Science and Technology Group
Annual Report FY2023

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1 Introductions

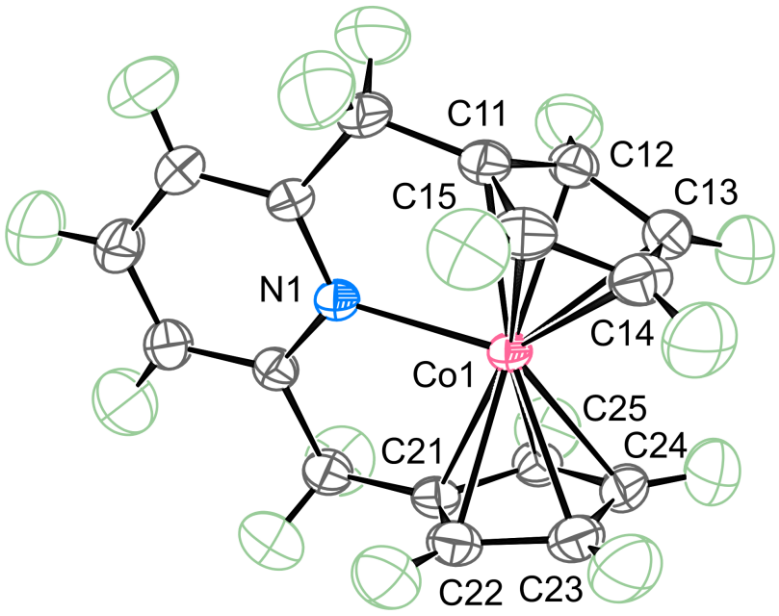
Synthesis of >20 electron metallocene derivatives

Metallocenes are highly versatile organometallic compounds. The versatility of the metallocenes stems from their ability to stabilize a wide range of formal electron counts. To date, d-block metallocenes with an electron count of up to 20 have been synthesized and utilized in catalysis, sensing, and other fields. However, d-block metallocenes with more than formal 20-electron counts have remained elusive. The synthesis and isolation of such complexes are challenging because the metal–carbon bonds in d-block metallocenes become weaker with increasing deviation from the stable 18-electron configuration. In this project , we aim to synthesize such complexes using a novel synthetic approach.

2 Activities and Findings

This year, we reported the synthesis, isolation, and characterization of a 21-electron cobaltocene derivative (https://www.nature.com/articles/s41467-023-40557-7). This discovery is based on the ligand design that allows the coordination of an electron pair donor to a 19-electron cobaltocene derivative while maintaining the cobalt–carbon bonds, a previously unexplored synthetic approach. Furthermore, we elucidate the origin of the stability, redox chemistry, and spin state of the 21-electron complex. This study reveals a synthetic method, structure, chemical bonding, and properties of the 21-electron metallocene derivative that expands our conceptual understanding of d-block metallocene chemistry. We expect that this report will open up previously unexplored synthetic possibilities in d-block transition metal chemistry, including the fields of catalysis and materials chemistry.

This research was highlighted at the reputed chemistry journal Nature Chemistry (https://www.nature.com/articles/s41557-023-01372-1) , and an established Japanese scientific newspaper, The Science News.



3 Collaborations

This project was carried out partly by corroboration with

- Dr. Robert R. Fayzullin (Arbuzov Institute of Organic and Physical Chemistry, FCR Kazan Scientific Center, Russian Academy of Sciences)
- Dr. Urs Gellrich (Institute of Organic Chemistry, Justus Liebig University Giessen, Germany)
- Prof. Kazunobu Sato (Department of Chemistry, Graduate School of Science, Osaka Metropolitan University)
- Prof. Ko Mibu (Graduate School of Engineering, Nagoya Institute of Technology)
- Dr. Hyung-Been Kang (Engineering section, OIST)
- Dr. Noriko Ishizu (Engineering section, OIST)

4 Publications and other outputs

Publication (*: corresponding authors)

(1) Takebayashi, S.*; Ariai, J.; Gellrich, U.*; Kartashov, S. V.; Fayzullin, R. R.*; Kang, H.-B.; Yamane, T.; Sugisaki, K.; Sato, K.
Synthesis and characterization of a formal 21-electron cobaltocene derivative
Nat. Commun. 2023, 14, 4979.
Highlighted at Nature Chemistry and The Science News.

(2) Hao Wu, Hiroki Hanayama, Max Coehlo, Yanwei Gu, Ze-Hua Wu, Satoshi Takebayashi, Gerhard Jakob, Serhii Vasylevskyi, Dieter Schollmeyer, Mathias Kläui, Grégory Pieters, Martin Baumgarten, Klaus Müllen*, Akimitsu Narita*, and Zijie Qiu*
Stable π-Extended Thio[7]helicene-Based Diradical with Predominant Through-Space Spin–Spin Coupling
J. Am. Chem. Soc. 2024, 146, 7480.

Presentation (*:presenter)

(1) Takebayashi, S.* Ariai, J.; Gellrich, U.; Kartashov, S. V.; Fayzullin, R. R.; Kang, H.-B.; Yamane, T.; Sugisaki, K.; Sato, K.
Synthesis and characterization of a formal 21-electron cobaltocene derivative
73rd Japan Society of Coordination Chemistry Conference, Mito, Japan, 2023.

(2) Takebayashi, S.* Ariai, J.; Gellrich, U.; Kartashov, S. V.; Fayzullin, R. R.; Kang, H.-B.; Yamane, T.; Sugisaki, K.; Sato, K.
Synthesis of a 21-electron cobaltocene derivative
25th Conference on Organometallic Chemistry (EuCOMC), Alcala, Spain, 2023.

(3) Takebayashi, S.* Ariai, J.; Gellrich, U.; Kartashov, S. V.; Fayzullin, R. R.; Kang, H.-B.; Yamane, T.; Sugisaki, K.; Sato, K.; Onoue, T.; Mibu, K.
Formal 21-electron cobaltocene and 20-electron ferrocene derivatives
Gorgon Research Conference in Organometallic Chemistry, Newport, RI, USA, 2023

Patent

(1) Milstein, D.; Takebayashi, S.
Iron-Catalyzed Metathesis Polymerization of Olefins.
PCT patent, published 2023, WO/2023/012789.

5 External fundings

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