Metal-containing molecules are usually comprised of a metal ion that is bound to organic ligands. Ligands that can easily tune the numbers of electrons stored in their chemical bonds are known as redox-active. Some redox-active ligands have been shown to induce a dramatic enhancement in the chemical reactivity of the bound metal ion. As a result, redox-active ligands have the potential to create molecules that function as new catalysts capable of enabling exquisite control of challenging chemical reactions of tremendous technological importance.

Recently, a team of researchers have shed light on a surprising electronic structure change due to a minor variation of a redox-active ligand: nickel complexes supported by bis(imino)pyridine ligands revealed that replacement of CH$_3$ side-groups with H atoms induces a dramatic transformation of a typical Ni(II)-ion with a square planar geometry to an unusual non-planar Ni(I) site. In other words, a minor change in the periphery of the ligand led to the intramolecular transfer of one unpaired electron from the ligand to the metal, concomitant with the conversion of a diamagnetic Ni(II) to a paramagnetic Ni(I) site with a $S = 1/2$ spin state. In effect, the H atom “reels in” an electron from the ligand to the nickel ion. (Figure 1), resulting in a dramatic change in the reactivity of this compound.

These conclusions result from high-magnetic-field electron paramagnetic resonance (EPR) experiments at the ultra-high microwave frequency of 406.4 GHz. (Figure 2)