How to Tame Palladium Terminal Oxos and Imidos

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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] Herein, I would like to report DFT (B2PLYP-D3(COSMO)/def2-TZVPP//B3LYP-D3/def2-TZVP) and CASSCF calculations, which predict which ligands are suitable for the thermodynamic stabilization of oxo and imido intermediates of palladium. [5,6] 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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