Hessisches Kompetenzzentrum
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Investigation of Photochemical Pathways to Metal-Nitrene Compounds From Azide Precursors II

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Project Term
2023 - 2024

Clusters
Lichtenberg II Cluster Darmstadt

Software
ORCA

Additional Software
CREST, pysisyphus, ChimeraX

Institute
Theoretical Physical Chemistry

University
Technische Universität Darmstadt

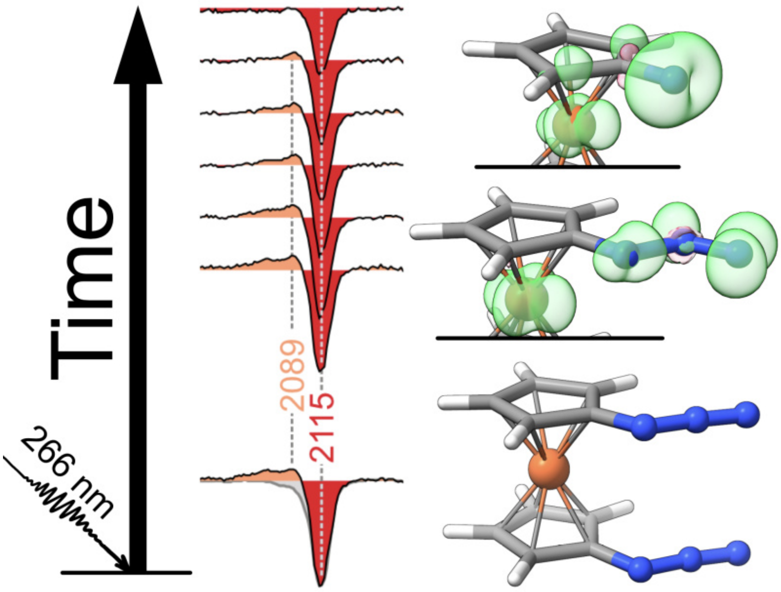

Figure 1: Ultrafast UV-pump-mIR-probe transient absorption spectroscopy signals show three distinct chemical species in the photochemical reaction. Quantum chemical calculations were used to identify these species and interpret the experimental results. Structures are shown with spin densities to the right.

Introduction

Azides are omnipresent in organic and inorganic chemical synthesis. They are readily introduced into molecules and allow for rich follow-up chemistry. The most important area where azides are routinely employed is in bioorthogonal Click chemistry, where the 1,3- dipolar cycloaddition reactions are used to efficiently link complex structures together. Dinitrogen is an excellent leaving group, essentially preventing the reverse reaction from taking place, rapidly driving equilibrium reactions to completion. Besides their broad use in thermally driven chemical transformations, azides feature a rich photochemical landscape. By photoexcitation, chemical reactivity patterns are enabled that would otherwise be impossible to achieve. By binding the azide to a transition metal ion in a coordination compound and exciting the complex electronically with light, a high-valent metal-nitrido species can be generated. Such intermediates often feature both a metal in an unusally high oxidation state as well as a single nitrogen atom bound to it, making them interesting from an electronic structure point of view as well as for nitrogen-atom transfer reactions. In this project we employ state-of-the-art quantum chemical methods in conjunction with sophisticated experiments to explore the photochemistry of various transition metal azide compounds and the electronic structure of the generated metal-nitrido species.

Methods

Recent advances in both quantum chemical theory and computing resources allow for highly sophisticated quantum chemical investigations to be performed in reasonable amounts of time. The methods used in this project comprise density functional theory (DFT), time-dependent density functional theory (TD-DFT), and complete active space selfconsistent field (CASSCF) calculations at a base level that are combined in higher level composite workflows to extract meaningful data and insightful visualiziations. Accurately describing these large molecular structures with heavy atoms require the use of appropriately large basis sets and dense integration grids. The computational effort of these kinds of calculations usually scales with $O(N^{6-7})$, where N is a measure for system size. High-performance computing clusters in conjunction with pragmatic approximations to reduce the computational effort are thus essential to performing these calculations.

Results

In the first phase of this project (May 2022 – April 2023) various computational protocols were explored with respect to their cost and accuracy. A breakthrough in this phase of the project was the identification of an intermediate with a bent azide moiety that is preorganizied for the release of dinitrogen. This motif proved to be almost universal for all investigated systems since and is consistent with literature for purely organic azides. In the second phase (April 2023 – May 2024) the established computational protocols were used in conjuction with femtosecond UV-pump-mIR-probe spectroscopy to follow the photoinitiated release of dinitrogen from 1,1’-diazidoferrocene. This joint theoretical and experimental study was then published in early 2024 (Collaboration between AK Krewald (Darmstadt), AK Sarkar (Stuttgart), AK Vöhringer (Bonn)).

Discussion

The theoretical work on this project thus far in conjunction with experimental ultrafast spectroscopy has proven to be a powerful way of understanding the photochemical processes. Our work shows that spin-orbit coupling effects can play an important role in the excited state dynamics, even in the absence of a heavy atom (as already known for e.g. DNA nucleobases).[1] With the initial work on 1,1’-diazidoferrocene done, the scope of the fine-tuned computational protocols can now be expanded to a variety of different transition metal azide compounds. While the basic photochemical process of dinitrogen release could be followed and rationalized, we now aim to improve our understanding even further. A major focus is to understand how spin-orbit coupling effects influence the photodissociation and how these spin-orbit coupling effects can be leveraged to obtain desired reactivity patterns. Such investigations of other transition metal azide compounds are currently underway together with our collaborators.

[1] This was known before, e.g., for DNA nucleobases.

Publications

Scherz, F; Bauer, M; Domenianni, L. I. ; Hoyer, C; Schmidt, J; Sarkar, B; Vöhringer, P; Krewald, V. Ultrafast photogeneration of a metal-organic nitrene from 1,1’-diazidoferrocene. Chem. Sci.,15, 6707-6715. (2024) https://doi.org/10.1039/D4SC00883A

Scherz, F; 25th International Symposium on the Photochemistry and Photophysics of Coordination Compounds, Investigation of photolytic dinitrogen release from 1,1’-diazidoferrocene (Poster), Ulm, Germany, 25.07-29.07 (2023)

Scherz, F; 2nd Pure and Data-driven Quantum Chemistry (PDQC) Meeting, Ultrafast photogeneration of a metal-organic nitrene (Presentation), Darmstadt, Germany, 01.08 (2023)

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