Synthesis and Characterization of Benzo[b]phosphaferrocene Derivatives

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S Supporting Information

ABSTRACT: The first examples of $(\eta^{5}$ -phosphindolyl)iron(II) species, which are planar-chiral, have been prepared and characterized by NMR spectroscopy and X-ray crystallography, and their partial optical resolution has been examined.



The phospholyl anion (phospholide) 2 is isoelectronic with cyclopentadienide 1 and is capable of coordinating to various transition-metal cations as a six-electron donor to form the corresponding phosphametallocenes 3 (Figure 1).¹ The



Figure 1. Comparison among cyclopentadienide, phospholide, and their benzannelated derivatives.

phosphorus atom in an η^5 -phospholide possesses a lone pair on it; phosphametallocenes are Lewis basic. Thus, they have been utilized as nucleophilic catalysts² or a new class of P-donor ligands.^{1,3-5} Due to an sp²-hybridized phosphorus atom, phosphametallocenes show unique electronic properties: in general, they are good π acceptors and poor σ donors.¹ Meanwhile, various chirally modified phosphaferrocenes, which include characteristic planar-chiral derivatives, have been prepared and applied to a wide range of metal-catalyzed asymmetric reactions as a new class of chiral ligands showing excellent performances.^{4,5}

The indenyl anion 4 and its derivatives also serve as η^5 sixelectron donors. Whereas (η^5 -indenyl)metal complexes show a clear contrast to (η^5 -cyclopentadienyl)metal species in their reactivity as well as in their steric characteristics, they share important positions in organotransition-metal chemistry.⁶ On the other hand, metal complexes of phosphaindenyl (phosphindolyl) anions 5 have attracted surprisingly less attention. To the best of our knowledge, examples of η^5 -phosphindolyl transition-metal complexes **6** are limited to those with Mn(I)⁷ and Sm(II).⁸ The X-ray crystal structure of a phosphindolyllithium also shows an η^5 coordination of the phosphindolide to a lithium cation.⁹ In addition to the species above, a couple of examples of (η^5 -isophosphindolyl)metal complexes were described recently.^{7b,10} The lack of "benzannelated" phosphametallocene chemistry can be partially attributed to the lack of convenient synthetic procedures of supplying various benzophospholes,^{7,8,11,12} which are the logical precursors to the phospholide anion dramatically decreases its ability for π coordination. For example, benzophospholides **5** and dibenzophospholides **9** tend to act as σ donors, occasionally bridging two metal centers (e.g., 7 and **10**),^{7,13,14} and the η^5 coordination of dibenzophospholides **9** has never been reported to date.¹⁴ The latter is a clear contrast to the η^5 coordination capability of fluorenyl anions **8**.

Among the numerous phosphametallocene complexes reported so far, those with a central iron(II) cation, i.e. phosphaferrocenes, have been arguably the most extensively investigated.¹ Considering these facts, it is quite surprising that the synthesis of $(\eta^5$ -phosphindolyl)iron(II) derivatives has not been achieved yet. In the paper published in 1982,^{7a} Mathey and co-workers examined a reaction of a phosphindolyl anion with FeCl₂, but the expected $bis(\eta^5$ -phosphindolyl)iron(II) species could not be obtained, probably because the benzannelation lowered the stability of the phosphaferrocenes. Here we wish to report the synthesis and characterization of a series of substituted benzo[b]phospholes (phosphindoles) and their application in the preparation of the first (η^5 phosphindolyl)iron(II) complexes. It should be noted that phosphindolyl anions are unsymmetrical, either substituted or unsubstituted, and their η^5 coordination to a transition-metal cation always induces planar chirality in the corresponding

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complexes.¹⁵ Thus, the benzo[*b*]phosphaferrocenes obtained here are also planar-chiral.

Preparation of Benzo[b]phospholes (Phosphindoles). One of the most versatile synthetic methods of phospholes known to date is the metallacycle transfer reaction from zirconium to phosphorus reported by Fagan and Nugent in 1988.¹⁶ Whereas various regio- and chemoselective methods of preparing substituted zirconacyclopentadienes have been developed,¹⁷ the metallacycle transfer process allows access to diverse phosphole derivatives in a highly selective manner. A typical method of generating the zirconacyclopentadiene species is the reductive coupling of two alkynes with a divalent zirconium reagent. Here the reaction of a zirconocene benzyne species with an alkyne reagent gives the corresponding zirconaindene derivative;^{18,19} the metallacycle transfer from the zirconaindene to an appropriate phosphorus compound should afford the benzophosphole derivative. Indeed, this possibility was demonstrated in a few previous reports.^{8,20} We also utilized the zirconaindene-mediated process for the preparation of a series of novel benzo[b] phosphole derivatives with slight modifications (Scheme 1).

Scheme 1. Zirconium Benzyne Mediated Synthesis of Benzo[b]phospholes 14



An equimolar mixture of zirconocene diphenyl 11, which was generated in situ from zirconocene dichloride and PhLi (2 equiv to Zr), and 3-hexyne in THF was heated to reflux for 8 h to give a deep red solution of zirconaindene 13a.^{19b-f} Subsequently, the solution of 13 was treated with CuCl (2 equiv to Zr) and PhPCl₂, followed by the addition of diethylamine to give 2,3-diethyl-1-phenylbenzophosphole (14a) in 67% yield as a colorless liquid. It was found that CuCl facilitated the metallacycle transfer process via the Zr to Cu transmetalation: the reaction took place faster and at lower temperature in the presence of CuCl.^{21,22} The metallacycle transfer reaction is sensitive to steric factors and becomes very sluggish, especially with sterically demanding substituents in THF, which is a conventional solvent for the zirconacycle formation. The solvent exchange from THF to dichloromethane accelerates the metallacycle transfer process in same cases,^{23,24} but the addition of CuCl is as effective as the use of the dichloromethane solvent and could avoid the bothersome solvent exchange.

With an unsymmetrical alkyne component, the benzophosphole could be in two regioisomeric forms. The reaction using 1- (trimethylsilyl)propyne, however, afforded α -silylbenzophosphole **14b** in 75% yield exclusively and the β -silyl isomer **14'b** was not detected, since the formation of **13b** was highly regioselective, giving the α -silylzirconaindene exclusively.^{19c,d} On the other hand, the analogous reaction using 1-phenyl-

propyne provided a mixture of 14c and 14'c,^{19g} which are difficult to separate, in 71% yield with the ratio 14c/14'c = 72/28.

The benzophospholes are thermally stable but slightly airsensitive. Diethyl derivative 14a was distilled under high vacuum and readily converted into the corresponding phosphole oxide 15a and phosphole sulfide 16a quantitatively by H_2O_2 or S_8 treatment, respectively.

Preparation and Characterization of Benzo[b]phosphaferrocenes. The preparation of the as yet unknown $(\eta^{5}$ -benzophospholyl)iron(II) species was examined. Treatment of an THF solution of 14a with excess lithium metal resulted in a dark red color in several minutes. A ³¹P NMR spectrum of the crude reaction mixture revealed a single sharp resonance at δ 23.2, indicating quantitative conversion to the corresponding lithium phosphindolide 17a. As an initial trial, the reactions of 17a with $FeCl_2$ or $Fe(acac)_2$ were examined. However, similar to the previous report,^{7a} the reactions did not afford any tractable iron-containing products. Then, we turned our attention to the preparation of benzo-fused monophosphaferrocene species. The THF solution of 17a, which contained equimolar PhLi, was treated with $\left[(\eta^6 \text{-mesitylene}) \right]$ FeCp]PF₆ (2 equiv to 17a) and the mixture was refluxed for 12 h.²⁵ After the usual workup, the crude material was purified by silica gel chromatography under nitrogen to afford benzomonophosphaferrocene 18a in 60% yield as a dark red viscous liquid (Scheme 2). The phosphaferrocene is thermally stable,





and the compound stored in an argon glovebox at room temperature for several months shows no sign of decomposition. On the other hand, **18a** is very sensitive to air: exposure of its hexane solution to air bleaches the dark red color in a few minutes and brown anonymous solids precipitate.

In the ¹³C NMR spectrum of **18a**, the two α -phosphindolyl carbons are detected as doublets at δ 95.4 (J_{PC} = 54.1 Hz) and 103.9 (J_{PC} = 60.4 Hz) with relatively large coupling constants, while the β -phosphindolyl carbons show smaller J_{PC} values at δ 93.7 (J_{PC} = 6.7 Hz) and 98.2 (J_{PC} = 4.0 Hz). The ³¹P NMR spectrum recorded in C₆D₆ shows a sharp singlet at high field at δ –85.3.

In the same way, **14b** could be converted to benzo[b]phosphaferrocene **18b** in 58% yield. Compound **18b** is crystallin, and deep red needles suitable for X-ray analysis can be grown from the hexane solution. The crystal structure of **18b** is shown in Figure 2 with the selected bond lengths and angles, which confirms the η^5 coordination of the phosphindolyl ligand to the Fe(II) center (see the Supporting Information for details). The phosphindolyl ligand in **18b** is planar: all of the atoms of the phosphindolyl core are located on a plane within 0.014 Å deviation. The phosphindolyl ligand and the Cp ligand are almost parallel with a dihedral angle of



Figure 2. ORTEP drawing of 18b with 50% thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Fe(1)-P(1) = 2.284(1), Fe(1)-C(1) = 2.127(3), Fe(1)-C(2) = 2.088(3), Fe(1)-C(3) = 2.056(3), Fe(1)-C(4) = 2.094(2), P(1)-C(1) = 1.792(3), P(1)-C(4) = 1.797(3), Fe(1)-phosphindolyl =1.656, Fe(1)-Cp = 1.659; C(1)-P(1)-C(4) = 89.7(1).

 3.73° in the nearly eclipsed conformation. The Fe–Cp (1.659 Å) and Fe–phosphindolyl (1.656 Å) distances are nearly the same.

Analytical Resolution and Diastereomeric Complexation of Planar-Chiral Benzo[b]phosphaferrocenes. Due to their unsymmetrical structure, benzo[b]phosphaferrocenes. Bue to their unsymmetrical structure, benzo[b]phosphaferrocenes. Bue to their unsymmetrical structure, benzo[b]phosphaferrocenes. 18 are planar-chiral,¹⁵ and optical resolution of *rac*-18a was examined. Nearly complete separation of the two enantiomers was achieved by HPLC on a chiral stationary phase (Daicel Chiralcel OD-H column) on an analytical scale (see the Supporting Information for details);²⁶ however, the HPLC method is not practical for the macroscale resolution of 18a due to the air-sensitive nature of the compound. An attempt at resolving *rac*-18a on a 5 mg scale resulted in decomposition of the benzo[b]phosphaferrocene and resolved 18a could not be obtained.

Then, we turned our attention to the enantioselective complexation of rac-18a with the chiral palladacycle (S)-Pd*.^{27,28} Treatment of *rac*-18a with a slight excess of $\lceil (S) \rceil$ $Pd^*]_2$ in dichloromethane afforded the pair of diastereometic complexes [(S)-Pd*][(S)-18a] and [(S)-Pd*][(R)-18a] at the time of mixing with complete consumption of free 18a (Figure 3b). The ³¹P{¹H} NMR spectrum of the mixture showed two clearly resolved resonances of equal intensities at δ 2.4 and δ 3.2. The use of less than stoichiometric $[(S)-\mathbf{Pd}^*]_2$ realized an uneven complexation between (S)- and (R)-18a. For example, a solution of *rac*-18a with 0.11 equiv of $[(S)-\mathbf{Pd}^*]_2$ in dichloromethane showed three signals in the ${}^{31}P{}^{1}H$ NMR spectrum at δ -89.1, 2.4, and 3.2 which are integrated with 79.1:12.7:8.2 relative intensities (Figure 3c). The enantiomeric purity of the unligated portion of 18a in this mixture, detected at $\delta_{\rm P}$ -89.1, was estimated to be ca. 6% ee. Although the selectivity of this asymmetric complexation is rather poor, the enantiomeric purity of the unligated 18a could be amplified to 27% ee in the mixture of rac-18a and $[(S)-Pd^*]_2$ with a 1.0/ 0.43 molar ratio, which shows the three 31 P resonances at δ -89.1, 2.4, and 3.2 with a 14.9/44.6/40.5 ratio (Figure 3d).

In summary, two novel benzo[b]phosphaferrocenes, which are the first examples of Fe(II) species with an η^5 phosphindolyl ligand, have been prepared and fully characterized by NMR spectroscopy and X-ray crystallography. The benzo[b]phosphaferrocenes are planar-chiral and are poten-



Figure 3. Reactions of *rac*-18a with chiral palladacycle (*S*)-Pd* and ${}^{31}P{}^{1}H$ NMR spectra at 162 MHz in CH₂Cl₂ at -90 °C: (a) free *rac*-18a; (b) *rac*-18a/[(*S*)-Pd*]₂ = 1.0/0.55; (c) *rac*-18a/[(*S*)-Pd*]₂ = 1.0/0.11; (d) *rac*-18a/[(*S*)-Pd*]₂ = 1.0/0.43.

tially resolvable by the chiral HPLC or the selective complexation with the chiral palladacycle species. However, complete and macroscale optical resolution of the phosphaferrocenes cannot be achieved due to the air sensitivity of the complexes.

ASSOCIATED CONTENT

S Supporting Information

Text giving experimental procedures and compound characterization data, figures giving NMR spectra (¹H, ¹³C, and ³¹P) for all the new compounds, and a CIF file giving crystallographic data for **18b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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