# Controlling the bonding situation of tetryliumylidenes with Ni(0) centers by denticity of the ligand scaffold

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Single center ambiphile ligands have been of growing interest, possessing an ion pair for coordination to a transition metal (TM) center and a vacant p-orbital enabling Lewis acidic reactivity at the ligand.[1] This allows for Metal ligand coordination (MLC) where both the ligand and the TM center participate in challenging bond-activation or catalytic processes.[2] Tetryliumylidenes are cationic group 14 element(II) centers, which posses an ion pair and two vacant p-orbtials, making them even more highly lewis acidic compared to their neutral counterparts. We have developed a series of cationic $E^{II}$ $Ni^0$ complexes **1** and **2** (E = Ge, Sn) and studied their bonding situation.[3][4]. The monodentate ligand leads to $Ni^0$ complexes **1** with a close to linear L-E-Ni angle (N-Ge-Ni 175.90(9) °, N-Sn-Ni 173.65(2) °). This results in a high degree of back bonding from $Ni^0$ to $E^{II}$, which in turn decreases its Lewis acidity. **1** has the shortest known E-Ni bonds (Ge-Ni 2.1596(7) Å, Sn- Ni 2.355(1) Å), the first known triple bonds between $E^{II}$ and $Ni^0$.[4] The denticity of these ligands can easily be increased by introduction of a chelating phosphine arm The bidentate ligand avoids back bonding due to its constrained binding leading to the $Ni^0$ complexes **2** with E-Ni bonds (Ge-Ni 2.1908(9) Å, Sn-Ni 2.4024(9) Å), which can best be described as single bonds. This results in a much higher Lewis acidity pertaining towards super lewis acidity, abstracting $F^-$ from $[SbF_6]^-$ and enabling catalytic hydrosilylation of alkenes and alkynes.[3]

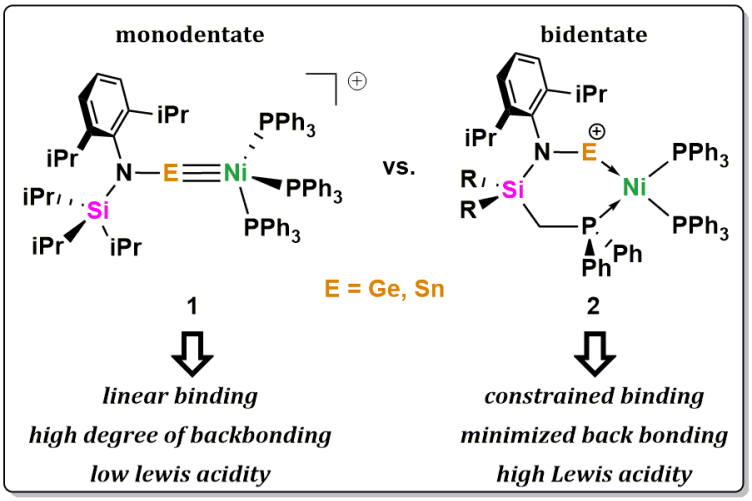


Fig 1 Comparison of the monodentate and bidentate cationic $E^{II}$ $Ni^0$ complexes **1** and **2**.

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[2] Khusnutdinova J. R., Millstein D. Metal-Ligand Cooperation. Angew. Chem. Int. Ed., 54, 12236–12273 (2015).

[3] Keil P. M., Hadlington T. J. Geometrically Constrained Cationic Low-Coordinate Terylenes; Highly Lewis Acidic σ -Donor Ligands in Catalytic Systems. Angew. Chem. Int. Ed., Accepted Author Manuscript (2021).

[4] Keil P. M., Hadlington T. J. Unpublished Results.

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