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Project Title | Harnessing Spin-Orbit Coupling to Tune Chemical Reactivity

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Spin-orbit coupling arises from the coupling between unpaired electronic spins and their orbital angular momentum. In paramagnetic metal compounds, increasing spin-orbit coupling impacts a variety of phenomena, such as by increasing magnetic anisotropy in magnetic materials and molecules, lengthening the duration of excited electronic states, providing unique selectivity to certain catalytic reactions, increasing the sensitivity of paramagnetic quantum sensors, and bringing about topological behavior in certain materials (Figure 1). To leverage spin-orbit coupling in the design of transition metal complexes with tailored properties, we require two key ingredients: synthetic access to molecular series within which we can systematically tune

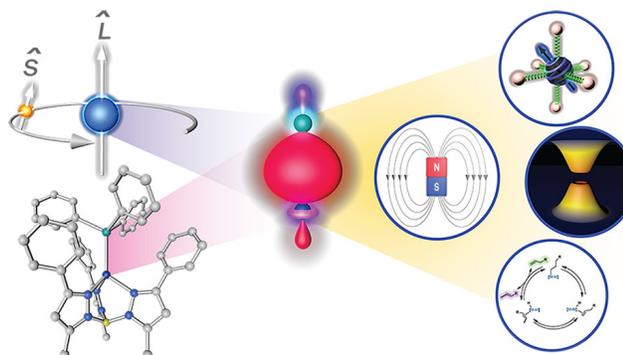


Figure 1: Spin-orbit coupling contributes to many fascinating properties including quantum coherence, permanent magnetism, topological non-triviality and reaction selectivity. We are leveraging spin-orbit coupling in bimetallic transition metal complexes through separation of the spin and orbital contributions.

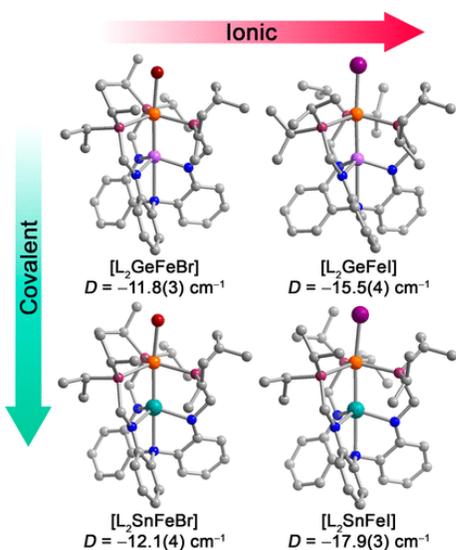


Figure 2: A series of Fe-main group metal molecules wherein the ionic and covalent contributions to magnetic anisotropy can be tuned through changing the halide (ionic) constituent and the main group (covalent) constituent.

spin-orbit coupling and, relatedly, a thorough understanding of how changing spin-orbit coupling changes the properties of transition metal complexes.

Towards these ends, we have developed a new research thrust within our lab wherein we design, synthesize, and measure the properties of heterobimetallic transition metal complexes with heavy elements either near the transition metal center or directly covalently bonded for catalysis. We then compare the properties of those compounds and determine the influence of changing spin-orbit coupling on their properties. To elucidate to what extent ligand-derived spin-orbit coupling can influence molecular properties, we prepared a separate series of molecules featuring direct bonds between iron and the heavy main-group elements tin and germanium, in addition to terminal bonds to either bromide or iodide ions. The aggregate of these results demonstrated that magnetic anisotropy crucially depends on the nature of the spin-bearing orbitals. In other words, the degree to which the spin-bearing orbitals interact with the heavy element seemed to strongly determine the magnetic anisotropy of the resulting complex. As a result, and counter to our initial hypothesis, the complexes exhibited greater magnetic anisotropy upon moving from bromide to iodide than from germanium to tin, simply as a result of greater relative π donation from the halides than

from the group XIV elements.

To allow the spin-bearing orbitals to interact with the heavy main-group metal, we explored weaker ligand fields

in slightly modified symmetries. The specific system we examined featured cobalt bound by three weak pyrazole donors (in the canonical Tp^- ligand scaffold) in approximate C_{3v} symmetry. We were then able to perform a simple metathesis reaction to replace the apical halide ligand on the cobalt complex with either a triphenyl tin or germanium substituent. Through examination of the complexes' electronic absorption spectra, we found that, even while correcting for differences in the ligand field strength of germanium and tin, the heavier tin atom contributed more to the spin-orbit interaction of the complex than did germanium. Further studies will focus on probing the degree of covalency in these metal-metal bonds. We will also focus on creating bonds between paramagnetic transition metals and even heavier main-group elements such as bismuth to maximize spin-orbit coupling.

Impact: This grant has allowed our group to explore a new area of research, and led to a publication. The results obtained from the research funded by this grant have revolutionized our understanding of how covalency vs. ionicity influence the magnetic and spectroscopic properties of transition metal complexes.

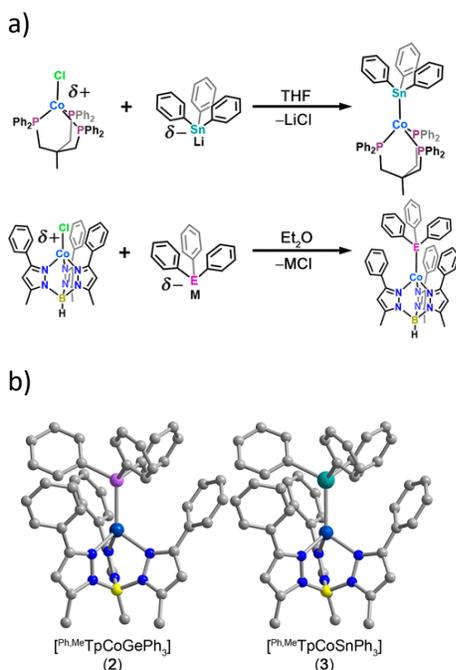


Figure 3: a) a scheme showing a typical synthetic pathway to reach the heterobimetallic $TpCo-Sn$ or $TpCo-Ge$ complexes b) the crystal structures of the $TpCo-Sn$ and $TpCo-Ge$ complexes.