

Reactions of ferrocenium with P-nucleophiles

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The formation of the quite stable ferrocenium cation $[\text{Fe}(\text{C}_5\text{H}_5)_2]^+$ by oxidation of ferrocene has been known for almost 70 years. However, its reactivity has been studied incomparably worse than the chemistry of the ferrocene itself. It is known that ferrocenium reacts with nucleophiles but those reactions almost always lead to products that are not interesting to the ordinary organometallic chemist. These include $[\text{FeX}_4]^-$ or $[\text{FeL}_6]^{n+}$, i.e. complete decomposition of the sandwich structure occurs.^[1]

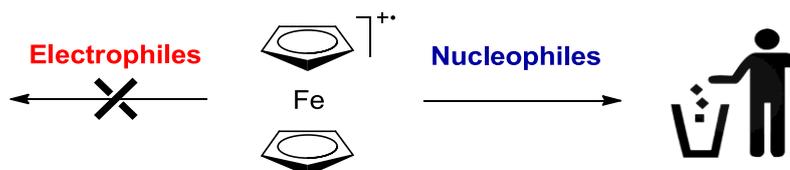
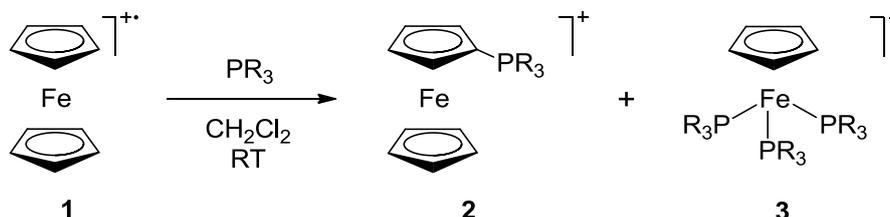


Figure 1. The reactions of ferrocenium with nucleophiles often lead to useless products.

Among all the nucleophiles, phosphorus compounds were greatly overlooked. We found that ferrocenium salts **1** react with diverse phosphorus reagents to form either ferrocenylphosphonium salts **2** or half sandwich complexes **3** (Scheme 1). The phenomenology of these reactions is totally new, and the investigation of the scope seems worthy task.



Scheme 1. Reaction of ferrocenium with P-nucleophiles. Counterions $\text{PF}_6^- / \text{BF}_4^-$ are omitted.

We showed that the reaction with PR_3 bearing electron donating groups (mainly tertiary phosphines and aminophosphines) leads only to the ferrocene derivatives **2**. In contrary, good π -acceptors (phosphites, phosphonites, secondary phosphines) favors the formation of complexes **3**. There are also a number of intermediate reactants that afford mixtures of both **2** and **3**.

In all cases, the formation of the product is accompanied by the equimolar formation of ferrocene. Only half of the original ferrocenium can be converted into **2** or **3**. That fact may be rationalized by the mechanism involving one-electron oxidation step so the initial ferrocenium salt acts, on the one hand, as a substrate for nucleophilic addition of the PR_3 and, on the other hand, as an oxidizing agent for one of the intermediate compounds.

The resulting individual compounds **2** and **3** were isolated and characterized (NMR, elemental analysis, XRD). We also successfully performed the synthesis of **2** in an electrochemical cell as the electrolysis of ferrocene in the presence of tertiary phosphine. Finally, on the basis of experimental data and DFT computations (M06L/6-311++G(d,p)) we proposed reaction pathways leading to **2** and **3** and discussed how do the properties of PR_3 affect them.

1. R. Prins, A. R. Korswagen, A. G. T. G. Kortbeek, *J. Organomet. Chem.* **1972**, 39, 335-344. DOI: 10.1016/S0022-328X(00)80459-3