

Direct Amination of Cobaltocenium Hexafluoridophosphate via Vicarious Nucleophilic Substitution

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Supporting Information

ABSTRACT: In this communication we report a convenient, as short as possible synthesis of aminocobaltocenium hexafluoridophosphate, a very useful compound for further functionalization in cobaltocenium chemistry. Via vicarious nucleophilic substitution of hydrogen of cobaltocenium hexafluoridophosphate with 1,1,1-trimethylhydrazinium iodide as nucleophile bearing its own leaving group, a one-step amination of cobaltocenium in 50% isolated yield is possible, a major improvement over the standard multistep procedure involving common Curtius rearrangement chemistry.



For about five years we have explored the chemistry of functionalized cobaltocenium salts,^{1–8} which have been rather neglected in comparison to their ubiquitous ferrocene relatives. Our motivation for this work stems from the belief that cobaltocenium salts might in principle be as useful as ferrocene derivatives, due to their isoelectronic 18-valence-electron structure, high stability, and reversible redox chemistry. However, in contrast to ferrocene compounds, cobaltocenium salts are per se highly polar, cationic species, which prevents their chemical functionalization by common organic reactions abundant in ferrocene chemistry.

In the course of these investigations, aminocobaltocenium hexafluoridophosphate³ turned out to be a very valuable starting material for highly reactive cobaltoceniumdiazonium bis(hexafluoridophosphate)³ that allowed access to mesoionic cobaltocenylidene gold(III) complexes by oxidative addition reactions⁵ as well as to iodo- and azidocobaltocenium hexafluoridophosphate by Sandmeyer-type reactions.³ These last two compounds are highly useful new organometallic precursors for further functionalization, including nucleophilic aromatic substitution,⁵ copper(I)-catalyzed azide–alkyne [3 + 2] cycloaddition (CuAAC-click chemistry),⁶ transition-metal-centered cycloaddition to afford cobaltoceniumyl-substituted tetraaza-1,3-butadiene (tetrazene) complexes,⁸ and palladium-catalyzed carbon–carbon cross-coupling (Suzuki reaction).⁹ Furthermore, the Heinze group has recently used deprotonated aminocobaltocenium hexafluoridophosphate in amide-coupling reactions to generate bioorganometallic, redox-responsive, short peptides.¹⁰ In related work, Heck and co-workers have prepared the corresponding 1-amino-1',2',3',4',5'-pentamethylcobaltocenium hexafluoridophosphate¹¹ and nitropentamethylcobaltocenium hexafluoridophosphate¹¹ that served as a valuable synthon for nucleophilic substitution reactions with water, alcohols or primary amines.¹²

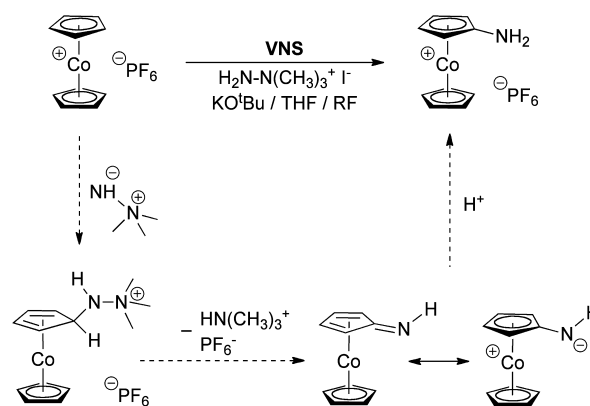
From a synthetic chemist's viewpoint, our best preparation of aminocobaltocenium hexafluoridophosphate,³ based in part on early work of Sheats and Rausch,¹³ involves a rather laborious multistep protocol via cobaltocenium/carboxylic

acid/acid chloride/acyl azide/Curtius rearrangement. Overall, this procedure makes aminocobaltocenium hexafluoridophosphate accessible in 32% yield.³ Clearly a less elaborate method would be highly desirable to foster further developments in cobaltocenium chemistry.

To this end, we reasoned that a direct nucleophilic amination of electrophilic cobaltocenium hexafluoridophosphate by a “vicarious nucleophilic substitution” (VNS) might be possible, similarly to what has been pioneered by Makosza^{14,15} and utilized by others^{16,17} for electron-deficient aromatic systems: e.g., (halo)nitroarenes.

To our delight, this approach proved successful (Scheme 1). Reaction of cobaltocenium hexafluoridophosphate with 1,1,1-trimethylhydrazinium iodide¹⁶ and 2 equiv of potassium *tert*-butoxide in dry tetrahydrofuran under reflux afforded the desired crude product in >80% yield according to ¹H NMR analysis, and after chromatographic purification over a short

Scheme 1. VNS of Cobaltocenium Hexafluoridophosphate with 1,1,1-Trimethylhydrazinium Iodide



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column of aluminum oxide, very pure aminocobaltocenium hexafluoridophosphate could be isolated in an average yield of 50% for approximately 50 reactions. We carefully optimized this reaction (for details see the [Supporting Information](#)), finding that inert conditions are highly important as well as reaction time, temperature, and type of solvent. For example, no reaction at all was observed in the VNS standard solvent dimethyl sulfoxide,¹⁶ and variations in stoichiometry or temperature proved less productive.

Mechanistically ([Scheme 1](#)), this amination consists most likely of a nucleophilic addition of a zwitterionic trimethylhydraziniumide at cobaltocenium, giving first a cyclopentadienyl substituted cyclopentadiene *endo*-hydride cobalt(I) complex, followed by base-promoted hydride removal by the internal trimethylamine moiety, thereby generating an η^4 -cyclopentadienimine cobalt(I) complex¹⁰ that is finally protonated under hapticity change from η^4 to η^5 to afford the desired aminocobaltocenium salt.

If aminocobaltocenium hexafluoridophosphate is only needed as the precursor for cobaltoceniumdiazonium bis(hexafluoridophosphate),³ then it is best to diazotize the crude amination product directly, thereby giving cobaltoceniumdiazonium bis(hexafluoridophosphate) in 66% isolated yield (see experimental details in the [Supporting Information](#)).

In conclusion, this direct amination of cobaltocenium is the first example of a vicarious nucleophilic substitution in organometallic chemistry. Conceptionally, it can be considered as a useful C–H activation process on an electron-poor cationic metallocene, potentially also applicable to other cationic sandwich or half-sandwich complexes. Synthetically, this VNS approach is a short and elegant access to aminocobaltocenium hexafluoridophosphate, thus greatly facilitating further progress in cobaltocenium chemistry.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.organomet.9b00205](https://doi.org/10.1021/acs.organomet.9b00205).

Experimental procedures and ¹H/¹³C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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