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



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Introduction

- Metal-nitrene (M=NR) species are excellent intermediates for direct olefin aziridination or C–H amination.[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 Macrocyclic Ligand[3]) 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?

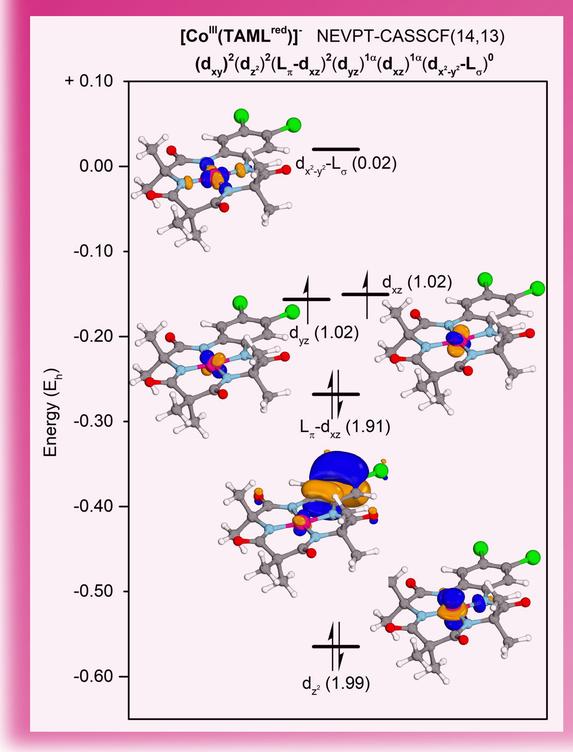
Double ligand-to-substrate single-electron transfer

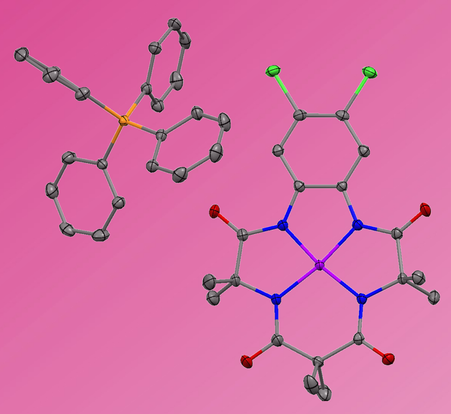
$PPh_4[Co^{III}(TAML^{red})]$

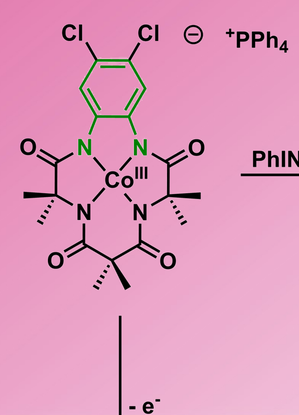
μ_{eff} = 2.94 μ_B, S = 1

XRD: fully reduced TAML

intermediate spin Co^{III}

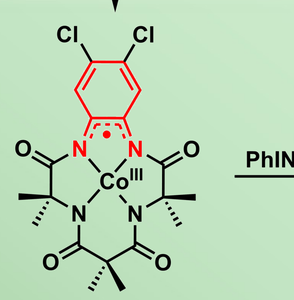






PhINNs (10 eq)

- e⁻



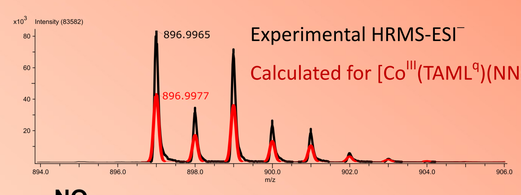
$PPh_4[Co^{III}(TAML^{q})(NNs)_2]$

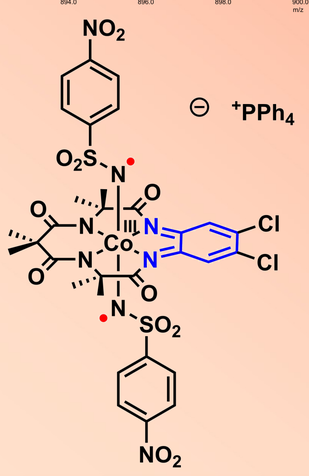
two one-electron reduced Fischer-type nitrene radicals

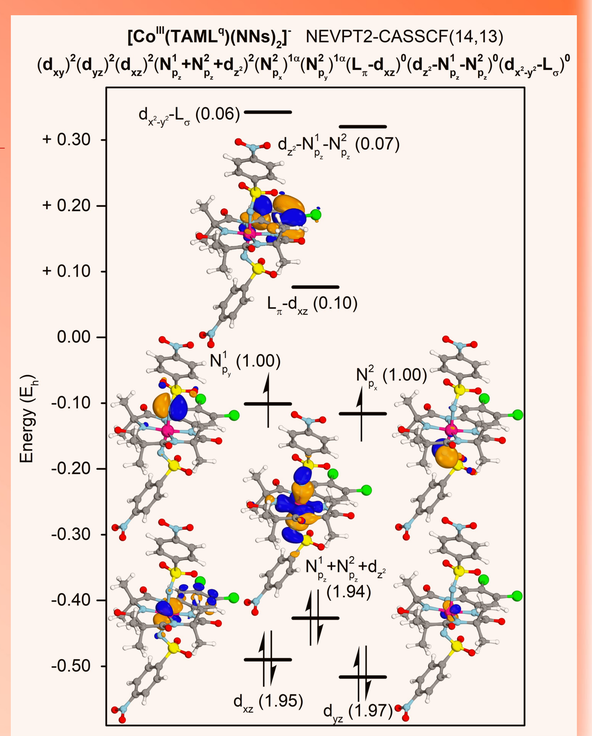
μ_{eff} = 2.75 μ_B, S = 1

fully oxidized TAML

low spin Co^{III}





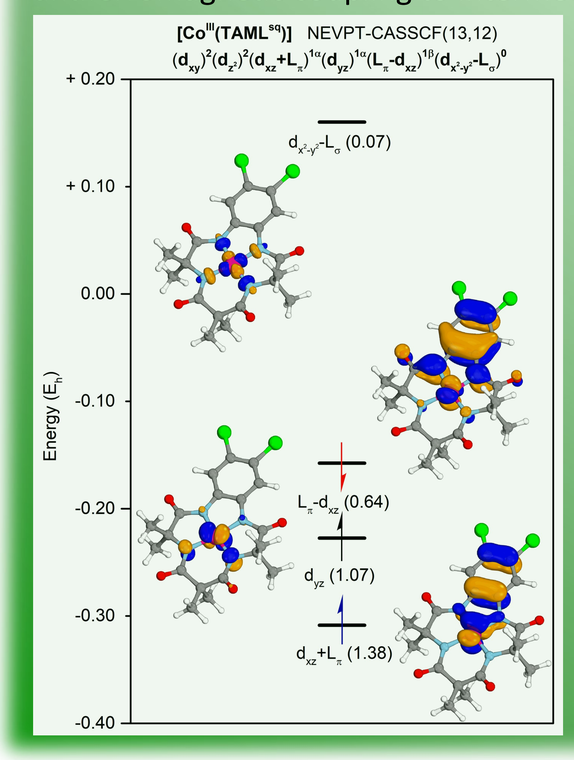


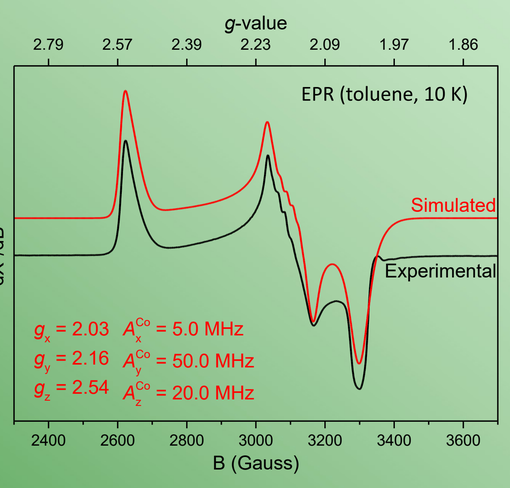
$[Co^{III}(TAML^{sq})]$

μ_{eff} = 1.88 μ_B, S = ½

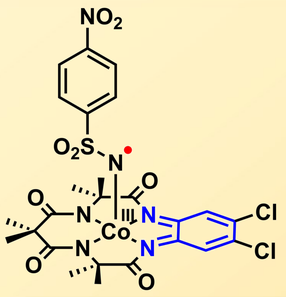
ligand-centered radical: MLCT band at λ_{max} = 623 nm

antiferromagnetic coupling to intermediate spin Co^{III}





PhINNs (10 eq)



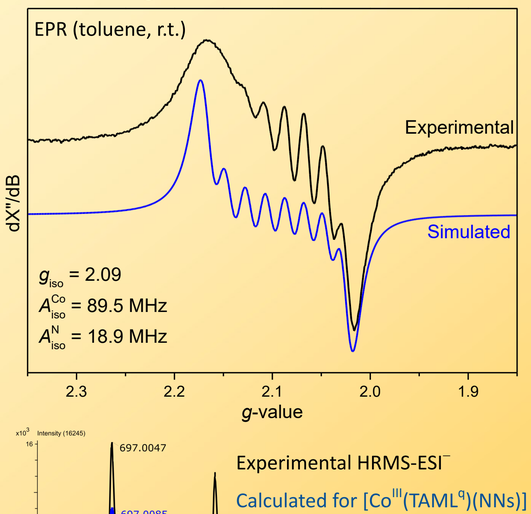
$[Co^{III}(TAML^{q})(NNs)]$

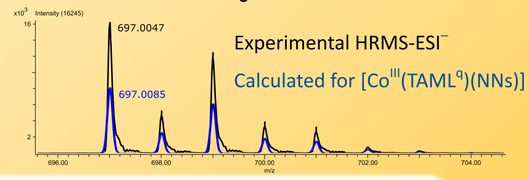
one-electron reduced Fischer-type nitrene radical

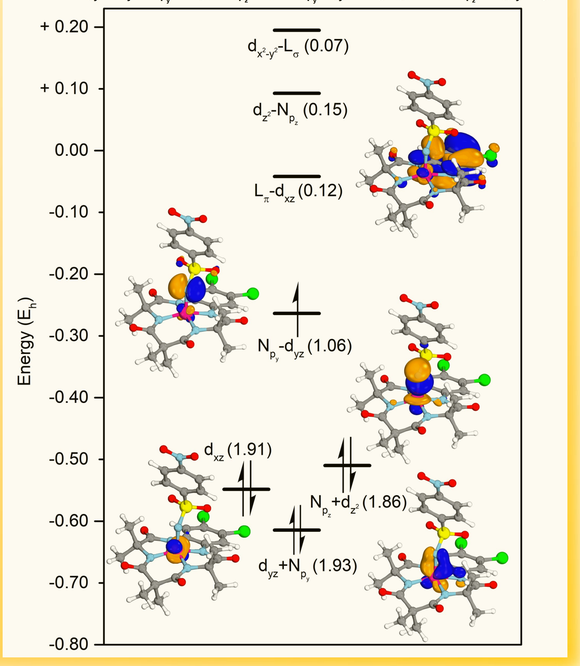
μ_{eff} = 1.53 μ_B, S = ½

fully oxidized TAML

low spin Co^{III}







Ligand-to-substrate single-electron transfer

Conclusions and outlook

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

References

[1] N. P. van Leest, R. F. J. Epping, K. M. van Vliet, M. Lankelma, E. J. van den Heuvel, N. Heijtbrink, R. Broersen, B. de Bruin, *Adv. Organomet. Chem.* **2018**, *70*, 71-180.

[2] P. F. Kuijpers, J. I. van der Vlugt, S. Schneider, B. de Bruin, *Chem. Eur. J.* **2017**, *23*, 13819-13829.

[3] T. J. Collins, R. D. Powell, C. Slebodnick, E. S. Uffelman, *J. Am. Chem. Soc.* **1991**, *113*, 8419-8425.