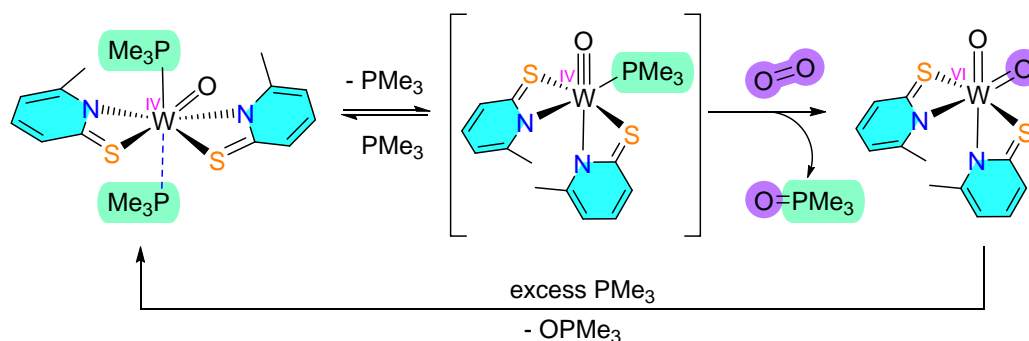


THE REDUCTION OF TUNGSTEN(VI) DIOXIDO COMPLEXES OPENS THE DOOR FOR NEW REACTIVITIES

Miljan Ćorović and Nadia C. Mösch-Zanetti

Institute of Chemistry, University of Graz, Graz, Austria

Studying tungsten(IV) oxo complexes' reactivity is crucial for understanding tungstoenzymes. However, only a few tungsten(VI) $[\text{WO}_2\text{L}_n]$ compounds are reported to undergo reduction rendering the reactivity studies of reduced species scarce.[1] For this reason, we investigated the reduction of high-valent tungsten compounds with PMe_3 as a reductant and reached tungsten(IV) oxo species. The reaction of $[\text{WO}_2(\text{SN})_2]$ (SN = bidentate ligand with S and N donors) with three equiv of PMe_3 required a conformational twist of two bidentate ligands to form $[\text{WO}(\text{SN})_2(\text{PMe}_3)_2]$. Due to their coordinative flexibility, this reactivity was possible only when using different pyridine-2-thiolate ligands. Tungsten(IV) oxo complex with simple pyridine-2-thiolate ligands showed reactivity toward dimethyl sulfoxide, mimicking the behavior observed for the DMSO reductase enzyme.[2] On the other hand, increasing the steric bulk around the W center by adding a methyl group into the same ligand system led to the isolation of the W(IV) compound $[\text{WO}(\text{6-MePyS})_2(\text{PMe}_3)_2]$ (6-MePyS = 6-methylpyridine-2-thiolate) with a complex solution behavior. This reduced species partially decoordinates one PMe_3 ligand in solution, creating a vacancy capable of splitting dioxygen (Scheme 1) or binding acetylene. The complex represents a rare example of a tungsten complex capable of performing oxygen atom transfer catalysis under aerobic conditions.[3]



Scheme 1. The behavior of $[\text{WO}(\text{6-MePyS})_2(\text{PMe}_3)_2]$ in solution and subsequent dioxygen activation

[1] Pättsch, S.; Correia, J. V.; Elvers, B. J.; Steuer, M.; Schulzke, C. *Molecules* **2022**, *27*, 3695.

[2] Ćorović M. Z.; Wiedemaier, F.; Belaj, F.; Mösch-Zanetti, N. C. *Inorg. Chem.* **2022**, *61*, 12415–12424.

[3] Ćorović M. Z.; Belaj, F.; Mösch-Zanetti, N. C. *Inorg. Chem.* **2023**, *62*, 5669–5676.