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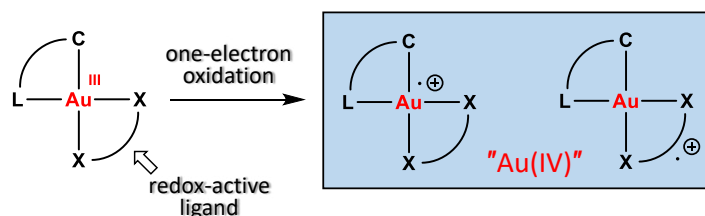
LABORATOIRE HÉTÉROCHIMIE FONDAMENTALE ET APPLIQUÉE
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Au(IV) Complexes: Fake or Reality?

Keywords: gold, redox-active ligands, single electron transfer, catalysis


Context: Despite major progress over the past 2-3 decades, the chemistry of gold still lags well behind that of the other transition metals. The unique properties of gold are now well-recognized and exploited in catalysis, material sciences as well as biology. Nonetheless, the chemical space of gold remains very limited. Only Au(I) and Au(III) complexes are known essentially. Other oxidation states remain curiosities or are simply unknown. About 10 years ago, my group has launched a research program aimed at opening and developing new avenues in gold chemistry thanks to ligand design. We have shown in particular that chelating/hemilabile/cyclometalated ligands efficiently trigger Au(I)/Au(III) redox cycles¹ and enhance π -back-donation from gold, enabling to stabilize reactive carbene and π/σ -complexes.²



Objectives and research plan: In a new long-term project funded by an ERC grant, it is my aim to expand further the chemical space of gold, in terms of structure, reactivity as well as applications. By designing suitable ligand frameworks and fine tuning the coordination sphere of gold, new redox states of gold may be discovered and exploited. This Master project will focus on Au(IV) complexes. Because of their peculiar electronic structures (radical cations), Au(IV) complexes will display enhanced reactivity and will open single-electron and radical paths, which are so far unprecedented with gold but very attractive synthetically.

The work will combine ligand synthesis and coordination studies. A cyclometalated ancillary ligand and a redox-active ligand will be installed at Au(III). Preliminary studies have shown that this combination indeed enable to achieve one-electron oxidation and to access stable cationic radical complexes. Special attention will be given to the electronic structure of the prepared complexes, by experimental and computational means. Is the oxidation taking place at gold or at the redox-active ligand? How to control it? Reactivity studies will be carried out. The photo-physical properties (absorption, emission) of the Au(IV) complexes will also be studied, and whenever relevant, light will be used to trigger challenging transformations.

This project will give the master 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.

Thesis funding ( ERC Gold-Redox) will be available at the start of the 2024 academic year.

Selected relevant references (with hyperlinks)

- 1 a) Zeineddine, A.; Estévez, L.; Mallet-Ladeira, S.; Miqueu, K.; Amgoune, A.; Bourissou, D. *Nat. Commun.* **2017**, *8*, 565 DOI: [10.1038/s41467-017-00672-8](https://doi.org/10.1038/s41467-017-00672-8); b) Rigoulet, M.; Thillaye du Boullay O.; Amgoune, A.; Bourissou, D. *Angew. Chem. Int. Ed.* **2020**, *59*, 16625 DOI: [10.1002/anie.202006074](https://doi.org/10.1002/anie.202006074); c) Rodriguez, J.; Vesseur, D., A.; Tabey, A.; García-Rodeja, Y.; Miqueu, K.; Bourissou, D. *ACS Catal.* **2022**, *12*, 993 DOI: [10.1021/acscatal.1c04580](https://doi.org/10.1021/acscatal.1c04580).
- 2 a) Rekhroukh, F.; Estévez L.; Bijani, C.; Miqueu, K.; Amgoune, A.; Bourissou, D. *Angew. Chem. Int. Ed.* **2016**, *55*, 3414 DOI: [10.1002/anie.201511111](https://doi.org/10.1002/anie.201511111); b) Zeineddine, A.; Rekhroukh, F.; Mallet-Ladeira, S.; Miqueu, K.; Amgoune, A.; Bourissou, D. *Angew. Chem. Int. Ed.* **2018**, *57*, 1306 DOI: [10.1002/anie.201711647](https://doi.org/10.1002/anie.201711647); c) Rigoulet, M.; Vesseur, D.; Miqueu, K.; Bourissou, D. *Angew. Chem. Int. Ed.* **2022**, *61*, e202204781 DOI: [10.1002/anie.202204781](https://doi.org/10.1002/anie.202204781); d) Holmsen, M. S.; Blons, C.; Amgoune, A.; Regnacq, M.; Lesage, D.; Sosa Carrizo, E. D.; Lavedan, P.; Gimbert, Y.; Miqueu, K.; Bourissou, D. *J. Am. Chem. Soc.* **2022**, *144*, 22722 DOI: [10.1021/jacs.2c10737](https://doi.org/10.1021/jacs.2c10737).