

Science and Technology Group Annual Report FY2024

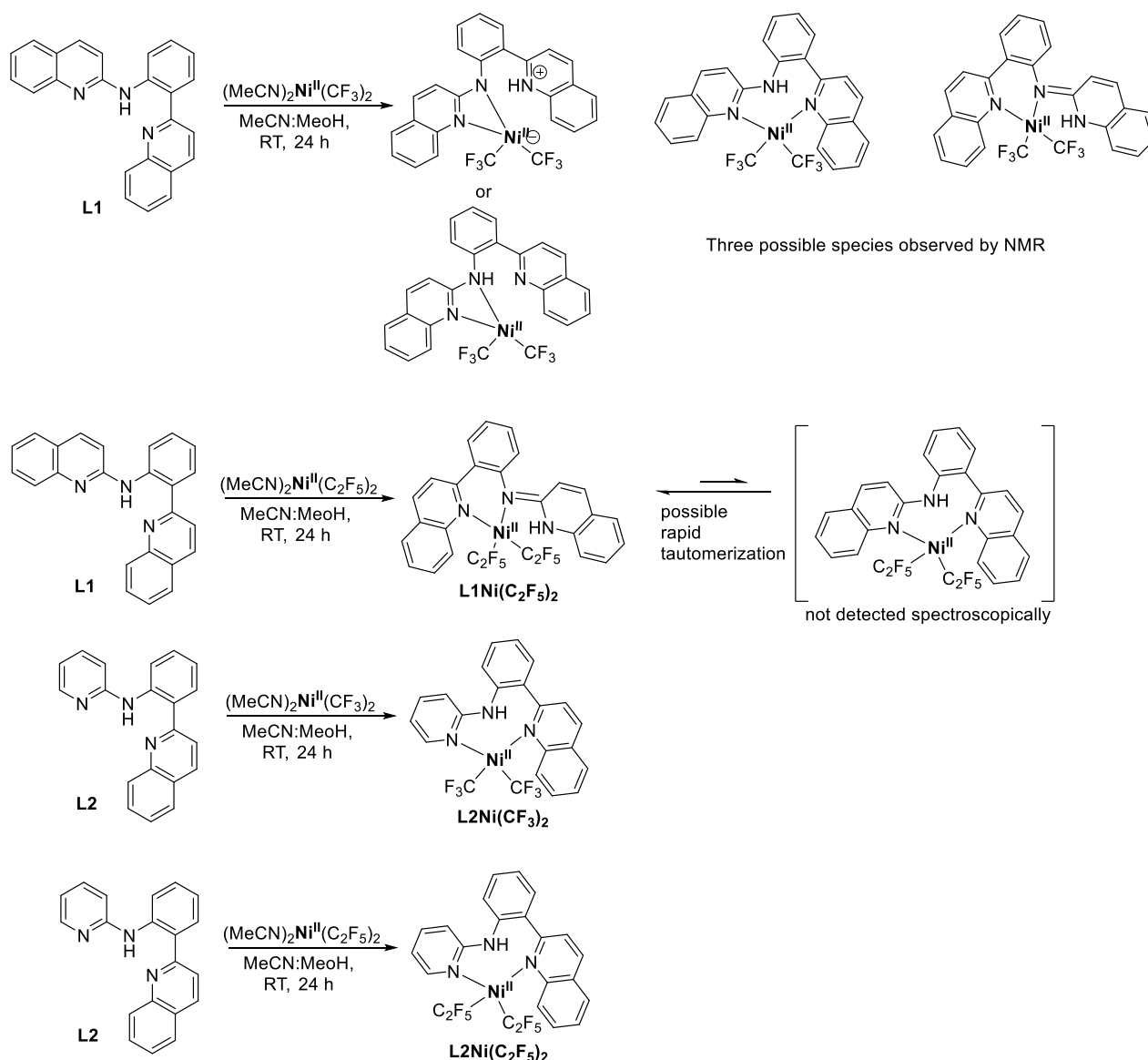
Eugene Khaskin

1 Introduction

During FY2024, as my main research output I published an article in which the collaboration with the Magne Sydnès group has cumulated.¹ The new ligand that was provided by his group, that had a quite unusual architecture, gave us a number of stable fluoroalkyl nickel complexes. We were unfortunately not able to reproduce our results of CF bond cleavage that we saw, and were led down some unproductive paths with other metals and metal precursors. Nevertheless, the work showed that small changes in electronics of the new ligand led to a completely different complexation pattern. There were also a number of works where my contribution was mainly in obtaining crystallographic data.

2 Activities and Findings

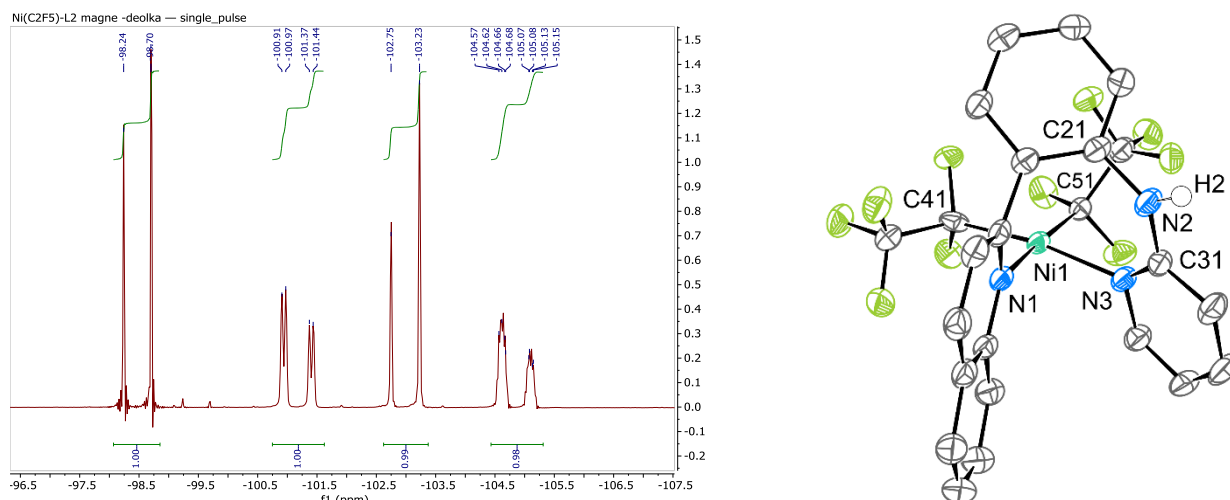
In the main published paper, we were able to observe three different complexation patterns with two ligands with nickel complexes (Scheme 1) and could see where fluoroalkyl group exchange was rapid on the NMR timescale. The paper also highlighted the unusual features of the fluorine NMR, where 3 bond FF coupling is not observed in fluoroalkyl NMR, while 4 bond coupling is readily seen.



Scheme 1. Synthesis of fluoroalkyl complexes.

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Scheme 3. ^{19}F NMR spectrum expansion of $\text{L2Ni}(\text{C}_2\text{F}_5)_2$ in THF-d_8 displaying $^4J_{\text{FF}}$ coupling of the magnetically inequivalent fluorine atoms of the CF_2 group with Molecular structure of $\text{L2Ni}(\text{C}_2\text{F}_5)_2$ in the crystal with anisotropic displacement ellipsoids at the 70% probability level. All hydrogen atoms except for [N]H are omitted for clarity.

I am continuing my collaboration with Dmitri Gusev and we managed to synthesize a Ru complex that is the best known catalyst to data for ester hydrogenation, based on our previous findings. We anticipate publishing the work that led us to this complex, as well as new results with it, as two separate papers in FY 2025. A project started with PNC pincer Pt complex with two interns in FY2024 will also have its first part published in FY 2025.

3 Collaborations

My work with OIST collaborators this year included measurement of crystal structures in a number of different fields and complexes, including with the Khusnutdinova group on the aerobic oxidation of fluoroalkyl groups attached to d10 metals. ² A greater contribution included contribution the bimetallic project with the Khusnutdinova group where measuring crystal structures involved closed cooperation with the first author, and where I more substantially helped with the manuscript preparation process. ^{3, 4} Finally, my first publication with the Narita group came entirely from measuring the crystal data and solving the initial structure of the molecule on which the article was based. ⁵

4 Publications and other output

Author list, *Title*, Journal or other reference, volume information (year)

- (1) Haaheim, K. S.; Deolka, S.; Fayzullin, R. R.; Lund, B. A.; Khaskin, E.; Sydnes, M. O. 2-Pyridinyl/quinolyl-phenylamino-quinoline Complexes With CF_3 and C_2F_5 Ligated Ni. *Eur. J. Inorg. Chem.* **2024**, 27 (25), e202400207.
- (2) Moradi, H.; Govindarajan, R.; Nguyen, H. G.; Deolka, S.; Dinh, H. M.; Khaskin, E.; Fayzullin, R. R.; Vasylevskiy, S.; Khusnutdinova, J. R. Synthesis and Aerobic Oxidation of Perfluoroalkyl d10 Metal Complexes Supported by 2,7-Dimethyl-1,8-Naphthyridine. *Eur. J. Inorg. Chem.* **2024**, 27 (23), e202400257.
- (3) Govindarajan, R.; Vardhanapu, P. K.; Fayzullin, R. R.; Khaskin, E.; Khusnutdinova, J. R. Facile methyl group transfer from PtII to gallium and indium. *Chem. Commun. (Cambridge, U. K.)* **2024**, 60 (56), 7216-7219.
- (4) Govindarajan, R.; Fayzullin, R. R.; Deolka, S.; Khaskin, E.; Vasylevskiy, S.; Vardhanapu, P. K.; Pal, S.; Khusnutdinova, J. R. Facile Access to Cationic Methylstannylenes and Silylenes Stabilized by E-Pt Bonding and their Methyl Group Transfer Reactivity. *Chem. - Eur. J.* **2024**, 30 (8), e202303789.
- (5) Marae, I. S.; Tan, J.; Yoshioka, R.; Ziadi, Z.; Khaskin, E.; Vasylevskiy, S.; Kabe, R.; Xu, X.; Narita, A. Synthesis and characterizations of highly luminescent 5-isopropoxybenzo[rst]pentaphene. *Beilstein J. Org. Chem.* **2025**, 21, 270-276.