

# UniSysCat Colloquium

Start Time: Wednesday, October 30, 2019 05:15 pm

End Time: Wednesday, October 30, 2019 06:45 pm

Chemistry Building, C264

Technische Universität Berlin, Straße des 17. Juni 115, 10623 Berlin

## EPR spectroscopy as a tool in earth abundant metal catalysis

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The earth abundant 3d metals are gaining increasing importance in homogeneous catalysis as alternative to the well-established but expensive platinum group metal catalysts. However, mechanisms for catalysis involving first row transition metals can be quite unique and frequently involve paramagnetic states hampering NMR analysis.

Routine and advanced electron paramagnetic resonance (EPR) spectroscopy will be introduced showcasing different applications ranging from Cu-catalysed Chan-Lam chemistry to investigations of biomolecular structure and function paired with the development of Cu-based spin labels.

The main part of the seminar will discuss recent insights on the Cr/PNP (PNP =  $(R^2)_2PN(R^1)P(R^2)_2$ ) catalyst system that underpins the commercially important selective ethylene oligomerisation ( $> 1 \text{ Mton a}^{-1}$ ). The active catalyst is formed by activating  $\text{Cr}^{\text{I}}$  or  $\text{Cr}^{\text{III}}$  precursors with alkylaluminium in presence of a PNP ligand and a weakly coordinating anion such as  $(\text{Al}(\text{OC}(\text{CF}_3)_3)_4)^-$ . The Cr/PNP complexes formed can undergo ligand redistribution, reduction and disproportionation, resulting in the formation of various species with different oxidation states and altered total electron spin.

Paramagnetic species from discrete catalyst precursors to ongoing catalysis were examined *in situ* by continuous wave EPR spectroscopy. For identifying different components and unravelling overlapping spectra relaxation filter-based pulse EPR methods were adapted to a mixture of discrete  $\text{Cr}^{\text{I}}$  and  $\text{Cr}^{\text{III}}$  precursors with different spin states. This is demonstrated on activated Cr precatalysts. To obtain additional structural information on these intermediates pulse EPR experiments such as transient nutation for assessing spin states and hyperfine spectroscopy have been applied.

The use of selectively isotope labelled substrates and catalyst precursors in EPR time course experiments has provided unequivocal evidence for the transient formation of a bis-ethylene chromium species that has been postulated early in the catalytic cycle but had until now eluded structural characterisation. Here we will present its EPR-derived structure and present insights into the mechanism of its formation derived from quantum chemistry.

Prof. Dr. Robert Bittl

Organizer