PROBING THE SPECIATION AND ELECTRONIC STRUCTURE OF ORGANOZINC REAGENTS USING X-RAY SPECTROSCOPY

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Organozinc reagents are essential for carbon-carbon bond formation in drug synthesis,[1] yet their chemistry is poorly understood. Understanding speciation and electronic structure in liquid-phase reactions is crucial. Problematically, zinc is spectroscopically quiet, mainly due to the filled 3d shell; investigating organozinc reagents is challenging using standard spectroscopies, e.g. UV-Vis, EPR, NMR. While X-ray absorption spectroscopy (XAS) is common for zinc-based compounds,[2] X-ray emission spectroscopy (XES) studies, particularly resonant XES (RXES), are rare.[3] Additionally, X-ray spectroscopy studies of organozinc compounds are limited.

On I20 at Diamond Light Source, high energy resolution fluorescence detection XAS (HERFD-XAS), valence-to-core XES (VtC-XES), VtC-RXES, and time-dependent density functional theory (TDDFT) were used to study the liquid-phase speciation and valence electronic structure of various organozinc samples. This combined approach revealed the linear geometric structure of 14 organozinc compounds in non-coordinating solvents and quantified the impact of coordinating solvent ratios on diorganozinc speciation. VtC-RXES, akin to UV-Vis spectroscopy,[4] allowed for the specific probing of Zn p-occupied to Zn p-unoccupied state transitions, helping to quantify the effects of 14 different substituents on diorganozinc species' electronic structure and reactivity (Figure 1). This study highlights the effectiveness of X-ray spectroscopic techniques in characterising the liquid-phase speciation and electronic structure of closed-shell diamagnetic complexes, including zinc.

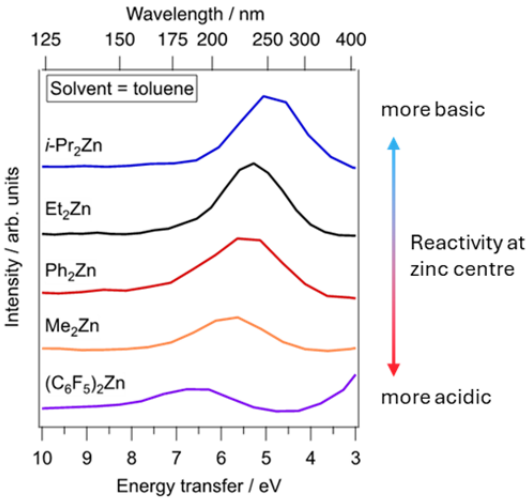

Figure 1. R-VtC-XES for Me_2Zn, Et_2Zn, *i*-Pr_2Zn, Ph_2Zn and $(C_6F_5)_2Zn$ in toluene.

[1] Huo *et al.*, *Science*, 2020, *367*, 559.

[2] Penner-Hahn, *Coord. Chem. Rev.*, 2005, **249**, 161.

[3] Clarke *et al.*, *J. Phys. Chem. A*, 2019, **123**, 9552.

[4] Glatzel *et al.*, *Catal. Today*, 2009, **145**, 294.