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## Ferrocene-based phosphonite–phosphine ligands, Pd and Rh complexes

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### Abstract

A variety of ferrocene-based 1-phosphonite-1'-phosphine ligands were prepared via 1-dichlorophosphino-1'-diphenylphosphinoferrocene from anionic ring opening of 1-phenyl-1-phospha-[1]ferrocenophane. The corresponding palladium and rhodium complexes have also been prepared and tested, in Heck and hydroformylation reactions. © 2000 Published by Elsevier Science Ltd. All rights reserved.

*Keywords:* ferrocenes; phosphine; phosphonite; palladium catalysts; rhodium catalysts.

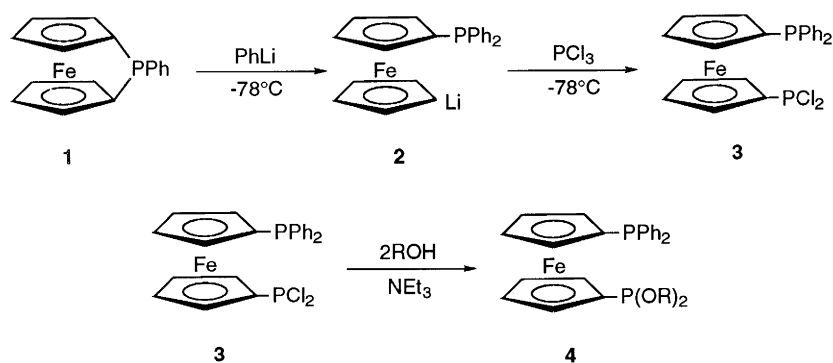
Ferrocenylphosphines have useful synthetic applications as ligands in the transition metal-catalyzed processes. Notable examples are the use of diphosphine ligands in 1,1'-bis(diphenylphosphine)ferrocene<sup>1</sup> and its dialkyl analogues. Different steric and electronic properties have been shown to provide various regioselectivity and efficiency in the Heck reaction for the palladium(II) chloride complex.<sup>2</sup> A chiral 1,1'-bisphosphine was also described which associated to rhodium catalyses various asymmetric hydrosilylation<sup>3a</sup> and hydrogenation.<sup>3b</sup> Recently, one chiral ferrocene-based 1,1'-diphosphonite was synthesized and used to prepare hydrogenation catalysts by reaction with Rh(cod)<sub>2</sub>BF<sub>4</sub>.<sup>4</sup>

There has been many reports dealing with non-metallocenic unsymmetrical chelating ligands such as phosphite–phosphine,<sup>5</sup> phosphinite–phosphine,<sup>6</sup> phosphonite–phosphine<sup>7</sup> or phosphonate–phosphine.<sup>8</sup> However, to the best of our knowledge there are no reported examples of 1,1' unsymmetric ferrocenyl analogues. We speculated that chelating 1-phosphonite-1'-phosphine ferrocenyl species constitute accessible ligands with attractive features because steric, chiral and electronic properties could easily be modulated owing to the phosphonite element.

In this paper, we report the first synthesis of 1-phosphonite-1'-phosphine ferrocenyl ligands from phosphorus-bridged [1]ferrocenophane and phenol, racemic or chiral diols.

The synthesis shown in Scheme 1 was accomplished in five steps starting from ferrocene (ferrocene → 1,1'-dilithioferrocene · TMEDA → **1** → **2** → **3** → **4**).

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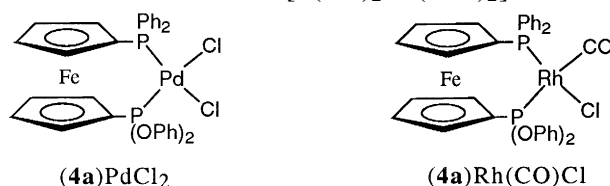


Scheme 1.

1-Phenyl-1-phospha-[1]-ferrocenophane **1** was synthesized using a procedure described by Manners et al.<sup>9</sup> Ring opening of **1** with phenyllithium gave **2**<sup>10</sup> (56% yield) which was transformed to **3**<sup>10</sup> (51% yield) with  $\text{PCl}_3$  in hexane, at  $-78^\circ\text{C}$ . Typical examples of the last step are the reaction of **3** in presence of triethylamine with phenol, 1,2 ethanediol and binaphthol (rac. and (*R*)), leading, respectively, to **4a**, **4b**, **4c** and **4d**<sup>11</sup> in quantitative yield.

A complementary procedure was developed by Lai and Dong<sup>12</sup> or Butler and Davies<sup>13</sup> to obtain **2** starting from alternative precursors (ferrocene→1,1'-dibromoferrocene→1-bromo-1'-lithioferrocene→1-bromo-1'-diphenylphosphinoferrocene→**2**). As shown in Scheme 1, the lithium derivative **2** gave **3** by nucleophilic attack of **2** on phosphorus trichloride. Reetz et al.<sup>4</sup> reports the same overall transformation but in two steps via the diethylaminophosphino derivative. Another synthetic route towards **4** involving the readily available building block  $\text{ClP}(\text{OR})_2$  and its reaction with lithiated ferrocene failed.

As first elements of our efforts to develop the use of **4** as ligands and applications in transition metal-catalyzed syntheses, we studied the reaction of **4a** [ $\text{P}(\text{OR})_2=\text{P}(\text{O}^i\text{Pr})_2$ ] with  $\text{PdCl}_2$ <sup>14</sup> and  $[\text{RhCl}(\text{CO})_2]_2$ .<sup>15</sup>



The ferrocene based **(4a)PdCl<sub>2</sub>** was compared to a series of other ferrocenylphosphines as a catalyst precursor for the Heck reaction. In the usual conditions,<sup>2</sup> **(4a)PdCl<sub>2</sub>** added to iodobenzene and methyl acrylate mixture led to *Z*-cinnamate with 80% isolated yield. In comparison, the yield for dppf was 7% and 96% for diisopfp.<sup>2</sup>

Preliminary attempts of hydroformylation of oct-1-ene in presence of **(4a)Rh(CO)Cl** (catalyst:octene=1:200) showed an effective transformation of the starting olefin. After 16 h reaction time ( $80^\circ\text{C}$ ; 10 atm with  $\text{CO}:\text{H}_2=1$ ), no products of hydrogenation or isomerization were detected. However, and surprisingly, all possible isomeric aldehydes (nonanal:2-methyloctanal:2-ethylheptanal:2-propylhexanal=52:37:7:4) were characterized in the reaction mixture (conversion: 30%). The unusual rate of hydroformylation of internal olefins was confirmed by hydroformylation of cyclohexene using the same experimental conditions (conversion: 43%).

In summary, the synthesis of some ferrocene-based phosphonite-phosphine ligands has been achieved. In one case the metallocene ligand allowed the coordination of transition metals leading to effective complexes in catalytic Heck or hydroformylation reactions. Access to new ligands and their use in complexation for catalytic syntheses are topics of continuing research in this area.

## Acknowledgements

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10. Spectral data of **2**:  $^{31}\text{P}\{^1\text{H}\}$  NMR (200 MHz,  $\text{C}_6\text{D}_6$ ),  $\delta$  -17.1 (s,  $\text{PPh}_2$ ). Compound **3**:  $^1\text{H}$  NMR (200 MHz,  $\text{C}_6\text{D}_6$ ),  $\delta$  7.02–7.42 (m, 10H, phenyl),  $\delta$  4.28 (m, 2H, Cp'),  $\delta$  4.09 (m, 2H, Cp'),  $\delta$  4.01 (m, 2H, Cp');  $^{31}\text{P}\{^1\text{H}\}$  NMR (200 MHz,  $\text{C}_6\text{D}_6$ ),  $\delta$  162.8 (s,  $\text{PCl}_2$ ),  $\delta$  -20.0 (s,  $\text{PPh}_2$ ); anal. calcd for  $\text{C}_{22}\text{H}_{18}\text{FeP}_2\text{Cl}_2$ : C, 56.11%; H, 3.82%. Found: C, 56.02%; H, 4.14%; MS EI  $m/z$  (%): 470 (100) ( $\text{M}^+$ ), 435 (35) ( $\text{M}-\text{Cl}$ ) $^+$ , 500 (10) ( $\text{M}-\text{Cl}_2$ ) $^+$ .
11. All attempts to obtain analytically pure samples of **4** were unsuccessful. The sensitivity of phosphonite group has been previously underlined.<sup>4,7</sup> Spectral data of: **4a** (orange oil):  $^1\text{H}$  NMR (200 MHz,  $\text{C}_6\text{D}_6$ ),  $\delta$  6.69–7.48 (m, 20H, phenyl),  $\delta$  4.45 (m, 2H, Cp'),  $\delta$  4.25 (m, 2H, Cp'),  $\delta$  4.15 (m, 2H, Cp'),  $\delta$  4.11 (m, 2H, Cp');  $^{31}\text{P}\{^1\text{H}\}$  NMR (200 MHz,  $\text{C}_6\text{D}_6$ ),  $\delta$  159.0 (s,  $\text{P}(\text{OPh})_2$ ),  $\delta$  -19.4 (s,  $\text{PPh}_2$ ); MS EI  $m/z$  (%): 586 (90) ( $\text{M}^+$ ), 493 (100) ( $\text{M}-(\text{OPh})$ ) $^+$ , 700 (70) ( $\text{M}-(\text{OPh})_2$ ) $^+$ . Compound **4b** (orange powder):  $^1\text{H}$  NMR (200 MHz,  $\text{C}_6\text{D}_6$ ),  $\delta$  7.03–7.45 (m, 10H, phenyl),  $\delta$  4.43 (pseudo-t, 2H, Cp'),  $\delta$  4.19 (pseudo-q, 2H, Cp'),  $\delta$  4.13 (pseudo-t, 2H, Cp'),  $\delta$  4.04 (pseudo-q, 2H, Cp'),  $\delta$  3.66–3.54 (m, 4H,  $\text{CH}_2\text{CH}_2$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR (200 MHz,  $\text{C}_6\text{D}_6$ ),  $\delta$  163.8 (s, phosphonite),  $\delta$  -19.1 (s,  $\text{PPh}_2$ ); MS EI  $m/z$  (%): 460 (100) ( $\text{M}^+$ ), 432 (30) ( $\text{M}-(\text{CH}_2\text{CH}_2)$ ) $^+$ , 400 (7) ( $\text{M}-(\text{OCH}_2\text{CH}_2\text{O})$ ) $^+$ , 369 (20) ( $\text{M}-\text{P}(\text{OCH}_2\text{CH}_2\text{O})$ ) $^+$ . Compound **4c** (orange powder):  $^1\text{H}$  NMR (200 MHz,  $\text{C}_6\text{D}_6$ ),  $\delta$  6.93–7.72 (m, 22H, phenyl),  $\delta$  4.45 (m, 1H, Cp'),  $\delta$  4.38 (m, 1H, Cp'),  $\delta$  4.35 (m, 1H, Cp'),  $\delta$  4.29 (m, 1H, Cp'),  $\delta$  4.10 (m, 1H, Cp'),  $\delta$  3.85 (m, 1H, Cp'),  $\delta$  3.57 (m, 1H, Cp');  $^{31}\text{P}\{^1\text{H}\}$  NMR (200 MHz,  $\text{C}_6\text{D}_6$ ),  $\delta$  189.7 (s, phosphonite),  $\delta$  -19.4 (s,  $\text{PPh}_2$ ); MS EI  $m/z$  (%): 684 (100) ( $\text{M}^+$ ), 607 (10) ( $\text{M}-\text{Ph}$ ) $^+$ . Compound **4d** (orange powder, ( $[\alpha]_{\text{D}}^{25}=-338$ ,  $c$  2, THF)).
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15. Spectral data: (yellow powder):  $^1\text{H}$  NMR (200 MHz,  $\text{C}_6\text{D}_6$ ),  $\delta$  6.59–7.21/8.10 (m, 20H, phenyl),  $\delta$  4.64 (m, 2H, Cp'),  $\delta$  4.09 (m, 2H, Cp'),  $\delta$  3.81 (m, 4H, Cp');  $^{31}\text{P}\{^1\text{H}\}$  NMR (200 MHz,  $\text{C}_6\text{D}_6$ ),  $\delta$  155.0 (dd,  $J_{\text{P-Rh}}=300$  Hz,  $J_{\text{P-P}}=45$  Hz,  $\text{P}(\text{OPh})_2$ ),  $\delta$  25.0 (dd,  $J_{\text{P-Rh}}=150$  Hz,  $J_{\text{P-P}}=45$  Hz,  $\text{PPh}_2$ ); IR ( $\text{CH}_2\text{Cl}_2$ ),  $\nu_{\text{CO}}=2041$   $\text{cm}^{-1}$ ; anal. calcd for  $\text{C}_{35}\text{H}_{28}\text{FeP}_2\text{O}_3\text{RhCl}$ : C, 55.86%; H, 3.72%. Found: C, 55.86%; H, 3.64%; MS FAB  $m/z$  (%): 724 (35) ( $\text{M}-\text{CO}$ ) $^+$ , 689 (100) ( $\text{M}-\text{Cl}$ ,  $\text{CO}$ ) $^+$ .