

CHARLES UNIVERSITY
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Study programme: Inorganic Chemistry



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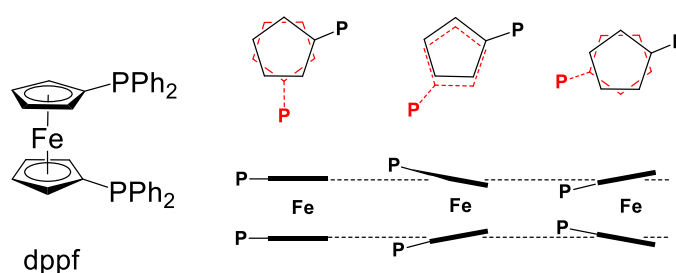
Electronically dissymmetric ferrocene bisphosphines

Expanded abstract of PhD Thesis

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One of the most frequently exploited properties of phosphorus derivatives is their ability to ligate transition metals. Thus, phosphines and related trivalent phosphorus ligands are the most important ancillary ligands in homogenous catalysis and in coordination and organometallic chemistry.¹ Even so, ferrocene-based phosphorus ligands have emerged as one of the most powerful ligand classes for chiral and achiral catalysis. 1,1'-Bis(diphenylphosphino)ferrocene (dppf) is the archetype of these compounds (Scheme 1).² This Thesis describes the synthesis, reactivity, coordination properties, and catalytic activity of novel electronically dissymmetric bisphosphines structurally related to dppf.



Scheme 1. 1,1'-Bis(diphenylphosphino)ferrocene (dppf), a successful donor in homogenous catalysis. Ferrocene provides a robust yet flexible backbone that allows stabilizing a variety of metal centers by various coordination modes of this ligand.

First, a methylene spaced dppf congener containing a primary phosphine group, which is stable in the air, $\text{Ph}_2\text{PfcCH}_2\text{PH}_2$ (fc = ferrocene-1,1'-diyl), was prepared. While studying its reactivity, an unprecedented, stable primary phosphine oxide, $\text{Ph}_2\text{PfcCH}_2\text{P}(\text{O})\text{H}_2$, was isolated. The primary phosphine, the corresponding phosphine oxide, dppf, and the known bis-tertiary phosphine $\text{Ph}_2\text{PfcCH}_2\text{PPh}_2$ were studied as ligands in Ru(II) complexes (Figure 1). The catalytic activity of the defined complexes was compared in two ruthenium-catalyzed reactions: cyclization of (*Z*)-3-methylpent-2-en-4-yn-1-ol into 2,3-dimethylfuran and isomerization of estragole to anethole. Unfortunately, the catalytic activity of the prepared Ru(II) complexes in the selected model reactions was only moderate.³ and the effect of the different ligands on the catalytic behavior was relatively marginal.

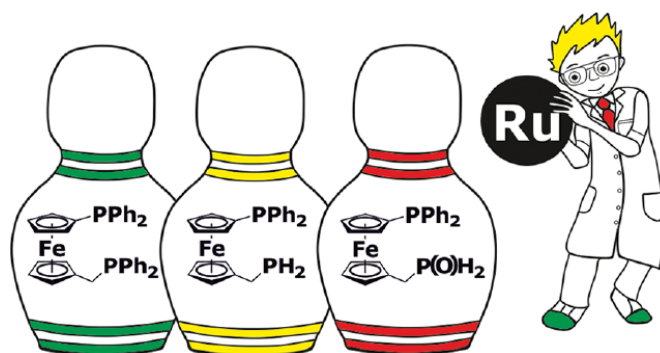
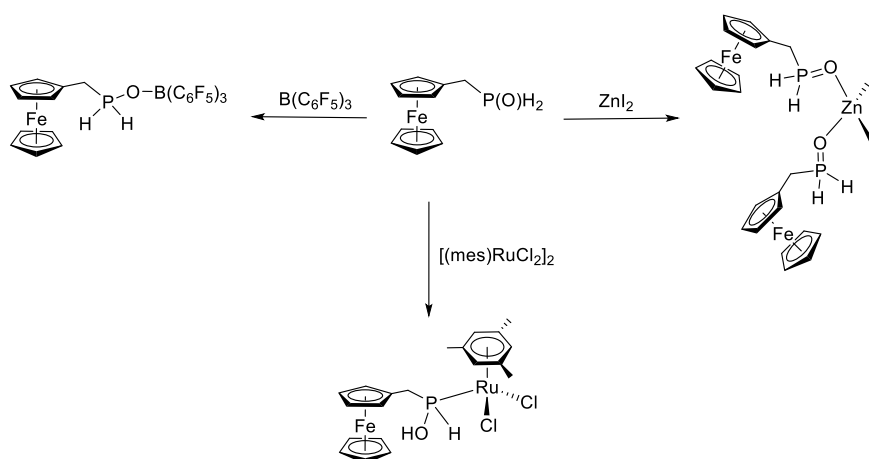
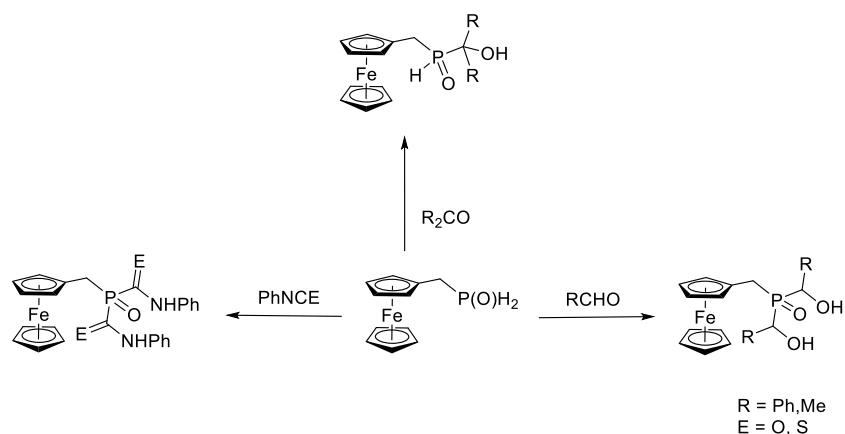


Figure 1. Methylene-spaced ferrocene bisphosphines studied as ligands in Ru(II) complexes.

Second, the remarkable stability of the prepared primary phosphine oxide called for a detailed investigation of this poorly described class of compounds.⁴ As a result, stable primary phosphine chalcogenides lacking steric protection $\text{FcCH}_2\text{P}(\text{Y})\text{H}_2$ (Fc = ferrocenyl; $\text{Y} = \text{O}, \text{S}, \text{Se}$) were isolated for the first time. These compounds were studied through reactions with borane and hard and soft Lewis acids ($\text{Zn}(\text{II})$ and $\text{Ru}(\text{II})$, Scheme 2). The reactivity of the P-H hydrogens was further examined in reactions with various unsaturated substrates (RCHO , R_2CO , PhNCE ; $\text{R} = \text{Me}, \text{Ph}$; $\text{E} = \text{O}, \text{S}$; Scheme 3). The reactivity in addition reactions was found to depend only on steric factors.



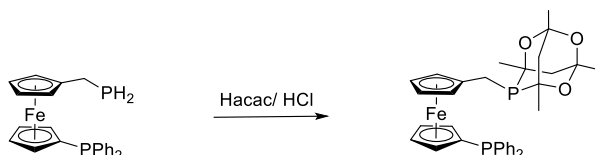
Scheme 2. Reactivity of the stable primary phosphine oxide $\text{FcCH}_2\text{P}(\text{O})\text{H}_2$.



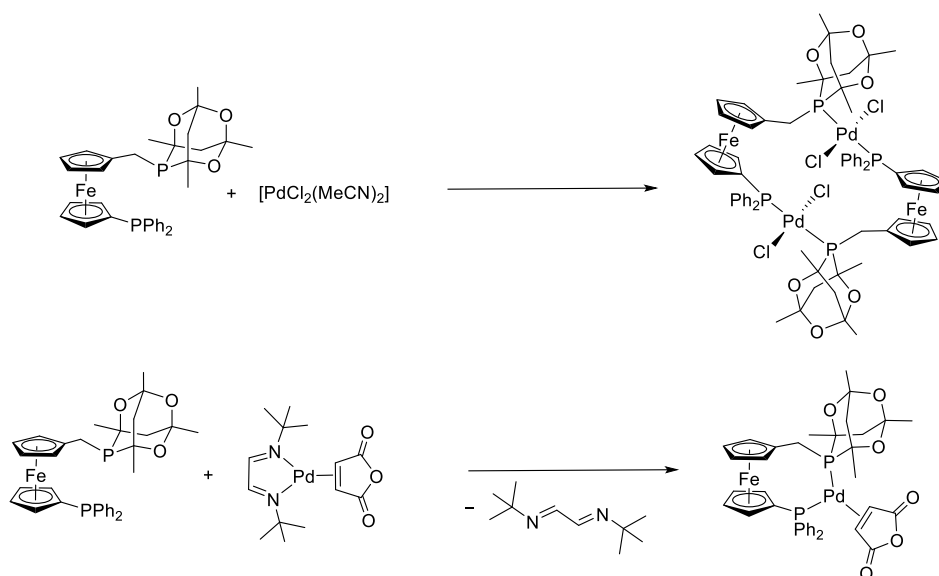
Scheme 3. Reactivity of primary phosphine oxide $\text{FcCH}_2\text{P}(\text{O})\text{H}_2$ in addition reactions.

Subsequently, bisphosphine $\text{Ph}_2\text{PfcCH}_2\text{PH}_2$ was employed in an acid-catalysed condensation reaction with acetylacetone to produce the bulky bis-phosphine $\text{Ph}_2\text{PfcCH}_2\text{PCg}$ ($\text{PCg} = 1,3,5,7$ -tetramethyl-2,4,6-trioxa-8-phosphaadamantyl, often denoted as “cage phosphine”, Scheme 4). Together with Ph_2PfcPCg as the direct dppf analogue, these bisphosphine ligands were used to prepare defined $\text{Pd}(0)$ and $\text{Pd}(\text{II})$ complexes (Scheme 5), and tested in selected catalytic reactions in comparison with their analogs derived from dppf . Specifically, the $\text{Pd}(0)$ complexes were applied to C-H arylation of benzoxazoles with aryl chlorides, in which they showed excellent catalytic activity and selectivity. Benzoxazole reacted satisfactorily with electron-poor and electron-rich aryl chlorides except when sterically hindered. Unfortunately, the efforts to expand the substrate scope (oxazole, oxazoline, benzothiazole, 1-methylbenzimidazole) were unsuccessful.

Conversely, the $\text{Pd}(\text{II})$ complexes were employed in cyanation of aryl bromides using $\text{K}_4[\text{Fe}(\text{CN})_6]$ as a non-toxic cyanide source and in the Suzuki-Miyaura reaction of benzoyl chlorides with arylboronic acids to give benzophenones. The catalytic activity of the new palladium(II) complexes with ferrocene cage ligands was comparable with the reactivity of dppf and already published catalysts.⁵

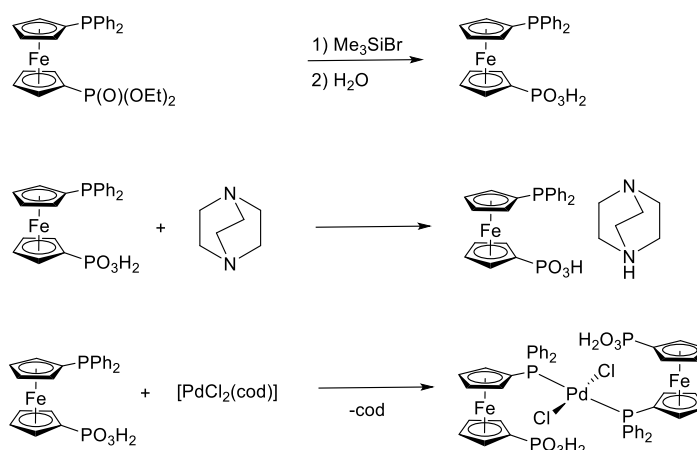


Scheme 4. Buckler-Epstein reaction of ferrocene bisphosphine $\text{PPh}_2\text{fcCH}_2\text{PH}_2$.



Scheme 5. Synthesis of Pd(0) and Pd(II) complex with bulky bis-phosphine $\text{Ph}_2\text{PfcCH}_2\text{PCg}$.

Last but not least, a new polar bidentate ligand $\text{Ph}_2\text{PfcPO}_3\text{H}_2$ was prepared by hydrolysis of the corresponding ethyl ester.⁶ However, although the ligand, its ammonium salts, and even Pd(II) complexes were prepared and fully characterized, they gradually decomposed upon storage, which prevented further studies into the catalytic properties of these compounds (Scheme 6).



Scheme 6. Synthesis of hybrid ligand $\text{PPh}_2\text{fcPO}_3\text{H}_2$, its salt, and palladium(II) complex.

References

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