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RESEARCH GROUP: Ligands Bifonctionnels et Polymères Biodégradables (LBPB)

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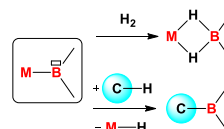
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PhD in Molecular Chemistry, Toulouse (France) Gold boryl complexes

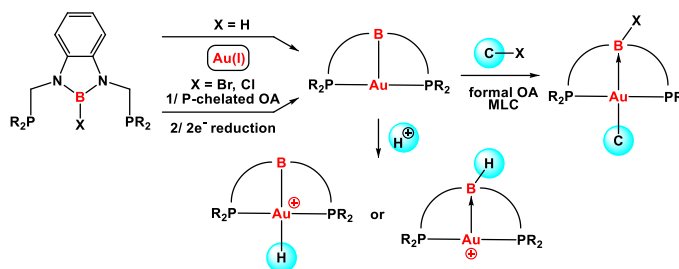
Keywords: pincer ligands, metal-ligand cooperativity, boryl to borane shift, Umpolung

Context and objectives: Boryl ligands are known to be among the strongest σ -donor ligands, resulting in very high *trans* effect. Moreover, the presence of the empty orbital at boron can lead to metal-ligand cooperativity for the activation of strong σ -bonds (such as in H_2). Boryl complexes are also key intermediates in C–H borylation reactions.



Compared to other heteroatom-based X-type ligands such as amides, phosphides and silyls, boryl ligands remain however relatively underexplored due to difficulties in accessing and stabilizing boryl complexes. In particular, gold complexes featuring boryl ligands are scarce with only 3 boryl complexes disclosed to date.

Research plan: This project is targeting pincer complexes in which the Au-boryl moiety is supported by two P sidearms (see the Scheme below for a representative PBP ligand). Two synthetic strategies will be investigated in parallel: direct reaction of B–H proligands with Au(I) precursors, or P-chelation assisted oxidative addition of B–halogen proligands with Au(I) precursors followed by 2e-reduction. The prepared complexes will be thoroughly characterized by spectroscopic and crystallographic means. Their bonding situation will be analyzed in depth computationally.



Because of their unique structure (T-shape geometry with a strong σ -donor boryl moiety), the PBP pincer Au(I) complexes are expected to be electron-rich, in contrast to most gold complexes (ligand-induced Umpolung). This will be inferred experimentally and theoretically by studying their protonation. « Oxidative addition » across the Au–B bond (metal-ligand cooperativity) will also be investigated. Inducing a shift from boryl to borane complexes, it would represent a complementary redox-neutral approach for the activation of C–X bonds at gold. It is most attractive for strong C–Cl, C–F bonds (unprecedented so far at gold) as well as Ar–OR, Ar–OCOR substrates (for which O→B interactions may assist the bond cleavage, in a similar way to that we observed recently in the activation of acyl chlorides across Pd–borane bonds).

The work will combine ligand synthesis and coordination studies. Special attention will be given to the bonding / structure analysis of the prepared complexes, by experimental and computational means. Reactivity studies will be carried out. Catalytic applications will be investigated, with major interest for reactions involving cooperativity between the transition metal and the Lewis acid moiety.

This project will give the PhD student the opportunity to work under inert atmosphere, to use a number of advanced analytical methods (multi-nuclear NMR, X-ray diffraction, UV-vis, electrochemistry...) and to discover the interplay between calculations and experiments (thanks to our collaboration with expert theoreticians). The candidate should be very enthusiastic and enjoy working closely with a team.

SALARY(net) ~1650 €/month, **START DATE** September-October 2023, ANR PROJECT FeBAu

Selected relevant references

For the coordination of Lewis acids as Z-type ligands and transition metal / Lewis acid cooperativity, see: a) Amgoune, A.; Bourissou, D. *Chem. Commun.* **2011**, 47, 859 DOI: [10.1039/C0CC04109B](https://doi.org/10.1039/C0CC04109B); b) Bouhadir, G.; Bourissou, D. *Chem. Soc. Rev.* **2016**, 45, 1065 DOI: [10.1039/C5CS00697J](https://doi.org/10.1039/C5CS00697J).

For low-valent Pd complexes with ambiphilic ligands, and catalytic applications thereof, see: a) Kameo, H.; Yamamoto, J.; Asada, A.; Nakazawa, H.; Matsuzaka, H.; Bourissou, D. *Angew. Chem. Int. Ed.* **2019**, 58, 18783. DOI: [10.1002/anie.201909675](https://doi.org/10.1002/anie.201909675); b) Boudjelel, M.; Sadek, O. Mallet-Ladeira, S.; García-Rodeja, Y.; Sosa Carrizo, E. D.; Miqueu, K.; Bouhadir, G.; Bourissou, D. *ACS Catal.* **2021**, 11, 3822 DOI: [10.1021/acscatal.0c04287](https://doi.org/10.1021/acscatal.0c04287).

For cooperation between Ni(0)/Pd(0) centers and Lewis acids to activate Si–F bonds and achieve Sila-Negishi catalytic couplings, see: Kameo, H.; Yamamoto, H.; Ikeda, K.; Isasa, T.; Sakaki, S.; Matsuzaka, H.; García-Rodeja, Y.; Miqueu, K.; Bourissou, D. *J. Am. Chem. Soc.* **2020**, 142, 14039 DOI: [10.1021/jacs.0c04690](https://doi.org/10.1021/jacs.0c04690).