Redox Interconversion and Reactivities of Isoindoline-Based Polyprotic Cobalt(II)/(III) Pincer Complexes

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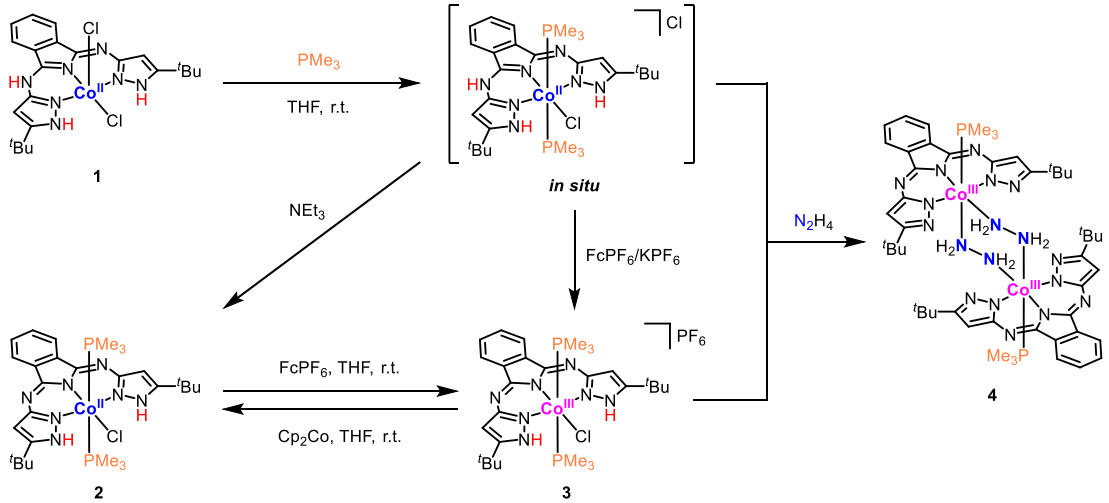
Protic pyrazole has been attractive ligands in coordination chemistry owing to their proton-responsive nature.[1] Recently, our group has introduced two protic pyrazoles into diiminoisoindoline framework to synthesize a new type of pincer ligand, $^{t\mathrm{Bu}}\mathrm{LH_3}$ (1,3-bis(5-*tert*-butylpyrazol-3-ylimino)isoindoline), which has a total of three ionizable NH groups. We have also isolated a series of its iron and cobalt complexes and explored their reactivity.[2,3] In this work, we investigated the redox interconversion between cobalt(II)/(III) complexes as well as their reactivity.

The reaction of $[\mathrm{CoCl_2}(^{t\mathrm{Bu}}\mathrm{LH_3})]$ (**1**) with $\mathrm{PMe_3}$ in a 1:2 ratio resulted in the formation of a cobalt(II) transient species, which was observed by ^{1}H NMR spectrum. Subsequent addition of an equimolar amount of $\mathrm{NEt_3}$ and $\mathrm{FcPF_6}$/$\mathrm{KPF_6}$ (Fc = $\mathrm{Cp_2Fe}$) afforded cobalt(II) and cobalt(III) bis(phosphine) complexes $[\mathrm{CoCl(PMe_3)_2}(^{t\mathrm{Bu}}\mathrm{LH_2})]^{n+}$ (n = 0 (**2**), 1 (**3**)) with a mono-deprotonated, $\mathrm{L_2X}$-type ligand, respectively. The interconversion of **2** and **3** could be achieved with $\mathrm{FcPF_6}$ and $\mathrm{Cp_2Co}$, which highlights the one-electron redox ability of the cobalt complexes. On the other hand, addition of hydrazine to the transient species or **3** afforded the hydrazine-bridged cobalt(III) complex $[\mathrm{Co(PMe_3)}(^{t\mathrm{Bu}}\mathrm{L})]_2(\mu_2\text{-}\mathrm{N_2H_4})_2$ (**4**) with dissociation of a phosphine ligand. The products **1**–**4** were fully characterized by X-ray diffraction analysis along with ESI-MS and ^{1}H, ^{31}P NMR spectroscopy.



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