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Équipe d'accueil: N (*SMAc • *Small Molecule* Activation*)
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French National Research Agency (ANR)-funded postdoc position

PUSH-PULL SYSTEMS FOR N_2 ACTIVATION: AMMONIA SYNTHESIS AND BEYOND

Since 1965, when Allen and Senoff isolated the first transition metal (M) dinitrogen complex,[1] the discovery of an efficient and mild process for dinitrogen reduction to ammonia or for its functionalization to organonitrogen chemicals (amines, amides, nitriles, etc.) became a holy grail for chemists. Although much progress has been made in the last two decade in the field of artificial nitrogen fixation, the number of catalytic systems for N_2 conversion under homogeneous conditions remains limited.[2] Therefore, new molecular design strategies must be explored to overcome the current scientific barriers and to gain access to optimized N_2 conversion. Inspired by the Mo-nitrogenase enzymes, which efficiently catalyze the reduction of dinitrogen to ammonia at ambient temperature and pressure,[3] the central idea of this ANR-funded project is to reproduce in synthetic complexes key features of their active site (FeMo-co). One approach is to combine N_2 complexes with Lewis acids (LAs) to mimic the H-bond donors present in the second coordination sphere of FeMo-co. These LAs interact with metal-bound N_2 resulting in the enhancement of metal back-bonding (i.e. pulling electron density from the metal) and thus its polarization and activation (*push-pull* mechanism).[4]

Our team has reported a series of combination of group VI N_2-complexes with boron Lewis acids and we have shown they display interesting reactivity that relate to the frustrated Lewis pair chemistry.[5] Recently, we have managed to associate a tungsten N_2 complex with a diborane exhibiting Lewis super-acidic properties. Beyond the extreme push-pull activation that could be expected, we have observed that the diborane shifts its coordination to the N_2 ligand to accompany electronic and structural changes at the metal. Remarkably, the N–B linkage can swap from covalent to dative upon the storage of hydrides at tungsten, leading to a very important push-pull activation of the N_2 ligand. This adaptability recalls the flexibility of secondary-sphere interaction that helps activate or stabilize active site-bound substrates and intermediates in enzymes.[6]

Building on these preliminary results, we wish to explore the benefit of diborane coordination in the secondary sphere for protonation and electron transfers, key steps to initiate reduction of N_2 into ammonia. Reactivity tests aiming at the functionalization of N_2 taking advantage of enhanced push-pull activation will also be considered. The syntheses of other ditopic Lewis acids, as well as the exploration of the biologically relevant metal iron are planned. If the results are encouraging, catalytic tests of ammonia synthesis may be performed. The project is conducted in collaboration with the Department of Molecular Chemistry of the University of Grenoble (coordinator: Dr. M. Gennari).

For this 1-year (renewable) contract, we are looking for an experienced organometallic (or main group) chemist who is familiar with air-free techniques (Schlenk line, glove-box, etc) and masters a large range of spectroscopies. Knowledge in EPR and electrochemistry would certainly be welcomed to tackle the proposed chemistry. The researcher will be welcomed into the "Small Molecules Activation" (SMAc) team led by Drs. S. Bontemps and A. Simonneau at the Laboratory for Coordination Chemistry (LCC) of the CNRS (www.lcc-toulouse.fr). The LCC provides very well-equipped technical and analytical platforms for the daily support of scientific work. With more than 70 researchers divided into 15 teams, research at the LCC places coordination chemistry as a central tool for tackling current issues related to climate change, energy transition and life sciences. More than 100 trainee, doctoral and post-doctoral students of different nationalities are present at the LCC, thus ensuring a stimulating work environment. Please address your CV, a cover letter and two to three recommendation letters. **Application via the CNRS Employment Portal is mandatory**: https://emploi.cnrs.fr/Offres/CDD/UPR8241-ANTSIM-007/Default.aspx.

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