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Diastereoselective Synthesis of Planar Chiral Phosphoramidites with a Ferrocenophane Scaffold

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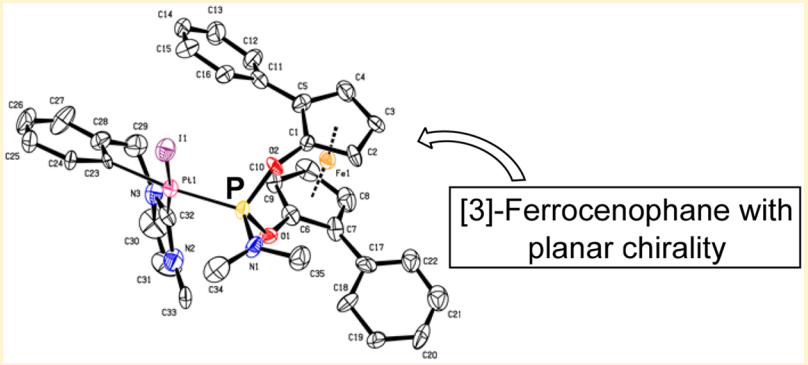
Supporting Information



ABSTRACT: A new family of planar chiral phosphoramidites with a [3]ferrocenophane structure was synthesized. The synthetic strategy involved diastereoselective formation of the chiral ferrocene units from suitable substituted bis-cyclopentadienyl derivatives. Preliminary coordination studies of these ligands were undertaken with the synthesis of palladium and platinum complexes.

INTRODUCTION

Chiral phosphoramidites represent one of the major classes of phosphorus ligands for asymmetric organometallic catalysis.[1] They stand out especially among monodentate chiral ligands[2] for their efficiency in reactions such as rhodium-promoted hydrogenation of olefins,[3] copper-promoted conjugate 1,4-additions,[4] iridium-promoted allylic substitutions,[5] and gold-catalyzed cycloisomerizations.[6] Chiral phosphoramidites usually display cyclic structures derived from C_2-symmetric chiral diols, mainly axially chiral biaryl diols, e.g. BINOL **I**, spiranic diols **II**, or diols with central chirality, e.g. TADDOL **III** (Figure 1). On the other hand, it may be noted that chiral phosphoramidites based on planar chiral scaffolds have been rather neglected so far.[7] The main achievement in this field has been the recent disclosure of unsymmetric phosphoramidites based on a [2.2]paracyclophane scaffold and their successful use in copper-catalyzed conjugate additions.[7b] In this context, inspired by the high potential of planar chirality in other series of phosphorus ligands, including ferrocene-derived phosphines,[8] we have started recently to develop various synthetic approaches to phosphoramidites displaying C_2-symmetric planar chiral scaffolds. Thus, in 2016 we have disclosed the synthesis of phosphoramidites displaying the [3.4]-paracyclophane scaffold **IV** and their use in gold-promoted cycloisomerizations.[9] The macrocyclic paracyclophane structure **IV** is made of two arylidene units tethered by O−P−O and biphenylene units. Planar chirality is generated by the presence

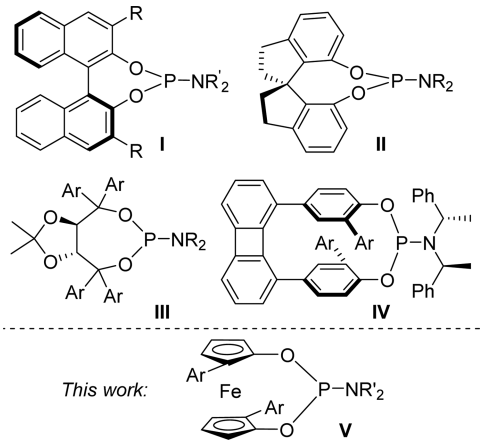


Figure 1. Representative phosphoramidites with axial, central, and planar chiral backbones.

of aryl substituents on both of the arylidene units, ortho to the O−P−O tether. Unlike phosphoramidites **I**−**III**, the diol precursor of **IV** is an achiral species and planar chirality is generated at the cyclization step which involves the achiral diol

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and a suitable dichlorophosphoramidite. In the synthesis of **IV** this step displayed moderate diastereoselectivity, as it afforded a complex mixture of the *d,l* and *meso* isomers.

In parallel studies, wishing to access a more diverse range of planar chiral phosphoramidites, we have investigated the unprecedented use of 1,3-dioxa-2-phospha[3]ferrocenophanes as structural units. The targeted structures **V** are shown in Figure 1. This paper reports on our first achievements in this field.

RESULTS AND DISCUSSION

1,3-Dioxa-2-phospha[3]ferrocenophanes with various phosphorus functions have been known since the late 1980s (phosphonates, phosphorochloridates,[10] phosphonites,[11] phosphites, phosphates, phosphorochloridites[11b,12]); however, phosphoramidites have not been described so far. Moreover, only one of the known ferrocenophanes above display substituted ferrocene units, as required for planar chiral derivatives.[13] Recently, a 2,2′-dimethyl-substituted ferrocenophane phosphate has been isolated as an inseparable mixture of *meso* and *d,l* isomers from lithiation/methylation of the unsubstituted 1,3-dioxa-2-phosphaferrocenophane.[12b]

Thus, the rather poor development of this field encouraged us to investigate the new class of planar chiral phosphoramidites **V**. In principle, the desired phosphoramidites **V** should be available from the corresponding 2,2′-diaryl-1,1′-ferrocenediols that, as far as we know, have not been described so far (Figure 2).

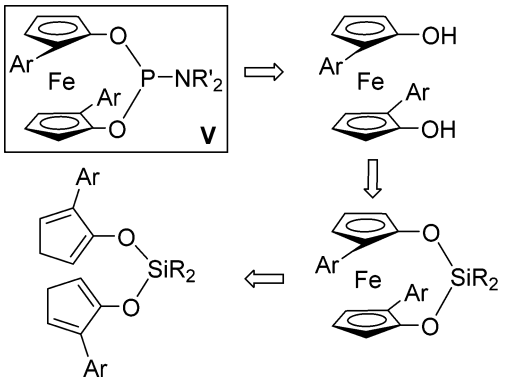


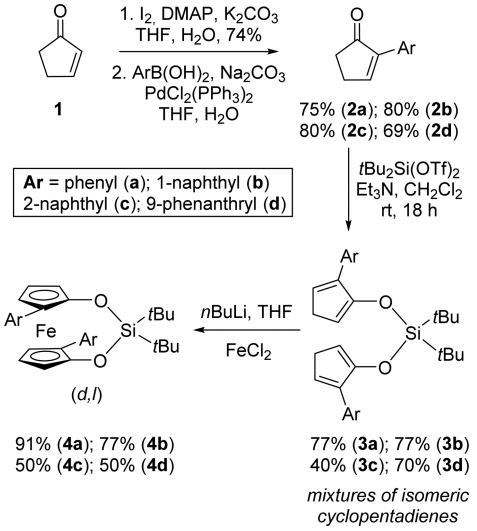
Figure 2. Retrosynthetic pathway leading to phosphoramidites **V**.

The surprisingly scarce development of this class of ferrocene derivatives might be related to their high air sensitivity, as reported for the parent 1,1′-ferrocenediol.[11a,14] Thus, the first step of our work has been the search for a suitable access to these diols, with the additional challenge of controlling the diastereoselectivity of their synthesis, since only the *d,l* isomer is relevant to our purposes. With this in mind, we have envisioned to assemble the substituted ferrocene directly from $FeCl_2$ and bis-cyclopentadienyl derivatives tethered by an O–Si–O chain (Figure 2).[15] This strategy relies on the reasonable hypothesis that steric constraints at the cyclization step will induce some diastereoselectivity in the assembly of the ferrocene unit. Removal of the silicon group will then generate in situ the desired diol.

Previous work of Plenio et al. has shown that ferrocenyl 1,1′-bis-silyl ethers can be obtained easily from symmetrically substituted cyclopentadienyl silyl ethers and $FeCl_2$ and that they can serve as synthetic equivalents of hydroxyferrocenes.[16]

Thus, we have adapted the same strategy to O–Si–O tethered cyclopentadienyls, in order to access the corresponding ferrocenophanes, as shown in Scheme 1. The key feature of

Scheme 1. Diastereoselective Synthesis of Aryl-Substituted O–Si–O Tethered Ferrocenes



the targeted bis(cyclopentadienyloxy)silanes **3** are the aryl substituents on their 2-positions. A variety of aryl groups can be entered in this position by palladium-promoted Suzuki coupling of 2-iodocyclopentenone with arylboronic acids. The method is illustrated in Scheme 1. Starting from cyclopentenone **1**, a regioselective iodation was accomplished using a literature procedure[17] (I_2, 4-dimethylaminopyridine (DMAP), K_2CO_3 in a H_2O/THF 1/1 mixture). The 2-iodocyclopent-2-enone was obtained in 74% yield on a 10 g scale. Subsequently, Suzuki couplings between this iodide and four different boronic acids were accomplished in the presence of $PdCl_2(PPh_3)_2$ as the catalyst and sodium carbonate as the base. The desired 2-phenyl-, 2-(1-naphthyl)-, 2-(2-naphthyl)-, and 2-(9-phenanthryl)cyclopent-2-enones **2a–d** were obtained in 69–80% isolated yields. This easy approach to the aryl-substituted enones **2** is crucial for the development of the new family of phosphoramidites, as it ensures a modular and flexible access to the corresponding ferrocenes, as shown hereafter. Next, our strategy involves formation of the bis(cyclopentadienyl) silyl ethers **3** as the key intermediates.[18] This step has been accomplished through reaction of cyclopentenones **2** with di-*tert*-butylsilyl bis-trifluoromethanesulfonate, in the presence of triethylamine. It generates the desired bis(5-arylcyclopenta-1,4-dienyloxy)silanes **3a–d** in 40–77% yields as mixtures of isomers, since the basic conditions of these reactions enable migration of the double bonds to various positions of the cyclopentadiene rings. For clarity reasons, Scheme 1 displays only one of these isomeric species.

Starting from **3a–d**, deprotonation of the cyclopentadiene units with *n*BuLi at −78 °C followed by treatment of the resulting anions with $FeCl_2$[19] afforded the desired O–Si–O tethered ferrocenes **4a–d** in 50–91% yields. Most notably, these reactions take place with excellent stereocontrol, leading to ferrocenes **4** as single diastereomers. These diastereomers were demonstrated to be the chiral *d,l* forms through further experiments and X-ray studies disclosed hereafter. The *d,l* isomers are expected to be largely favored by steric effects, since

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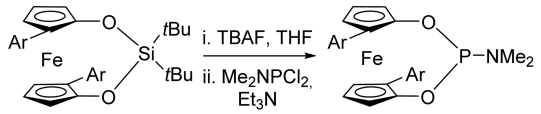
the two aryl substituents will be located on opposite faces of the O−Si−O bridges. The observed high stereocontrol means that the synthetic method largely benefits from the template effect of the tethered cyclopentadienes, as anticipated in our initial design.

The last step of the reaction sequence leading to the ferrocenophane-type phosphoramidites **5** is typified in Scheme 2. It involves replacement of the O−Si(tBu)$_2$−O linker by a O−P(NMe$_2$)−O linker following a one-pot desilylation/phosphorylation procedure, in order to avoid isolation of the air-sensitive intermediate 1,1′-dihydroxyferrocenes.

Scheme 2. One-Pot Conversion of the 1,3-Dioxa-2-sila[3]ferrocenophanes 4 into the Corresponding Phosphoramidites 5



4a-d

5a, Ar = Ph, 41%
5b, Ar = 1-naphthyl, 36%
5c, Ar = 2-naphthyl, 30%
5d, Ar = 9-phenanthryl, 53%

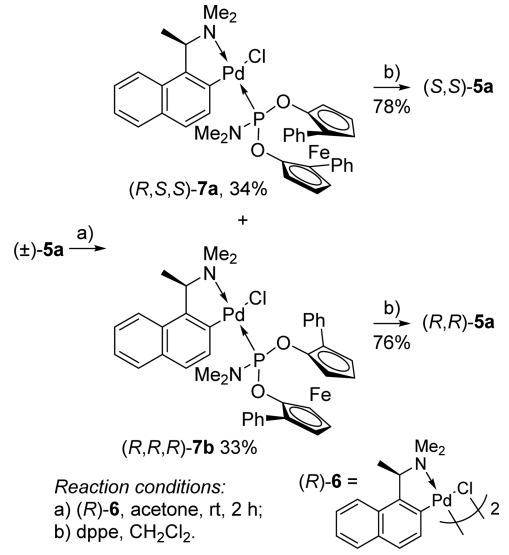
Cleavage of the silicon bridge has been carried out with tetrabutylammonium fluoride (TBAF)[16b] in THF at room temperature. After a workup, the crude mixture was diluted in THF, and then triethylamine and Me$_2$NPCl$_2$ were added and the reaction mixture was stirred for 4 h at room temperature. The desired phosphoramidites **5a−d** were purified by column chromatography on silica gel and isolated in 30−53% yields over two steps, as single isomers. Thus, the reaction conditions of the one-pot procedure above allow total retention of the stereochemistry of the planar chiral ferrocene scaffold. We have also considered alternative methods for the cyclization step, such as the use of P(NMe)$_3$ as the phosphorus reagent, but they did not afford improved yields. The new phosphoramidites **5a−d** have been fully characterized by spectroscopic methods, but unfortunately, we could not get crystals suitable for X-ray diffraction studies.

Overall, these preliminary investigations have highlighted a suitable method for the diastereoselective synthesis of unprecedented phosphoramidites displaying 2-phospha[3]-ferrocenophane scaffolds. Reactions in Scheme 2 show that the ferrocene substituents can be modulated easily. The size of the aryl substituents does not affect the cyclization step markedly, which looks promising for further extension of the method.

The following step of this study (Scheme 3) allowed us to both isolate pure enantiomers of the representative phosphoramidite **5a** and to validate the structural assignment of **5a** by X-ray diffraction of a palladium complex. For the optical resolution of racemic **5a** we have applied the standard procedure involving separation of diastereomeric palladium(II) complexes.[20] The chiral metallacyclic complexes **7a,b** have been formed by reacting the cyclopalladated (*R*)-*N*,*N*-dimethyl-1-naphthylethylamine complex (*R*)-**6**[21] with (±)-**5a** at room temperature in acetone. They have been separated easily by flash chromatography on silica gel.

After isolation of the pure diastereomers, we could grow crystals of **7b** suitable for X-ray diffraction studies. An ORTEP drawing is shown in Figure 3. The phosphorus ligand occupies the trans-to-N position in the palladacycle complex.[22]

Scheme 3. Resolution of the Phosphoramidite 5a via Chiral Palladacyclic Complexes



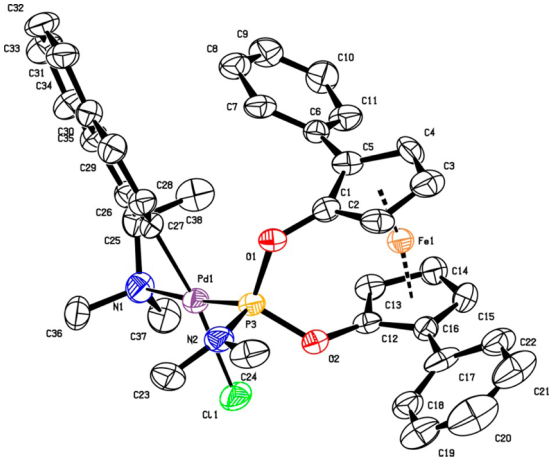


Figure 3. ORTEP view of complex (*R*,*R*,*R*)-**7b**. Selected bond distances (Å) and angles (deg): P−O(1) = 1.639(5), P−O(2) = 1.629(6), P−N, 1.618(8), P−Pd = 2.190(2), O(1)−C(1) = 1.38(1); O(1)−P-O(2) = 104.1(3), P−O(1)-C(1) = 129.5(5); P−O(2)-C(12) = 126.3(5); O(1)−C(1)−C(2) = 123.4(7); O(1)−C(1)−C(5) = 129.1(7); O(2)−C(12)−C(13) = 126.7(7); O(2)−C(12)−C(16) = 121.9(7).

Measurements reveal bond angle and distance values in the normal range for the phosphoramidite unit. However, they highlight a significant bending of the ferrocene unit due to ring strain: the oxygen atoms remain coplanar with the respective cyclopentadienyl rings, while the two cyclopentadienyl rings are tilted toward each other, forming an angle of 11.9°. Thus, the tilt of the flexible ferrocene unit balances the strain generated by the short O−P−O tether.

Finally, the enantiomerically pure phosphoramidites (*S*,*S*)-**5a** and (*R*,*R*)-**5a** have been removed from their palladium complexes by stirring with 1 equiv of 1,2-bis(diphenylphosphino)ethane (dppe) at room temperature in CH$_2$Cl$_2$. The same resolution procedure has been applied to complexes **5c,d** (see the Supporting Information).

As a preliminary investigation of the coordinating behavior of these ligands, we have considered the synthesis of platinum(II) metallacyclic complexes of the general formula **9** (Scheme 4).

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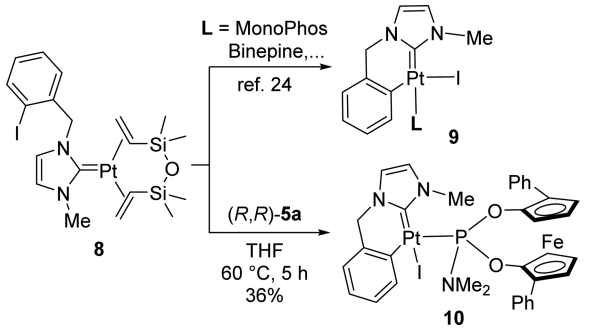
Scheme 4. Synthesis of the Platinum(II) Complex 10



These complexes display six-membered platinacyclic units containing NHC− and σ-aryl−platinum bonds. Complexes of this class had been investigated extensively by our group.[23] The platinacycles were generated from a NHC−Pt^0(divinyltetramethyldisiloxane) complex, such as **8**, by intramolecular oxidative addition of the aryl iodide and then combined in situ with a monodentate phosphorus ligand so as to complete the coordination sphere of platinum(II). We had shown notably that a variety of monodentate phosphoramidites coordinate platinum(II) easily to generate such complexes.[24] In most of the square-planar complexes **9** the phosphorus ligand L (L = phosphine, phosphoramidite) enters trans to the carbene ligand, but cis coordination is also possible. Thus, as a complement to these previous studies, we have envisioned the synthesis of analogous complexes by reacting phosphoramidite (*R*,*R*)-**5a** with the (NHC)Pt^0(dvtms) complex **8**. The reaction afforded the expected platinum complex, as a single isomer (^{31}P NMR δ 145.8 (J_{P-Pt} = 3008 Hz)).

The crystal structure of **10** (Figure 4) revealed that phosphoramidite **5a** coordinates cis to the NHC ligand. This

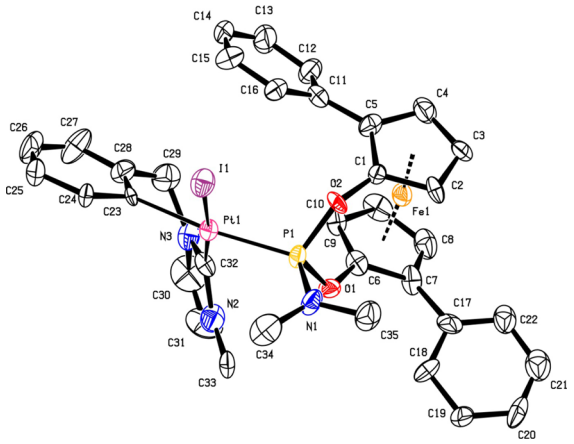


Figure 4. ORTEP view of complex **10**. Selected bond distances (Å) and angles (deg): Pt−P = 2.266(4), Pt−C(32) = 1.96(2), Pt−C(23) = 2.09(2), Pt−I = 2.666(1), P−N = 1.64(1), P−O(1) = 1.655(9), P−O(2) = 1.63(1); P−Pt−C(32) = 95.5(5), P−Pt−I = 90.5(1), I−Pt−C(23) = 90.1(4), P−Pt−C(23) = 172.8(4).

coordination mode had been encountered previously with a TADDOL-derived phosphoramidite.[24c] The preference for cis coordination had been tentatively assigned to the increased steric hindrance of the TADDOL phosphoramidite, with respect to Monophos and other phosphoramidites. Formation of the cis complex **10** might corroborate this hypothesis, as phosphoramidite **8** is a significantly bulky species, the steric bulk of the ferrocene unit being increased further by the phenyl substituents, ortho to the O−P−O bridge.

The platinacyclic complex **10** displays an additional axial chirality, since its unsymmetrical NHC ligand is oriented "orthogonally" to the square-planar platinum complex[25] and two different ligands are located ortho to the NHC (P and C in Figure 5). In principle, this axially chiral core combined with the planar chiral phosphoramidite should generate a mixture of diastereomeric complexes **10**.[24]

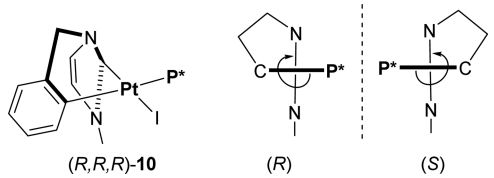


Figure 5. Schematic view of complex **10**, with stereochemical descriptors.

The reaction leading to **10** (Scheme 4) proved to be totally diastereoselective, as only the *R*,*R*,*R* diastereomer has been isolated. From the X-ray structure, it can be seen that the *R*,*R*,*R* relative configuration minimizes the steric hindrance between the phenyl substituent of the phosphoramidite and the platinacyclic unit. This might account for the diastereoselectivity observed in this reaction.

CONCLUSION

In summary, we have disclosed here a suitable synthetic approach to planar chiral phosphoramidites with [3]-ferrocenophane structures. As the key step, the method involves diastereoselective building of the ferrocene units from suitable bis-cyclopentadienyl derivatives displaying an O−Si−O tether. The phosphoramidites have been obtained in enantiomerically pure form by resolution of their racemic mixtures. In spite of their high steric bulk, these new phosphoramidites proved to be suitable ligands for palladium and platinum square-planar complexes. Investigations of the catalytic properties of these phosphoramidites as chiral ligands are currently ongoing.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications Web site. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00700.

General information, experimental procedures, X-ray crystal structure determinations, and NMR spectra (^{1}H, ^{13}C, ^{31}P) (PDF)

Accession Codes

CCDC 1543585 and 1543727 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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