

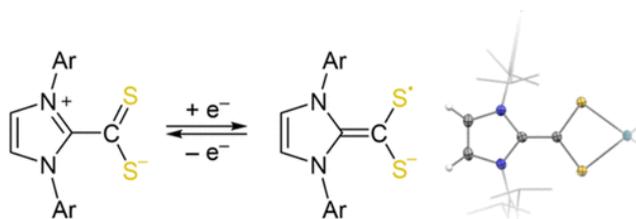
Carbene–CS₂: Redox-active Radical Ligands

Youngsuk Kim

Department of Chemistry, Pusan National University

E-mail: youngsuk.kim@pusan.ac.kr

Singlet carbenes are recognized for their ability to stabilize various main group radicals; however, carbene-derived, sulfur-based radicals remain rare. Here, I present two advances in carbene-stabilized sulfur radical chemistry. First, I will report the synthesis and characterization of novel palladium diradical complexes featuring sulfur-based radical ligands derived from carbene–CS₂ adducts.^[1] These complexes exhibit an open-shell singlet ground state, confirmed through spectroscopic analysis, computational studies, and proton NMR relaxometry, with the unpaired electrons antiferromagnetically coupled on each ligand. The complexes display ligand-centered redox behavior, demonstrating the redox-active nature of these novel sulfur-based radical ligands. Second, I will introduce a new class of stable sulfide radical cations. Sulfide radical cations have recently garnered significant attention as key intermediates in both organic synthesis and in biological electron transfer processes. We have successfully synthesized exceptionally stable sulfide radical cations supported by two carbene moieties.^[2] These radical cations, characterized through EPR spectroscopy, X-ray crystallography, and DFT calculations, show remarkable stability to air, water, various chemical reagents, and elevated temperatures. Beyond establishing a new class of stable sulfur-based radicals, this work illustrates how strategic molecular design can enhance the stability of traditionally reactive species.



NHC-derived Sulfur-based Radical as Redox-active Ligand

References

- [1] S. Park, J.-Y. Hwang, J. Shin*, Y. Kim*, N-Heterocyclic Carbene-Derived Carbon Disulfide Radical Ligands for Palladium Diradicals, *J. Am. Chem. Soc.* **2024**, *146*, 28508.
- [2] D. Kang, M. Kim, H. Choi, J.-Y. Hwang, G. Lim, J. Kim, Y. Kim*, Air- and Water-Stable Sulfide Radical Cations Supported by Cyclic (Alkyl)(amino)carbenes, *J. Am. Chem. Soc.* **2025**, *147*, 35829.