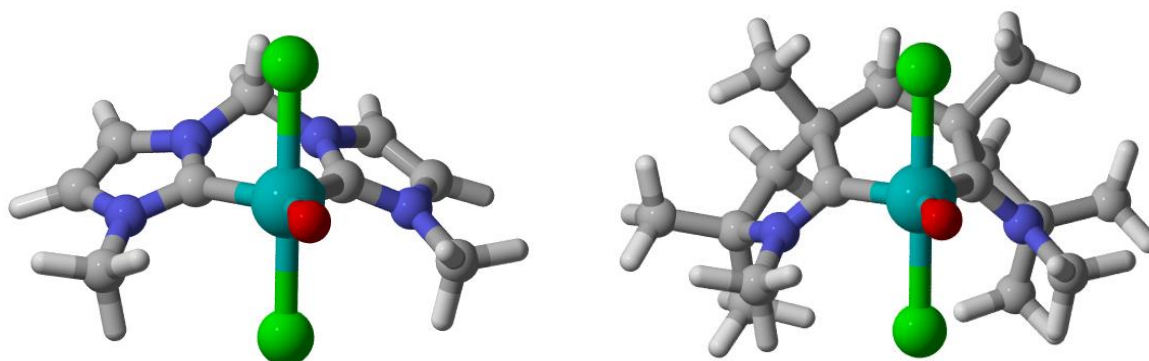# What Makes a Palladium Terminal Oxo Stable?

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For decades, the isolation of late transition metal complexes featuring multiple bonds to pnictogen or chalcogen atoms like imido- or oxo-substituents has been a huge challenge. [1] Even more so, well characterized examples for the group 10 metals remain elusive. [2] Excitingly, such species have been proposed as intermediates for the catalytic activation of CH bonds or redox processes related to the conversion of small molecules as found for example in catalytic converters of cars.[3] Redox active cyclic (alkyl)(amino)carbene ligands (CAACs) have received considerable attention for the stabilization of reactive intermediates, radicals and low valent transition metals due to their strong π-acceptor properties, which exceed those of conventional NHC ligands considerably. [4] However, the stabilization of transition metal terminal oxo and imido compounds with such ligands has not yet been explored. Herein, I would like to report DFT (B2PLYP-D3(COSMO)/def2-TZVPP//B3LYP-D3/def2-TZVP) and CASSCF calculations, which predict that CAAC ligands will be very efficient for the thermodynamic stabilization of oxo and imido intermediates for palladium(II). [5] Importantly, the calculations rationalize in which way σ-donor and π-acceptor properties of a range of different carbene and related P or N donor ligands contribute to the electronic structure and spin state of Pd(II) or respectively Pd(IV) oxo complexes. Accordingly, the electronic properties of a huge variety of different ligands could be correlated to the expected thermodynamic stability of palladium oxo complexes.

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[3] P. R. Sharp *J. Chem. Soc. Dalton Trans.* **2000**, *16*, 2647-2657.
[4] M. Soleilhavoup, G. Bertrand *Acc. Chem. Res.* **2015**, *48*, 256-276.
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