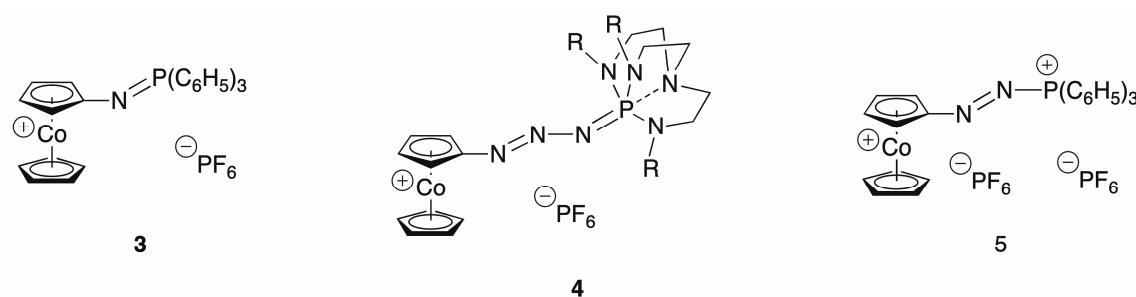


Organometallic aza-phospha compounds containing cobaltoceniumyl substituents

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In continuation of our exploration of functionalized cobaltocenium compounds [1] we report here on three new phosphine derivatives of azidocobaltocenium hexafluoridophosphate **1** and cobaltoceniumdiazonium bis(hexafluoridophosphate) **2** (Scheme 1). Staudinger reaction of **1** with triphenylphosphine afforded the expected phosphazene **3** under evolution of N₂. Interestingly, no further aza-Wittig reaction of **3** with aldehydes or ketones proved possible, due to the strongly electron-withdrawing, cationic cobaltoceniumyl substituent. However, Staudinger reaction of **1** with Verkade's superbases [2] allowed access to phosphazide **4**, a new organometallic member in the limited number of isolable phosphazides [3]. Reaction of **2** with triphenylphosphine gave dicationic azophosphonium salt **5**, an unusual redox-active azo dye. Spectroscopic and structural properties of these novel aza-phospha organometallic compounds will be presented.



Scheme 1. Aza-phospha cobaltocenium salts

[1] Vanicek, S.; Kopacka, H.; Wurst, K.; Müller, T.; Hassenrück, C.; Winter, R. F.; Bildstein, B.; *Organometallics* **2016**, *35*, 2101–2109.

[2] Tang, J.; Dopke, J.; Verkade, J. G.; *J. Am. Chem. Soc.* **1993**, *115*, 5015–5020.

[3] Bebbington, M. W. P.; Bourissou, D.; *Coord. Chem. Rev.* **2009**, *253*, 1248–1261.