Small molecules containing refractory elements are important keys to understanding the connection between the gas-phase and solid-state constituents of the interstellar medium. They also have relevance for the origin of life and the delivery of the biogenic elements to planet surfaces. Studies of these types of molecules in interstellar space have clearly been driven by laboratory spectroscopy. For almost three decades, the Ziurys lab has been conducting measurements of rotational spectra of highly reactive metal and phosphorus-bearing species, and subsequently searching for these molecules in interstellar space with radio telescopes. Critical to this endeavor has been the development of unusual synthetic methods to create these unstable molecules, and the challenge of unraveling spectra of states with high spin and orbital angular momenta. Molecules of particular interest include metal dicarbides and metal-phosphorus species. An overview of this spectroscopy will be presented, as well as new results for SiP and VO, and the current astrophysical implications.