Ligand Redox Non-Innocence in [Co\textsuperscript{III}(TAML)]\textsuperscript{0/-} Complexes Affects Nitrene Formation

**Introduction**
- Metal-nitrene (M=NR) species are excellent intermediates for direct olefin aziridination or C-H amination.\textsuperscript{1,2}
- Generation of such species from cheap and sustainable reagents, preferably directly from amines, is desired.
- This requires characterisation of the proposed key catalytically active (radical) nitrene intermediates.
- The cobalt-TAML (TAML = Tetra-Amido Macroyclic Ligand) platform is selected to study this.
- Ligand redox non-innocence of [Co(TAML)] complexes is questioned since 2006.
- No [Co(TAML)(NR)] species have been described up to date. Potential redox non-innocence of the TAML scaffold on cobalt and formation of nitrene adducts were therefore investigated.

**Research questions**
1) Is the ligand in [Co(TAML)] complexes redox non-innocent?
2) Can the [Co(TAML)] platform be used to generate catalytically competent cobalt-nitrene (radical) species?
3) What is the influence of the (ligand) oxidation state on the (electronic) structure of the targeted nitrene (radical) species?

**References**

**Conclusions and outlook**
- Oxidation of [Co\textsuperscript{II}(TAML\textsuperscript{III})\textsuperscript{+}] to [Co\textsuperscript{II}(TAML\textsuperscript{III})\textsuperscript{+}] is ligand-centered: TAML on cobalt is redox active.
- Electronic structure of [Co\textsuperscript{II}(TAML\textsuperscript{III})\textsuperscript{+}] is best described as intermediate spin Co\textsuperscript{II} antiferromagnetically coupled to a ligand-centered radical.
- Nitrene-radical formation occurs through double or single ligand-to-substrate single-electron transfer from [Co\textsuperscript{II}(TAML\textsuperscript{III})\textsuperscript{+}] or [Co\textsuperscript{II}(TAML\textsuperscript{III})\textsuperscript{+}], respectively.
- Follow-up work focusses on catalytic activity of nitrene-radical species in aziridination reactions.