

A New Class of Ferrocenyl Phosphines

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Abstract: A new series of ferrocenyl diphosphines have been synthesized by Suzuki coupling of diboronic acid of ferrocene with bromo-substituted triphenylphosphine oxides, followed by reduction with HSiCl_3 .

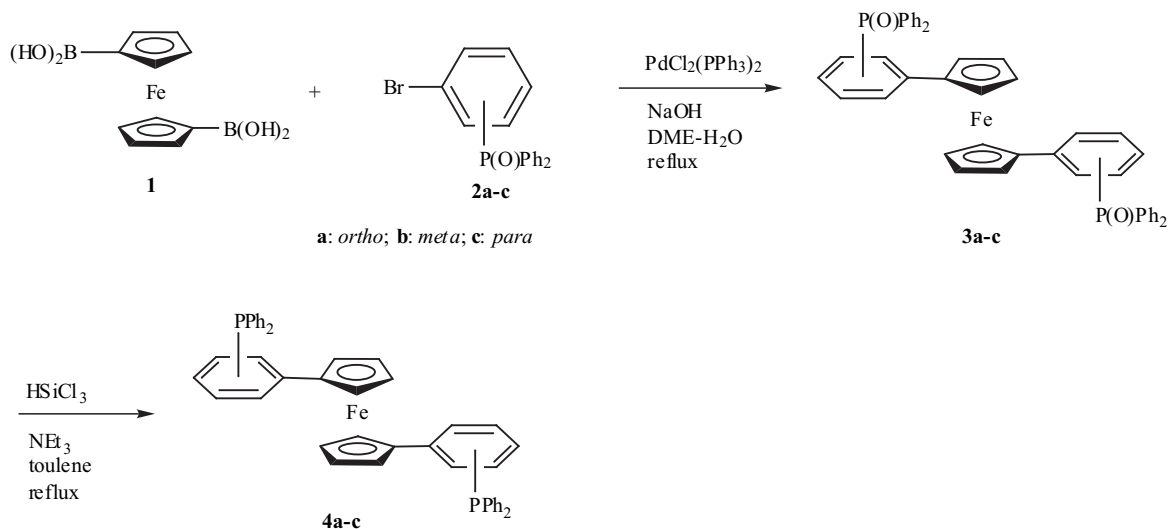
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INTRODUCTION

Ferrocenyl phosphines have found extensive applications in homogeneous catalysis. Examples that readily come to mind include various cross coupling reactions, hydrogenation, hydroformylation, allylic substitution, and Aldol condensation [1]. Apart from the well-known 1,1'-bis(diphenylphosphino)ferrocene (dppf), however, few other aromatic diphosphines based on the ferrocenyl backbone are known. We have recently reported several catalytic methodologies for the synthesis of various aryl phosphines [2]. In continuing our effort in search for methods that allow for easy access to modular phosphines, we report herein the synthesis of a new class of ferrocenyl diphosphine ligands, which are based on a bisarylated ferrocene backbone.

palladium-catalysed Suzuki coupling of the diboronic acid of ferrocene **1** with a desired aryl halide. There are a few scattered examples in the literature where **1** has been coupled with common aryl halides such as iodobenzenes [3,4]. We found this chemistry [3] could be applied to the halophosphine oxides **2**, thereby constructing precursors to a new series of ferrocenyl phosphines in only one step. The coupling reaction can be readily effected by heating a mixture of **1** and **2** in the presence of $[\text{PdCl}_2(\text{PPh}_3)_2]$ in ethylene glycol dimethyl ether (DME) with aqueous sodium hydroxide as base, furnishing the *ortho* and *para*-positioned diphosphine oxides **3a** and **3c** in >70% yields. The yield of **3b** was lower, at 54%, reflecting probably less electron density depletion at the *meta* position than at the other two



Scheme 1. Synthesis of ferrocenyl diphosphines **4** via Suzuki coupling.

RESULTS AND DISCUSSION

The diphosphines are 1,1'-bis[(diphenylphosphino)phenyl]ferrocenes with phosphorus at the *ortho*, *meta* and *para* positions (Scheme 1). The key synthetic step is a

positions by the electron-withdrawing phosphoryl moiety, which presumably renders the oxidative addition of the C-Br bond at the former position more difficult. The phosphine oxides **2** were prepared using bromiodobenzenes according to the P-C coupling protocol of Steltzer [5]. The coupling reactions were facile in the case of the *ortho*- and *para*-bromiodobenzenes; but *meta*-bromiodobenzene was difficult to couple, giving reduced yields.

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The free phosphines **4** were obtained in quantitative yields by reduction with HSiCl_3 in refluxing toluene in the presence of NEt_3 . As expected, reduction of **3** to **4** was accompanied by an upfield shift in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. Unexpectedly, **4a** was shifted by 5-6 ppm more than **4b** and **4c**. This may be ascribed to the neighbouring group effect arising from the ferrocene Cp rings. Interestingly, while **4b** and **4c** were found to be relatively stable, **4a** decomposed readily in solution upon exposure to air. Although **4a** is more congested and hence could be less stable, the exact reason for its instability is not clear to us at this time. Previously it has been noted that some (*o*-substituted phenyl)ferrocenes are more readily oxidized in acidic media than the corresponding *p*-substituted isomers, probably due to a stabilizing effect of the substituent, e.g. *o*-acetyl, on the proton bound to the ferrocene iron atom, an intermediate thought to be the precursor to the oxidised ferrocene [6].

In summary, we have developed a simple, catalytic method for the synthesis of ferrocenyl arylphosphines. Because the essential ligand framework is created by a one-step Suzuki coupling and other halophosphine oxides should be equally applicable, the method provides a modular approach that should make a diverse range of ferrocenyl diphosphines readily accessible. The catalytic properties of **4** remain to be seen.

EXPERIMENTAL

Phosphine oxide **2** (1.3 g, 3.7 mmol) and diboronic acid **1** (500 mg, 1.8 mmol) were heated in the presence of $[\text{PdCl}_2(\text{PPh}_3)_2]$ (0.064 g, 9.1×10^{-2} mmol) in DME (20 ml) containing 2 M NaOH solution (2 ml) at 90 °C with stirring for 12 h, before being poured into a saturated solution of ammonium chloride (50 ml) and extracted with dichloromethane (3 x 20 ml). The organic extracts were washed with water (3 x 20 ml), separated and then dried over magnesium sulphate.

An example of reduction is given for **3c**. Triethyl amine (2.1 ml, 15 mmol), trichlorosilane (1.6 ml, 15 mmol) and toluene (20 ml) were added to the ferrocenyl phosphine oxide **3c** (0.44 g, 0.77 mmol) and the mixture was refluxed for 12 h. Under nitrogen, sodium hydrogen carbonate solution was added to destroy excess silane. The mixture was filtered under nitrogen and the toluene extracts were reduced by oil pump, affording **4c** in quantitative yield.

1,1'-Bis[2-(Diphenylphosphinyl)Phenyl]Ferrocene (3a)

The compound was obtained as a red powder from flash chromatography in 71% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 3.71 (t, $J = 1.8$ Hz, 4H), 4.65 (t, $J = 1.8$ Hz, 4H), 6.99-7.09 (m, 4H), 7.24-7.29 (m, 8H), 7.32-7.37 (m, 6H), 7.47-7.56 (m, 8H), 7.86 (d, $J = 7.4$, 1H), 7.88 (d, $J = 7.4$, 1H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 70.9, 72.8, 88.4, 125.8 (d, $J_{\text{C-P}} = 12.8$ Hz), 128.4 (d, $J_{\text{C-P}} = 12.0$ Hz), 131.4 (d, $J_{\text{C-P}} = 102.3$ Hz), 131.4 (d, $J_{\text{C-P}} = 2.4$ Hz), 131.8 (d, $J_{\text{C-P}} = 15.2$ Hz), 131.8 (d, $J_{\text{C-P}} = 2.9$ Hz), 133.6 (d, $J_{\text{C-P}} = 104.7$ Hz), 133.7 (d, $J_{\text{C-P}} = 9.6$ Hz), 134.5 (d, $J_{\text{C-P}} = 12.8$ Hz), 144.3 (d, $J_{\text{C-P}} = 8.0$ Hz); $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 30.9; Anal. calcd. for $\text{C}_{46}\text{H}_{36}\text{FeP}_2\text{O}_2$: C, 74.80; H, 4.91. Found: C, 74.83; H, 4.93.

1,1'-Bis[3-(Diphenylphosphinyl)Phenyl]Ferrocene (3b)

The compound was obtained as an orange powder from flash chromatography in 54% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 4.07 (t, $J = 1.9$ Hz, 4H), 4.38 (t, $J = 1.7$ Hz, 4H), 7.15-7.20 (m, 2H), 7.27-7.27 (m, 6H), 7.45-7.60 (m, 12H), 7.65-7.77 (m, 8H); $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 30.1; Anal. calcd. for $\text{C}_{46}\text{H}_{36}\text{FeP}_2\text{O}_2$: C, 74.80; H, 4.91. Found: C, 75.13; H, 4.97.

1,1'-Bis[4-(Diphenylphosphinyl)Phenyl]Ferrocene (3c)

The compound was obtained as an orange powder from flash chromatography in 78% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 4.23 (t, $J = 1.9$ Hz, 4H), 4.47 (t, $J = 1.9$ Hz, 4H), 7.39-7.56 (m, 20H), 7.65-7.71 (m, 8H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 68.7, 71.7, 84.1, 125.8 (d, $J_{\text{C-P}} = 12.0$ Hz), 128.5 (d, $J_{\text{C-P}} = 12.0$ Hz), 129.6 (d, $J_{\text{C-P}} = 107.1$ Hz), 131.9 (d, $J_{\text{C-P}} = 3.2$ Hz), 132.1 (d, $J_{\text{C-P}} = 9.6$ Hz), 132.2 (d, $J_{\text{C-P}} = 10.4$ Hz), 132.6 (d, $J_{\text{C-P}} = 103.9$ Hz), 143.1 (d, $J_{\text{C-P}} = 2.4$ Hz); $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 30.4; Anal. calcd. for $\text{C}_{46}\text{H}_{36}\text{FeP}_2\text{O}_2$: C, 74.80; H, 4.91. Found: C, 75.22; H, 4.93.

1,1'-Bis[2-(Diphenylphosphino)Phenyl]Ferrocene (4a)

The phosphine was obtained as a red orange powder. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 4.08 (t, $J = 1.8$ Hz, 4H), 4.32 (dt, $J = 1.7$ Hz, 4H), 6.80-6.84 (m, 2H), 7.05-7.25 (m, 24H), 7.70-7.74 (m, 2H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 70.0, 72.4 (d, $J = 8.8$ Hz), 88.4, 128.2, 128.3 (d, $J_{\text{C-P}} = 10.4$ Hz), 129.0, 131.4 (d, $J_{\text{C-P}} = 4.8$ Hz), 133.8 (d, $J_{\text{C-P}} = 20.0$ Hz), 135.5 (d, $J_{\text{C-P}} = 16.0$ Hz), 137.9 (d, $J_{\text{C-P}} = 12.0$ Hz), 144.8 (d, $J_{\text{C-P}} = 26.4$ Hz); $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ -11.1; Anal. calcd. for $\text{C}_{46}\text{H}_{36}\text{FeP}_2$: C, 78.19; H, 5.14. Found: C, 77.97; H, 5.13.

1,1'-Bis[3-(Diphenylphosphino)Phenyl]Ferrocene (4b)

The phosphine was obtained as an orange red wax: $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 3.92 (t, $J = 1.8$ Hz, 4H), 4.18 (t, $J = 1.8$ Hz, 4H), 7.00-7.41 (m, 28H); $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ -4.0; Anal. calcd. for $\text{C}_{46}\text{H}_{36}\text{FeP}_2$: C, 78.19; H, 5.14. Found: C, 78.23; H, 5.19.

1,1'-Bis[4-(Diphenylphosphino)Phenyl]Ferrocene (4c)

The phosphine was obtained as an orange powder, which crystallized in hexane/ CH_2Cl_2 . $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 4.20 (t, $J = 1.9$ Hz, 4H), 4.43 (t, $J = 1.9$ Hz, 4H), 7.15 (dd, $J = 7.6$ Hz, 4H), 7.25-7.33 (m, 24H); $^{13}\text{C NMR}$ (101 MHz, CD_2Cl_2) δ 69.1, 71.8, 85.9, 126.7 (d, $J_{\text{C-P}} = 7.2$ Hz), 129.2 (d, $J_{\text{C-P}} = 7.2$ Hz), 129.3 (d, $J_{\text{C-P}} = 21.6$ Hz), 134.4 (d, $J_{\text{C-P}} = 19.2$ Hz), 134.5 (d, $J_{\text{C-P}} = 20.0$ Hz), 135.1 (d, $J_{\text{C-P}} = 10.4$ Hz), 138.4 (d, $J_{\text{C-P}} = 11.2$ Hz), 140.1; $^{31}\text{P NMR}$ (162 MHz, CD_2Cl_2) δ -4.8; Anal. calcd. for $\text{C}_{46}\text{H}_{36}\text{FeP}_2$: C, 78.19; H, 5.14. Found: C, 78.05; H, 5.13.

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