*)-**1** (p*S*,*R*)-**2** *rac*-**3**

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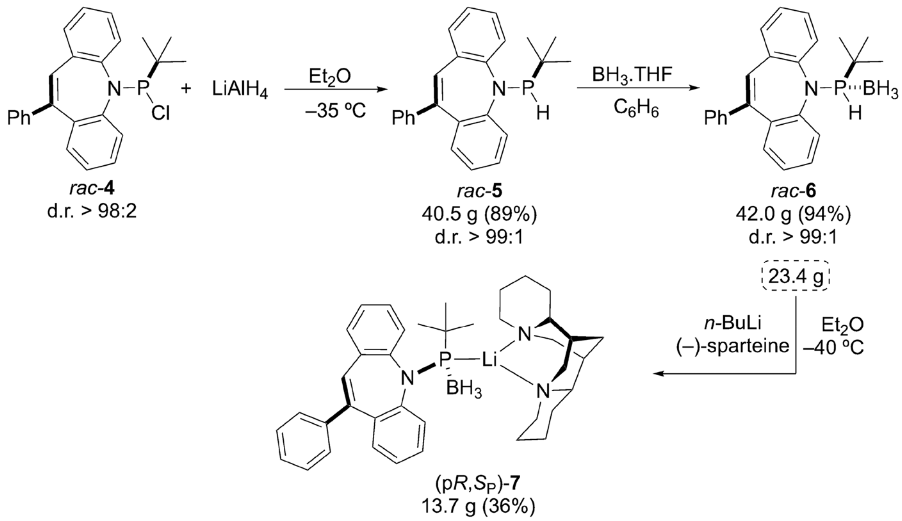


Scheme 1 Synthetic route to the enantiopure crystalline phosphide (p*R*,S_P)-**7**.

Results and discussion

We opted for Livinghouse's protocol for the synthesis of optically pure P-stereogenic phosphines *via* chiral phosphide intermediates obtained by enantioselective deprotonation of secondary phosphine-boranes, which then are quenched with organic electrophiles.[17] In our case, the diastereomerically pure, BH_3-protected, secondary phosphinamide *rac*-**6** (Scheme 1) is prepared by reducing diastereomerically enriched (d.r. > 98 : 2) chlorophosphine *rac*-**4** with $LiAlH_4$ to almost diastereopure *rac*-**5** followed by protection with BH_3·THF. Deprotonation of 23.4 g of *rac*-**6** with the *n*-BuLi/(−)-sparteine mixture in Et_2O at −40 °C, yields 13.7 g of phosphide (p*R*,S_P)-**7**. Non-decoupled NMR spectra of the ^{31}P, ^{11}B, and ^{7}Li nuclei display multiplets centered at 96.5, 31.6, and 0.8 ppm, respectively. The molecular mass for **7**, estimated by DOSY-NMR (585 g mol^{-1}) corresponds to a monomer (MW = 612 g mol^{-1}). Single crystals of **7** grow from 1,2-difluorobenzene/Et_2O and XRD analysis confirms its absolute configuration and monomeric structure featuring a P–Li bond (see Fig. 1) contrasting Livinghouse's chiral phosphide, in which the borane moiety bridges the Li-sparteine complex.[18] Unlike Livinghouse's dynamically resolving system, we think that in our case the BuLi/sparteine deprotonation enables resolution of the lithium phosphide sparteine complex by diastereoselective crystallization[19] from cold Et_2O solutions, which might explain the modest yields of (p*R*,S_P)-**7**. The (p*S*,R_P)-antipode is accessible by using (+)-sparteine (see the SI for details).

With optically pure phosphide (p*R*,S_P)-**7** in hand we first validated its utility as a stereospecific nucleophile for the synthesis of our well-understood P-alkene *rac*-**3** since earlier attempts of stereospecific C–N bond formation between lithium phenyldibenzoazepinate[20] and enantiopure (*R*)-(Me)(*t*Bu)PBr(BH_3) (Imamoto's method)[21] only afforded *rac*-**3** albeit in diasteromerically pure form. Gratifyingly, methyl iodide reacts smoothly with (p*R*,S_P)-**7** to produce the protected phosphinamide (p*R*,R_P)-**8** in 99% ee (Scheme 2), which is deprotected to (p*R*,R_P)-**3** by

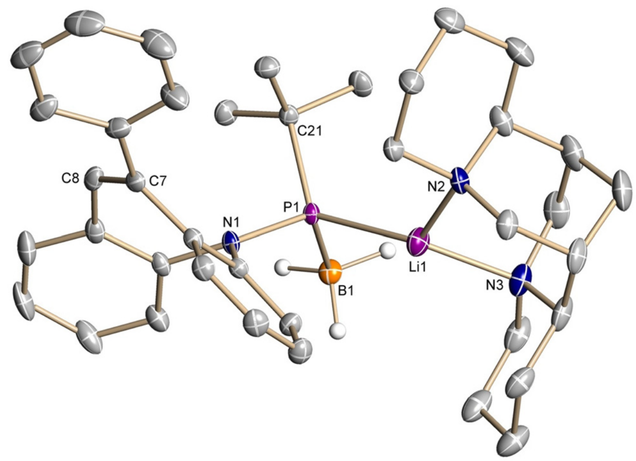
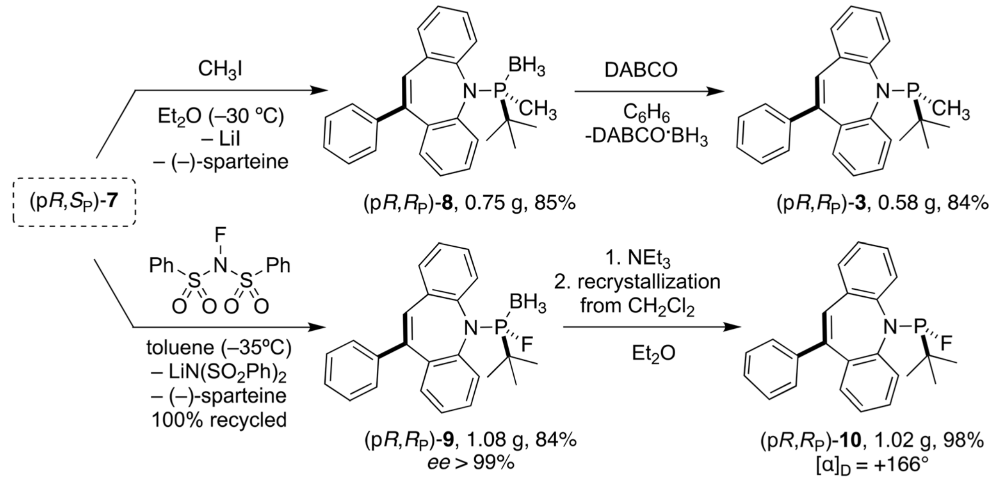


Fig. 1 Crystal structure of (p*R*,S_P)-**7** (50% displacement ellipsoids, most H atoms are omitted). Selected distances (Å) and angles (deg): Li1–P1 2.488(3), Li1–N2 1.995(4), Li1–N3 2.024(4), P1–B1 1.956(2), P1–N1 1.7469(15), P1–C21 1.8790(17), C7–C8 1.355(3), N1–P1–Li1 106.06(10), C21–P1–Li1 121.50(10), N1–P1–C21 112.88(9), N1–P1–C21 103.46(7).

DABCO. Its precise stereochemistry is established by the crystal structure of the Rh(I) complex **11** (see below and Fig. S1).

Likewise, phosphide (p*R*,S_P)-**7** reacts with *N*-fluorobenzenesulfonimide[22] with retention of configuration at phosphorous to the BH_3-protected diastereo- and enantiopure amido-*t*-butyl fluorophosphine (p*R*,R_P)-**9** (Scheme 2).[23] P–F bond formation is evident in ^{31}P{^{1}H} and non-decoupled ^{19}F NMR spectra, which show a doublet of multiplets and a doublet of quartets centered at 155.9 ($J_{PF} \approx 1050$ Hz) and −109.4 ppm ($J_{FP} \approx 1050$ Hz, J_{FH} = 16.1 Hz), respectively (Fig. S26). The ^{1}H NMR spectrum shows a doublet at 1.09 ppm and broad multiplets between 0.45–0.26 ppm corresponding to the *t*Bu and BH_3 moieties. Enantiopurity was confirmed by chiral HPLC (Fig. S41 in the SI). Fig. 2 shows the crystal structure of (p*R*,



Scheme 2 Syntheses of enantiopure (pR,R_P)-**3** and fluorophosphinamide (pR,R_P)-**10**.

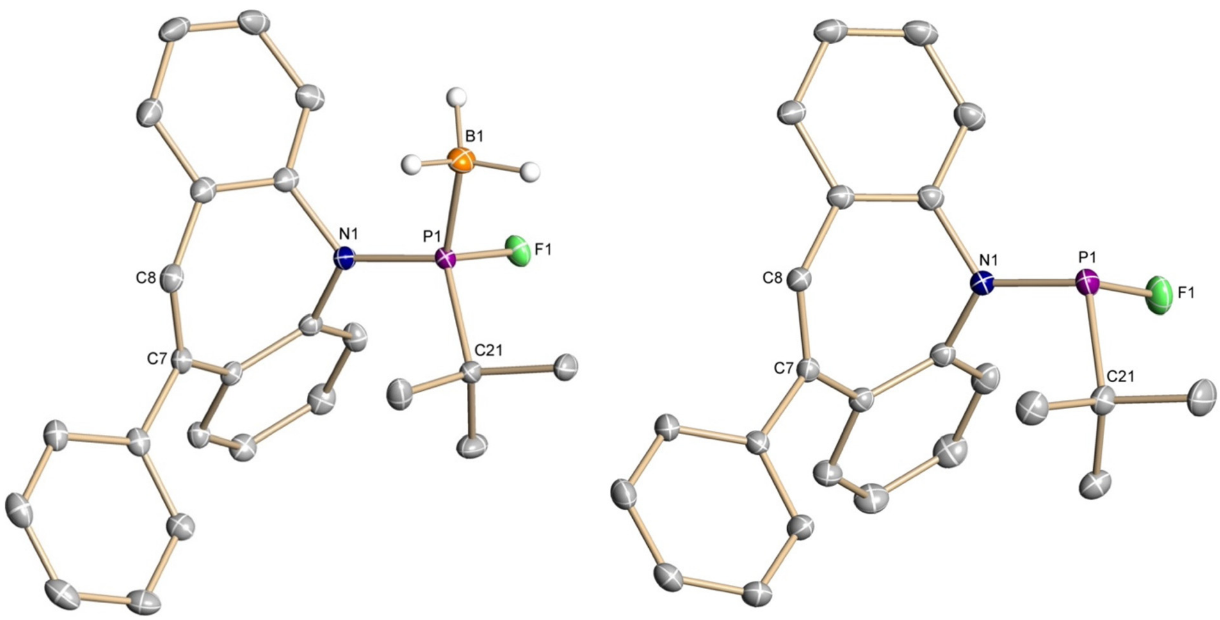
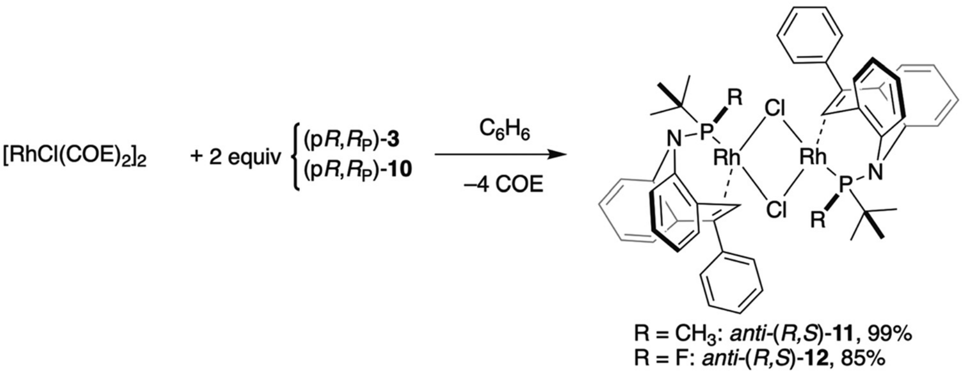


Fig. 2 Crystal structures of (pR,R_P)-**9** and (pR,R_P)-**10** (50% displacement ellipsoids, most H atoms are omitted). Selected distances (Å) and angles (deg) for (pR,R_P)-**9**: P1–F1 1.5851(10), P1–N1 1.6509(14), P1–B1 1.899(2), P1–C21 1.8303(17), C7–C8 1.348(2), F1–P1–N1 106.13(6), F1–P1–B1 109.60 (7), F1–P1–C21 100.51(7), N1–P1–B1 112.98(8). For (pR,R_P)-**10**: P1–F1 1.6286(10), P1–N1 1.6805(12), P1–C21 1.8579(15), C7–C8 1.3540(18), F1–P1–N1 103.19(6), F1–P1–C21 97.10(6), N1–P1–C21 106.08(6).

R_P)-**9**, which confirms the formation of the P–F bond (d_{P-F} = 1.585(10) Å), the absolute configuration of the P-atom, and the planar chirality of the dibenzoazepine ring, which are (pR,R_P). Importantly, expensive (−)-sparteine can be recycled quantitatively. The basicity of the P-donor in (pR,R_P)-**9** seems lower than in (pR,R_P)-**3**,[24] because removal of the BH_3 moiety from (pR,R_P)-**9** is achieved with NEt_3, instead of DABCO affording diastereo- and enantiopure free fluorophosphinamide (pR,R_P)-**10** in excellent yields. To make sure deprotection did not erode enantiopurity, (pR,R_P)-**10** was re-protected with BH_3·THF giving back (pR,R_P)-**9** in > 99% optical purity. ^{31}P and ^{19}F NMR spectra show new doublets at 176.7 ppm and −132.3 ppm, respectively, with J_{PF} = 970.6 Hz. In the ^{13}C NMR spectrum, the quaternary carbon and the methyl groups of the *t*Bu moiety, appear at 35 ppm as a doublet of doublets at 35.0 (J_{CP} = 25.3 Hz, J_{CF} = 12.1 Hz) and 25.4 ppm (J_{CP} = 19.5 Hz, J_{CF} = 1.7 Hz), respectively. The crystal structure confirms the unaltered configuration in (pR,R_P)-**10** and shows significant elongation of both the P–F (to 1.6286(10) Å) and P–N bonds compared with (pR,R_P)-**9** (Fig. 2). Deprotected (pR,R_P)-**9** is surprisingly robust: It is air-stable in the solid state and withstands boiling chloroform and toluene solutions without showing signs of decomposition or epimerization.

(pR,R_P)-**3** and (pR,R_P)-**10** both react with $[RhCl(COE)_2]_2$ (COE = cyclooctene) to form the respective P-alkene ligated dinuclear complexes (pR,R_P)-**11** (see Fig. S1 in the SI for its crystal structure) and (pR,R_P)-**12**[25] according to eqn (1). The $^{31}P\{^1H\}$ spectrum of (pR,R_P)-**12** shows the formation of a single isomer with a doublet of doublets centered at 231.5 ppm (J_{PF} = 1066 Hz, J_{PRh} = 249.6 Hz), and the non-decoupled ^{19}F spectrum exhibits a doublet of doublets at −104.8 ppm (J_{F-P} = 1065 Hz, J_{F-Rh} = 16.4 Hz). The alkene–C–H resonates at relatively low frequency as a singlet at 5.70 ppm, indicating alkene coordination. (pR,R_P)-**12** crystallizes as red blocks from benzene solution, and its crystal structure in Fig. 3 confirms the bidentate coordination of the ligands in an *anti*-fashion to the Rh_2Cl_4 butterfly core, which spans an angle of 99° between the square coordination planes around the Rh atoms. The P–F bond is shorter than in the free ligand and is comparable to the P–F bond in borane complex **8**. The P–F bond in complex (pR,R_P)-**12** is significantly shorter than the P–Me bond in complex (pR,R_P)-**11**, measuring 1.58 *vs.* 1.82 Å, respectively (1.63 *vs.* 1.82 Å in the respective free ligands). Including the H-atoms of the methyl substituent an even larger difference in the respective van-der-Waals volumes is expected. Fluorine substitution at the P-donor also shortens



(1)

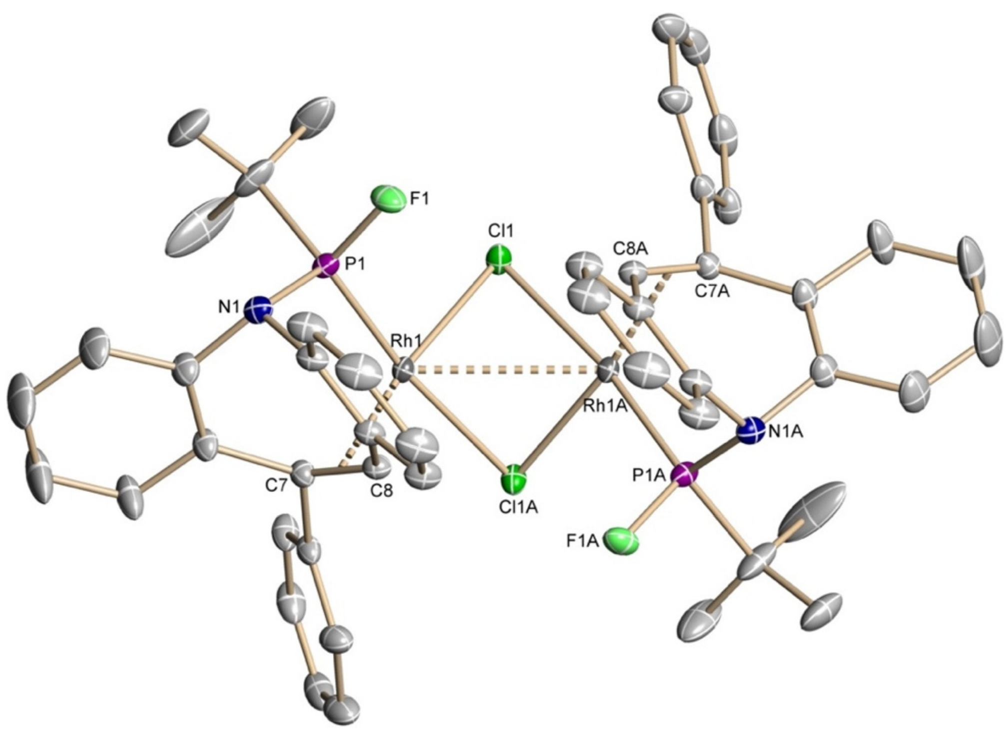
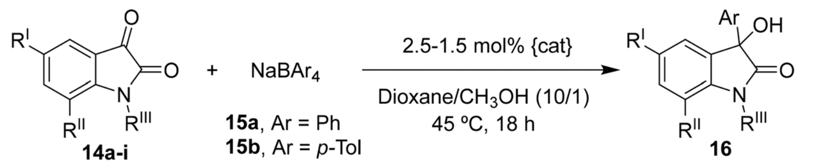


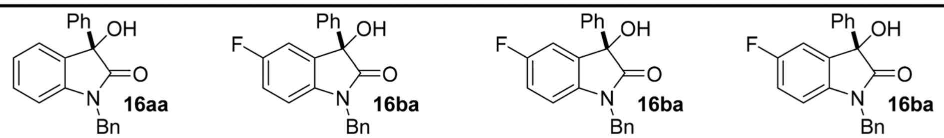
Fig. 3 Crystal structure of (pR,R_P)-**12** (50% displacement ellipsoids, H atoms are omitted). Selected distances (Å) and angles (deg): Rh1–Cl1 2.3685 (3), Rh1–Cl1A 2.5010(3), Rh1–P1 2.132(4), Rh1–C7 2.1654(13), Rh1–C8 2.1107(13), C7–C8 1.4330(19), P1–F1 1.5845(10), P1–N1 1.7035(12), F1–P1–Rh1, 113.35(4), F1–P1–N1 98.17(6), F1–P1–C21 100.23(8)

the Rh–P bond in complex (p*R*,R_P)-**12** (2.132(4) Å) compared to (p*R*,R_P)-**11** (2.1622(9) Å); a small but statistically significant difference.

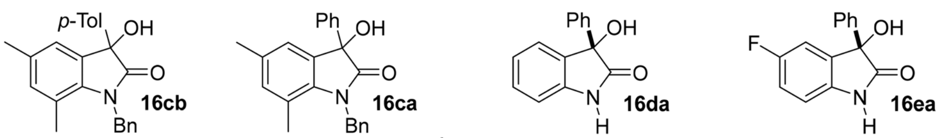
The P–F ligand (p*R*,R_P)-**10** was then benchmarked against ligands (p*R*,R_P)-**2** and (p*R*,R_P)-**3** of identical planar chirality in the base-free arylation of isatins with sodium tetraarylborates[26] to biologically important 3-aryl-3-hydroxyoxindoles (Table 1).[27] The arylation of benzyl-protected isatin **14a** with $NaBPh_4$, is catalyzed by (p*R*,R_P)-**12** bearing the P–F ligand affords **16aa** quantitatively in 86% ee, whereas the previously reported cationic complex [Rh((p*R*,*R*)-**2**)$_2$][BF_4][12a] and (p*R*,R_P)-**11** bearing ligands (p*R*,R_P)-**2** and (p*R*,R_P)-**3**, respectively, give conversions of <10%. Only with the electron-poor isatin **14b** do these catalysts afford relevant quantities of **16ba**. For this product, catalyst (p*R*, R_P)-**11** exhibits good enantioselectivity compared with the much more active but less selective (p*R*,R_P)-**12**. The sense of induction of the ligands with the Me- and the F-substituted P-donors is identical.[28] *In situ* generation of the cationic catalyst [Rh((p*R*,*R*)-**10**)$_2$][NTf] pushes the ee of the protected dimethyl hydroxyoxindole **16ca** up to 96%. Surprisingly, catalyst (p*R*,R_P)-**12** works even better with unprotected NH isatins[29] at reduced catalyst loadings. Electron-donating substituents at R^I *para* to the NH function appear to favor enantioselectivity affording hydroxyoxindoles of very high enantiomeric purity (compounds **16fa**, **16ha** and **16ia**), while *N*-protection and the use of tetra-*p*-tolylborate **15b** significantly erode enantioselectivity.

Table 1 Benchmarking of ligand (p*R*,R_P)-**10** in the water- and base-free catalytic arylation of isatins with tetraarylborates

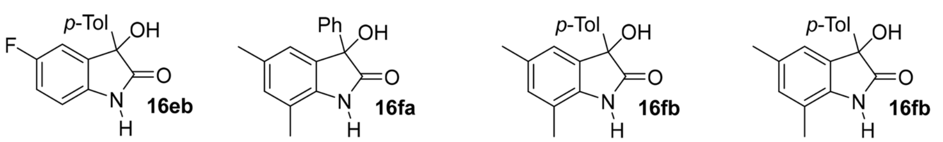




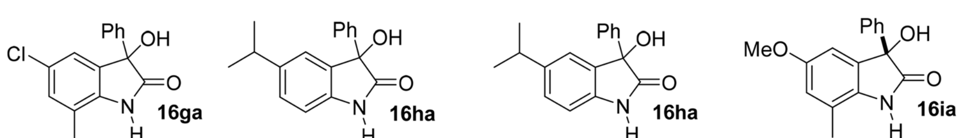
16aa	16ba	16ba	16ba
{(p*R*,R_P)-**12**}	{[Rh(p*R*,*R*)-**2**)$_2$][BF_4]}	{(p*R*,R_P)-**11**}	{(p*R*,R_P)-**12**}[a]
2.5 mol%	5 mol%	2.5 mol%	2.5 mol%
Conv. 100%	Conv. 30%	Conv. 20%	Conv. 100%
ee 86% (*S*)	*ee* 5% (*S*)	*ee* 80% (*S*)	*ee* 71% (*S*)



16cb	16ca	16da	16ea
{(p*R*,R_P)-**12**}	{[Rh((p*R*,*R*)-**10**)$_2$][NTf]}[b]	{(p*R*,R_P)-**12**}	{(p*R*,R_P)-**12**}
2.5 mol%	5mol%	2.5 mol%	1.5 mol%
Conv. 100%	Conv. 100%	Conv. 100%	Conv. 96%
ee 92%	*ee* 96%	*ee* 91% (*S*)	*ee* 93% (*S*)



16eb	16fa	16fb	16fb
{(p*R*,R_P)-**12**}[c]	{(p*R*,R_P)-**12**}	{(p*R*,R_P)-**12**}	{(p*R*,R_P)-**12**}[c]
1.5 mol%	1.5 mol%	1.5 mol%	1.5 mol%
Conv. 100%	Conv. 81%	Conv. 100%	Conv. 96%
ee 63%	*ee* 98%	*ee* 88%	*ee* 89%



16ga	16ha	16ha	16ia
{(p*R*,R_P)-**12**}	{(p*R*,R_P)-**12**}	{[Rh((p*R*,*R*)-**10**)$_2$][NTf]}[b]	{(p*R*,R_P)-**12**}
1.5 mol%	1.5 mol%	5 mol%	1.5 mol%
Conv. 94%	Conv. 80%	Conv. 89%	Conv. 100%
ee 87%	*ee* 96%	*ee* 98.5%	*ee* 99.5% (*S*)

[a] Reaction performed at 35 °C for 4 d. [b] Catalyst formed *in situ* from (p*R*,R_P)-**12** + 2 equiv. (p*R*,R_P)-**10** + 2 equiv. AgNTf (for experimental details, see the SI). [c] Reaction performed with 1 equiv. of **15b**.

Conclusions

We report a significant advance in the long-standing synthetic challenge of preparing a stereochemically stable P-stereogenic fluorophosphines of the type PR^1R^2F. This was achieved *via* enantiospecific electrophilic fluorination of the crystalline alkene-phosphide (p*R*,S_P)-**7**, yielding the configurationally stable fluorophosphinamide (p*R*,R_P)-**10** in gram quantities. This compound introduces a novel donor motif for chiral ligand design and functions as a bidentate ligand in the Rh(I) complex (p*R*,*R*)-**12**. In rhodium-catalyzed, water- and base-free arylations of isatins using $NaBAr_4$ nucleophiles, (p*R*,R_P)-**10** performs favorably compared to benchmark planar-chiral ligands **2** and **3**, particularly in the arylation of unprotected NH-isatins. This transformation marks the first application of a fluorophosphinamide in asymmetric catalysis. Notably in this context, the P(*t*-Bu)F synthon outperforms the generally effective P*(*t*-Bu)(Me) analog.[13] Furthermore, the crystalline phosphide (p*R*,S_P)-7 provides a versatile platform for accessing new classes of P-stereogenic P-alkene hybrid ligands, the exploration of which is currently underway.

Conflicts of interest

The authors declare no conflicts of interest.

Data availability

Synthetic procedures, X-ray crystallographic data, NMR spectra, and HPLC traces for this study are available as Supplementary Information. See DOI: **https://doi.org/10.1039/d5qi01994j**.

CCDC 2390089–2390093 contain the supplementary crystallographic data for this paper.[30a–e]

Acknowledgements

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