Taming arenes: A comparative and systematic study

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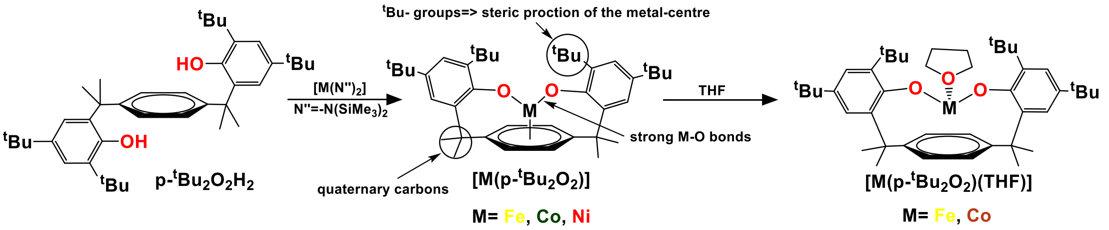
Multidentate ligands featuring a central arene (tethered arene) in an apical position poised to interact with metal centres, have been shown to be advantageous supporting architectures towards promoting multielectronic small molecule reduction. Specifically, when coordinated to heavier transition metals[1] or f-block elements[2], arenes can be formally reduced even twice. Hence, complexes of reduced tethered arenes react with small molecules promoting electron transfers with electrons originated from both the arene and the metal centre. Nevertheless, this reactivity has not been widely expanded to the cheap and readily available 3d metallic centres. Thus, we derived the ligand p-$^{t}Bu_2O_2H_2$ (Scheme 1), a potential L_3X_2 donor, which has the above attributes and is used to implement the concept of "arenes acting as electron reservoirs'' in 3d-metals, with ultimate goal to develop (electro)catalytic processes. The phenolate donors secure strong M-O bonding and the quaternary benzylic carbon atoms, adjacent to the anchor arene, hinder acid-base reactions, making the above ligand a suitable candidate to chase this cause.



Scheme 1: The synthetic route towards [M(p-$^{t}Bu_2O_2$)] and [M(p-$^{t}Bu_2O_2$)(THF)] complexes by using the ligand p-$^{t}Bu_2O_2H_2$. The color code used reflects the true color of the isolated compounds.

Up to now, we were able to isolate three hitherto unknown complexes [M(p-$^{t}Bu_2O_2$)] (M= Fe, Co, Ni), along with their THF adducts [M(p-$^{t}Bu_2O_2$)(THF)] (M= Fe, Co) and characterized them spectroscopically and structurally. IR serves as a qualitative proxy to identify the degree of the metal-arene interaction, while cyclic voltammetry studies on both the solvated and non-solvated species, indicate a possible correlation of the M-arene interaction with the reduction potential of the complexes.

References:

[1]. M. Keener, R. A. K. Shivaraam, T. Rajeshkumar, M. Tricoire, R. Scopelliti, I. Zivkovic, A.-S. Chauvin, L. Maron, M. Mazzanti, J. Am. Chem. Soc. 145 (2023) 16271-16283.
[2]. J. Buss, T. Agapie, Nature 529 (2016) 72-75.