Ruthenium-based precatalysts for olefin metathesis are amongst the most studied complexes in the field of organometallic catalysis. All the ligands around the metal center have been modified imposing a significant impact on the catalyst’s stability, activity and selectivity. One of the most important modifications was the introduction of strong sigma-donating carbene ligands, like NHCs and more recently CAACs. These ligands improved the stability of the catalytic species and allowed control over selectivity in olefin metathesis reactions. Another impactful modification to the ruthenium complexes was the use of S-chelating benzylidenes to afford latent precatalysts, useful for polymerizations and orthogonal chemistry. In my talk I introduce the first S-chelated Ru-CAAC complexes, present their synthesis and characterization, show how the differences in substituents on both CAAC and S-chelating benzylidenes affect the reactivity of the complexes in various thermally and photo-induced polymerization reactions, and present the unusual selectivity of these complexes towards non-metathetic side reactions catalyzed by typical ruthenium olefin metathesis catalysts under harsh conditions.