

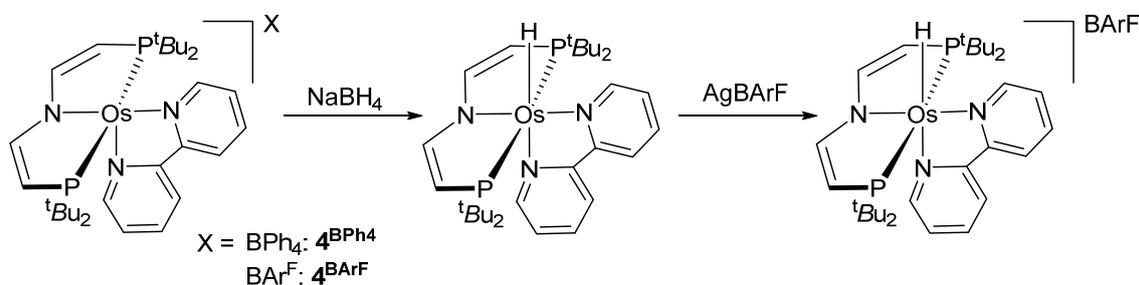
SYNTHESIS AND CHARACTERIZATION OF STABLE OSMIUM (III) HYDRIDE COMPLEXES

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Numerous examples of osmium hydride complexes are described in the literature [1]. These complexes have been reported in various oxidation state; however, the number of octahedral metal hydride complexes with the osmium metal center in the oxidation state of (III) is scarce. Taube et al reported a stable osmium (III) monohydride complex in solid state, which goes under disproportionation to the oxidation state of II and IV in solution [2]. To the best of our knowledge, this is the only example of a stable octahedral osmium (III) hydride complex reported so far.

In this contribution, we present the design of a framework to achieve a series of osmium complexes in various oxidation state. The combination of a tridentate pincer and an auxiliary bidentate ligand was chosen. Pincer ligands provide a robust environment and the available space in the coordination sphere of the metal is mostly determined by the steric demand of the pincer side arms, such as PR₂ groups. The PNP ligand (PNP = N(CHCHP^tBu₂)₂, Scheme 1) is a well-known ligand to stabilize late transition metal complexes in a broad range of oxidation states[3]. The electronic properties of the complexes are further tuned by choice of the additional auxiliary ligand; here 2,2'-bipyridine; that is located trans to the hydride. By this design we have accomplished to synthesize and fully characterize an osmium (III) hydride complex which not only stable in the solid state but also in the solution.



Scheme 1. Synthesis of osmium (II) and (III) hydride complexes

- [1] Hu, Y., Shaw, A. P., Estes, D. P., & Norton, J. R. (2016). Transition-metal hydride radical cations. *Chemical Reviews*, **116**(15), 8427-8462.
- [2] McQueen, J. S., Nagao, N., Eberspacher, T., Li, Z. W., & Taube, H. (2003). Synthesis and Characterization of trans-[Os(en)2py(H)]²⁺ and Related Studies. *Inorganic chemistry*, **42**(12), 3815-3821.
- [3] Alig, L., Fritz, M., & Schneider, S. (2018). First-row transition metal (de) hydrogenation catalysis based on functional pincer ligands. *Chemical reviews*, **119**(4), 2681-2751.