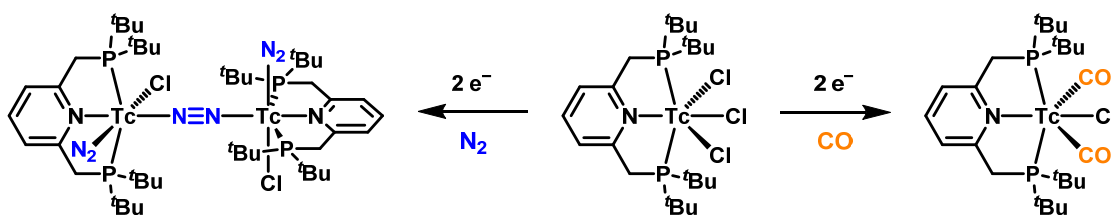


⁹⁹Tc-PNP Pincer Complexes Interacting with Small Molecules

Manuel Luca Besmer, Henrik Braband, Roger Alberto

University of Zurich, Department of Chemistry, Switzerland

Industrial scale reactions often rely on the use of fossil fuel based feedstocks, which led to the search for the implementation of alternatives such as N₂, O₂, H₂ or CO₂ gas. The activation of these small molecules (SMA) with transition metal catalysts has gathered increased attention over the past years. Catalysts with pincer-type ligands are among the most prominent examples due to their high-level tunability. Exciting results have been published on a multitude of chemical transformations, for example a Mo-pincer complex that is active in the fixation of N₂ to NH₃.^[1] Pyridine based PNP ligands (e.g., ^{Pyr}PNP^{tBu}) found applications in diverse bond activation processes in combination with different metal centers via metal-ligand cooperativity (MLC). Literature on SMA chemistry with Tc is sparse, leaving a knowledge gap between Mn and Re. We reported the synthesis of the first *mer*-Tc^{III}-PNP pincer complex [Tc(^{Pyr}PNP^{tBu})Cl₃] and its interaction with N₂ upon reduction.^[2]



The two electron reduction of [Tc(^{Pyr}PNP^{tBu})Cl₃] leads to the formation of the electron-deficient, reactive [Tc(^{Pyr}PNP^{tBu})Cl]²⁻ intermediate followed by the coordination of N₂ or CO, depending on the reaction conditions. In the case of N₂, the dinuclear complex [(Tc(^{Pyr}PNP^{tBu})Cl(N₂))₂(μ-N₂)] is obtained. The *trans*-[Tc(^{Pyr}PNP^{tBu})(CO)₂Cl] complex is obtained if the reduction is performed under CO, allowing for experiments on metal-ligand cooperativity (MLC) as it has been reported with the *cis*-[Re(^{Pyr}PNP^{tBu})(CO)₂Cl].^[3] There, deprotonation of the pincer backbone with a strong base yields the dearomatized *cis*-[Re(^{Pyr}PNP^{tBu*})(CO)₂] (asterisk indicates dearomatization), capable of reacting with H₂, CO₂ and nitriles. In analogous fashion, deprotonation of *trans*-[Tc(^{Pyr}PNP^{tBu})(CO)₂Cl] with KO^tBu yielded the dearomatized *cis*-[Tc(^{Pyr}PNP^{tBu*})(CO)₂], which reacts with H₂ and CO₂ gas correspondingly. The reactivity and high *Lewis* and *Brønsted* basicity of the pincer backbone sparked the idea to investigate reactions with substrates that contain weakly acidic protons. Substrate classes, such as alkynes, imidazolium ions and heterocyclic molecules have so far not been reacted with dearomatized PNP complexes. Indeed, the *cis*-[Tc(^{Pyr}PNP^{tBu*})(CO)₂] complex reacts with these *via* initial deprotonation by the PNP backbone and subsequent coordination of the “remaining” anion. Our work contributes to the mitigation of the fundamental knowledge gap for Tc and to the field of MLC.

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[2] M. L. Besmer, *et al.*, *Inorg. Chem.* **2021**, *60*, 6696–6701.

[3] M. Vogt, *et al.*, *J. Am. Chem. Soc.* **2013**, *135*, 17004–17018.