Book of Abstract

FLUORINE FRONTIERS:

A Symposium Honoring the Legacy of Boris Žemva

Ljubljana, September 9-11, 2024

Book Of Abstracts

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CONTENTS

INTRODUCTION

Fluorine Frontiers: A Symposium Honoring the Legacy of Boris Žemva

Welcome to "Fluorine Frontiers: A Symposium Honoring the Legacy of Boris Žemva". We are delighted that you are able to join us to celebrate Boris Žemva's life and to explore his pioneering contributions to the field of fluorine chemistry. To begin, we would like to give you a brief overview of his life and achievements.

Prof. Dr. Boris Žemva's remarkable scientific journey began at the University of Ljubljana, where he pursued his passion for chemistry and earned his Ph.D. in 1971. His academic pursuits led him to the Jožef Stefan Institute, where he delved into the intriguing world of noble-gas chemistry and focussed on the reactions between xenon and fluorine. This research laid the foundation for his distinguished career as a prominent figure in the field.

Throughout his tenure from 1983 to 2006 as the head of the Department of Inorganic Chemistry and Technology at the Jožef Stefan Institute, Prof. Žemva's leadership and vision extended far beyond the confines of fluorine chemistry. Under his guidance, the department addressed a multitude of scientific challenges, ranging from basic research in fluorine chemistry to technological advancements. His commitment to education in chemistry further demonstrated his passion for cultivating knowledge and innovation in future generations of scientists. It is noteworthy that his involvement in this sphere is exemplified by his continued participation in the International Postgraduate School at the Jožef Stefan Institute, which served to emphasize his dedication to nurturing scientific excellence.

The collaborative efforts between research groups in Ljubljana and Berkeley paved the way for ground-breaking research that led to the syntheses of thermodynamically unstable high-oxidation-state fluorides. Prof. Žemva's impactful contributions in this area, alongside his colleague Prof. Neil Bartlett, were recognized by Nobel Laureate in Chemistry, Prof. Roald Hoffmann, who underscored their pioneering work on high-energy oxidants.

Prof. Žemva's influence extended globally, with over 150 published articles, numerous invited lectures, and pivotal editorial roles in esteemed scientific journals. His research results significantly contributed to our understanding of chemistry and are often described and cited in contemporary inorganic chemistry textbooks. His involvement in organizing international symposiums and conferences further solidified his role in the international fluorine chemistry community. He collaborated closely with numerous scientists and research groups from around the world, including Japan, Germany, France, Poland, the USA, and Canada. He often mentioned that close collaboration with people worldwide is invaluable and should be nurtured. He greatly enjoyed the company of his international friends and colleagues.

Notable accolades such as the Boris Kidrič Award, Alexander von Humboldt Research Award, American Chemical Society (ACS) Award, and the prestigious Zois Award exemplified the recognition of his outstanding contributions to the field of fluorine chemistry.
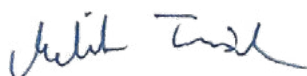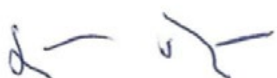
Beyond his scientific endeavours, Prof. Žemva found joy in diverse interests, including outdoor pursuits like hiking and skiing, appreciation of music, and savouring good food and wine.

A gathering at the Jožef Stefan Institute in Ljubljana is being organized to celebrate Prof. Žemva's illustrious career and scientific achievements in the field of fluorine chemistry. This event will serve as a tribute to his legacy, emphasizing the importance of his research and the impact he had on the scientific community. Your presence in Slovenia at this gathering of friends and colleagues is warmly anticipated, and promises to be a memorable and scientifically enriching experience that will provide opportunities for collaborations and reflection on the enduring legacy of Prof. Dr. Boris Žemva.
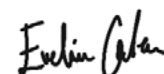
Sincerely yours,

The Symposium Organizing Committee:
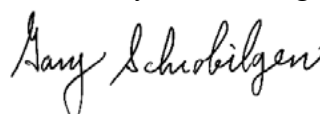
Assoc. Prof. Gašper Tavčar   Dr. Evelin Gruden

Dr. Hélène P. A. Mercier   Prof. Gary J. Schrobilgen

Dr. Melita Tramšek

TIMETABLE

	Sunday September 8
18:00–21:00	*Welcome Reception & Registration*

	Monday September 9	Tuesday September 10	Wednesday September 11
8:00–9:00	*Registration*	*Registration*	*Registration*
9:00–9:30	Welcome Address & Opening Session	Lecture Session 4	Lecture Session 8
9:30–10:00			
10:00–10:30			
10:30–11:00	*Coffee Break*	*Coffee Break*	
11:00–11:30	Lecture Session 1	Lecture Session 5	*Coffee Break*
11:30–12:00			Student Session
12:00–12:30			
12:30–13:00	*Lunch Break*	*Lunch Break & Group Photo*	Closing Remarks & Lunch
13:00–13:30			
13:30–14:00	Lecture Session 2	Lecture Session 6	
14:00–14:30			
14:30–15:00			
15:00–15:30	*Coffee Break*	*Coffee Break*	
15:30–16:00	Lecture Session 3	Lecture Session 7	
16:00–16:30			
16:30–17:00			*Tour of Ljubljana*
17:00–17:30			
17:30–18:00			
19:00–22:00		*Symposium Dinner*	

PROGRAM

Sunday, September 8, 2024

| 18:00–21:00 | *Welcome Reception & Registration* | Gallery |

Monday, September 9, 2024

| 8:00–9:00 | *Registration* | Gallery |

| 9:00–9:30 | Welcome Address | Main Lecture Hall |

| | **OPENING SESSION** | Main Lecture Hall |

| 9:30–10:00 | *Melita Tramšek & Gašper Tavčar* | |
| 10:00–10:30 | *Hélène P. A. Mercier & Gary J. Schrobilgen* | |

| 10:30–11:00 | *Coffee Break* | Gallery |

| | **LECTURE SESSION 1** | Main Lecture Hall |

11:00–11:30	L1	**The Intermediates of the Schmidt Reaction and a Pictorial of Boris** *Karl O. Christe, Thomas Saal, Antonina Nazarova, Ralf Haiges, David Dixon*	*p. 17*
11:30–12:00	L2	**A Personal Journey into Applications of XeF$_2$ in Synthetic Organic Chemistry and the Quest for the Xe-C Bond** *Yurii L. Yagupolskii*	*p. 18*
12:00–12:30	L3	**Fluoride ion and Alcohols: Good friends?** *Kazuhiko Matsumoto, Nozomi Yoneda, Kohei Tada*	*p. 19*

| 12:30–13:30 | *Lunch Break* | Gallery |

LECTURE SESSION 2				Main Lecture Hall
13:30–14:00	L4	**My Fluorine Chemistry and Ljubljana** *Konrad Seppelt*		*p. 20*
14:00–14:30	L5	**Fluorine-Forged Friendship** *Olga Boltalina*, Sebastian Balser, Steven H. Strauss		*p. 21*
14:30–15:00	L6	**Nucleophilic Fluorination Reagents Based on Difluorosilicates and Difluoroimidazoles** *Jaroslav Kvíčala*, Markéta Rybáčková, Šárka Bouzková, Adam Hroch, Michal Trojan, G. Tavčar		*p. 22*
15:00–15:30	*Coffee Break*			Gallery

LECTURE SESSION 3				Main Lecture Hall
15:30–16:00	L7	**Chemical In-Depth Analysis of (Ca/Sr)F_2 Core-Shell Like Nanoparticles by X Ray Photoelectron Spectroscopy with Tunable Excitation Energy** *E. Kemnitz*, A. Müller, Th. Krahl, B. Ritter, W. E. S. Unger		*p. 23*
16:00–16:30	L8	**Simplifying Fluoroalkylation Reactions with Nickel** *David A. Vičič*, Cherry Mae Ravidas, Scott T. Shreiber		*p. 24*
16:30–17:00	L9	**RuF_6, a stronger Oxidizing Agent than PtF_6: Oxidation of Halogen Pentafluorides with RuF_6** *Florian Kraus*, Björn N. Koch		*p. 25*

Tuesday, September 10, 2024

8:00–9:00	*Registration*		Gallery

LECTURE SESSION 4			Main Lecture Hall
9:00–9:30	L10	**Structural Peculiarities of some d-Transition Compounds in Fluorinated Environments** *Alain Tressaud*	*p. 26*
9:30–10:00	L11	**α-Silyl Carbanions Stabilized by Pentafluoroethyl Groups** *Berthold Hoge, Julia Landwehrmann*	*p. 27*
10:00–10:30	L12	**Fluorochemicals with Uniquely Important Applications in Electronics** *Robert (Bob) G. Syvret*	*p. 28*

10:30–11:00	*Coffee Break*		Gallery

LECTURE SESSION 5			Main Lecture Hall
11:00–11:30	L13	**Adventures in Xenon- and Mercury-Chemistry with Weakly Coordinating Perfluoroalkoxyaluminate Anions** *Ingo Krossing, Konstantin Kloiber*	*p. 29*
11:30–12:00	L14	**Novel two-dimensional quantum magnets based on Ag(II)** *Wojciech Grochala, Mateusz Domanski, Daniel Jezierski, Zoran Mazej*	*p. 30*
12:00–12:30	L15	**Tris(pentafluoroethyl)difluorophosphorane: A Versatile Fluoride Acceptor for Transition Metal Chemistry** *Udo Radius*	*p. 31*

12:30–13:20	*Lunch Break*		Gallery
13:20–13:30	*Group Photo*		Stairs in front of IJS main building

		LECTURE SESSION 6	Main Lecture Hall
13:30–14:00	L16	**Unusual Fluorine Containing Compounds: from Oxyfluorides and High Potential Oxidizers** *Sebastian Riedel*	*p. 32*
14:00–14:30	L17	**Fluorinated aminophospohonates and amino acids with olefinic motif – versatile peptidomimetics** *Henryk Koroniak, Marcin Kaźmierczak, Katarzyna Koroniak-Szejn, Karolina Paszek*	*p. 33*
14:30–15:00	L18	**One Of The Smallest Elements Of The Periodic Table, But The Diamond Of Our Life, Element F2** *Dayal T. Meshri, Sanjay D. Meshri, Elena Shembel, Ritesh Jain, Prakash Iyer*	*p. 34*
15:00–15:30		*Coffee Break*	Gallery

		LECTURE SESSION 7	Main Lecture Hall
15:30–16:00	L19	**Rhodium-Mediated C-H and C-F Bond Activation to Access Fluorinated Alkene Derivatives** *Thomas Braun, Cortney von Hahmann, Maria Talavera, Soodeh Mollasalehi*	*p. 35*
16:00–16:30	L20	**Unusual Reactivity Triggered By Fluorine – From Exotic Complexes To Novel Reaction Mechanisms** *Przemysław J. Malinowski, Magdalena Grochowska-Tatarczak, Michał Jadwiszczak, Kacper Koteras, Piotr J. Leszczyński*	*p. 36*
16:30–17:00	L21	**Theranostic Applications of Fluorinated Dendrimers** *Pierangelo Metrangolo*	*p. 37*

19:00–22:00	*Symposium Dinner*	Ljubljana Castle

Wednesday, September 11, 2024

8:00–9:00		*Registration*		Gallery

		LECTURE SESSION 8	Main Lecture Hall

9:00–9:30	L22	**Electrochemical Fluorination:** **Synthesis of Fluorine-Containing Building Blocks** *Maik Finze, Nikolai V. Ignat'ev, Leon N. Schneider, Tanja Knuplez, Younes K. J. Bejaoui, Roland Graf*	*p. 38*
9:30–10:00	L23	**High-pressure chemistry and physics of fluorides** *Dominik Kurzydłowski*	*p. 39*
10:00–10:30	L24	**Chloroimidazolium Deoxyfluorination Reagent with $H_2F_3^-$ Anion as a Sole Fluoride Source** *Gašper Tavčar, Jernej Iskra*	*p. 40*
10:30–11:00	L25	**Do We Still Need To Determine Crystal Structures Experimentally?** *Horst Borrmann*	*p. 41*

11:00–11.30		*Coffee Break*	Gallery

STUDENT SESSION			Main Lecture Hall

11:30–11:37	S1	**Phase Transitions in Compressed Palladium Trifluoride** *Sylwia Olszewska, Deepak Upadhyay, Sharad Babu Pillai, Kinga Zdun, Jakub Drapała, Klemen Motaln, Matic Lozinšek, Dominik Kurzydłowski*	*p. 45*
11:37–11:44	S2	**Preparation and Structural Characterisation of Salts Containing the Unique $[MF_3(XeF_2)_3]^+$ (M = Pd, Pt) Adduct Cations** *Klemen Motaln, Matic Lozinšek*	*p. 46*
11:44–11:51	S3	**Pyridine and pentafluoropyridine as ligands in transition metal complexes** *Michał J. Jadwiszczak, Przemysław J. Malinowski*	*p. 47*
11:51–11:58	S4	**Protective Role of Aluminium Against Fluoride Toxicity in THP-1 Monocytes** *Anja Pavlovič, Larisa Janžič, Lucija Sršen, Andreja Nataša Kopitar, Maja Ponikvar-Svet*	*p. 48*
11:58–12:05	S5	**Hydrosilylation of olefins on highly reactive calcium cation** *Magdalena Grochowska-Tatarczak, Kacper Koteras, Krzysztof Kazimierczuk, Przemysław J. Malinowski*	*p. 49*
12:05–12:12	S6	**Novel Xe^{II}−N-bonded compounds derived from cyanogen** *Erik Uran, Kristian Radan, Miha Virant, Mirela Dragomir, Matic Lozinšek*	*p. 50*
12:12–12:19	S7	**Trifluoromethylthiolation: A Strategy for Hydrophobic Peptide Development** *Jure Gregorc, Nathalie Lensen, Gregory Chaume, Thierry Brigaud, Jernej Iskra*	*p. 51*
12:19–12:26	S8	**Carboxylic Acids to Acyl Fluorides: An Easy Access for Amides and Esters** *Jan Jelen, Griša Prinčič, Nina Cankar, Jernej Iskra, Gašper Tavčar*	*p. 52*

12:30–14:00	Closing remarks *& Lunch*	Gallery

16:00–18:00	*Tour of Ljubljana*	Ljubljana city center

ABSTRACTS
Lecture sessions

The Intermediates of the Schmidt Reaction and a Pictorial of Boris

Karl O. Christe,[1]* Thomas Saal,[1] Antonina Nazarova,[1] Ralf Haiges,[1] David Dixon[2]

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Abstract

Boris was not only a brilliant scientist but also enjoyed life to the fullest. A series of pictures will be presented, demonstrating his joie de vivre.

A summary will be given about the isolation and characterization of the intermediates of the Schmidt reaction. Acyl azides, $RCON_3$, are the starting materials for both the Schmidt reaction and the Curtius rearrangement. However, these two reactions are very different. The Curtius rearrangement, the conversion of an acyl azide to an acyl isocyanate,

$$RCON_3 \rightarrow RNCO + N_2 \qquad (1)$$

is a simple one-step, intramolecular, thermal rearrangement with N_2 elimination. In contrast, the Schmidt reaction, the conversion of an acyl azide to an alkyl amine involving N_2 and CO_2 eliminations,

$$RCON_3 + H_2O \rightarrow RNH_2 + N_2 + CO_2 \qquad (2)$$
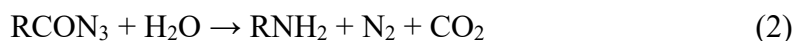
is a low-temperature, acid catalyzed, multi-step reaction whose complex mechanism had not been established before.

A Personal Journey into Applications of XeF$_2$ in Synthetic Organic Chemistry and the Quest for the Xe-C Bond

Prof. Dr. Yurii L. Yagupolskii*

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Among the pages of my research career that have been of most importance to me are those that chronicle the time I spent exploring the reactivity of XeF$_2$:
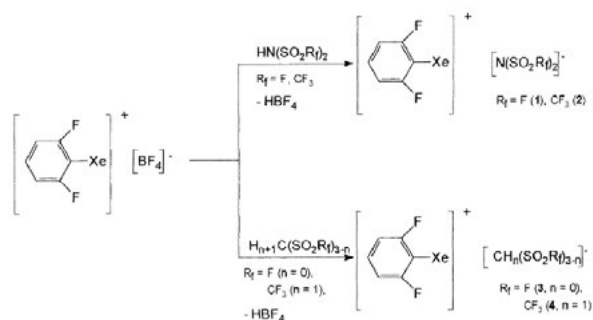
Perfluoroalkyl sulfur and selenium difluoride substituent ArS(orSe)F$_2$CF$_3$ construction [1]:

ArS(Se)CF$_3$ + XeF$_2$ → Ar SF$_2$(SeF$_2$)CF$_3$
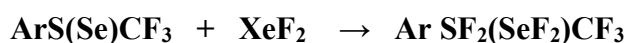
The syntheses of N-F compounds (RfCO$_2$)$_2$NF [2]:

(RfCO)$_2$NH + XeF$_2$ → (RfCO)$_2$NF

Long term search for Xe-N and Xe-C containing stable molecules [3]:

These were great and unforgettable times [4], which carry with them great memories of cooperations, meetings and friends in the fluorine community. Among them, it was the wise and friendly smile of Professor Boris Zemva.

References
[1] Yu.L.Yagupol'skii, T.I. Savina, Reaction of aryl trifluoromethyl sulfides and selenides with xenon difluoride // Zh. Org. Khim.- 1979.- Vol. 15(2).- P. 438-439 (Russ). (CA – Vol. 90 – 203618p).
[2] Yu. L.Yagupol'skii, T. I. Savina, Reaction of imides of perfluorodicarboxylic acids with xenon difluoride // J. Org. Chem. USSR (English Translation).- 1981.- Vol. 17(6).- P. 1180 – 1181. (Zh. Organ. Khim.- 1981.- Vol. 17(6).- P. 1330 – 1331).
[3] Yu.L.Yagupolskii, W.Tyrra, R.Gnann, N.Maggiarosa, Naumann D. 2,6-Difluorphenylxenon(II) bis(fluorsulfonyl)amid, -bis(trifluormethylsulfonyl)amid, tris(fluorsulfonyl)methanid und -bis(trifluormethylsulfonyl)methanid - neue C-Xe-N- und C-Xe-C-Verbindungen? // J. Fluorine Chem.- 2002.- Vol. 113, № 2.- P. 143-146.
[4] Yu.L. Yagupolskii, Introduction of Fluorine with Noble Gas Fluorides // Organo-Fluorine Compounds (Houben-Weyl). / Eds. B.Baasner, H.Hagemann, J.C.Tatlow.- Stuttgart, New York: Theme, 2000.- Vol. E 10a.- P. 219-233.

Fluoride ion and Alcohols: Good friends?

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[1] *Graduate School of Energy Science, Kyoto University, Yoshida, Sakyo-ku, Kyoto, JAPAN*
[2] *Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka, JAPAN*

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Interactions of alcohols and fluoride are of interest for researchers in view of its importance in the design of chemical[1,2] and electrochemical[3,4] reactions. In such systems, the interaction between fluoride ion and hydroxy group is a key factor to determine the activity of fluoride ion, and thus the structural insights on it attracts significant attentions. This study discusses the impact of fluorination of alcohols on their interaction with fluoride ion through experimental and theoretical data. The CsF-hexafluoroisopropanol (HFIP) system exhibits a significantly larger interaction energy than that of the CsF-isopropanol (IP) system (Figure 1) as indicated by the activity coefficient measurements.[5]
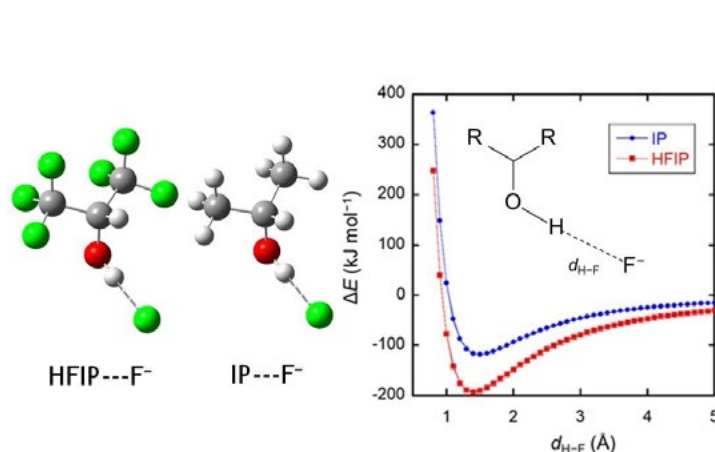

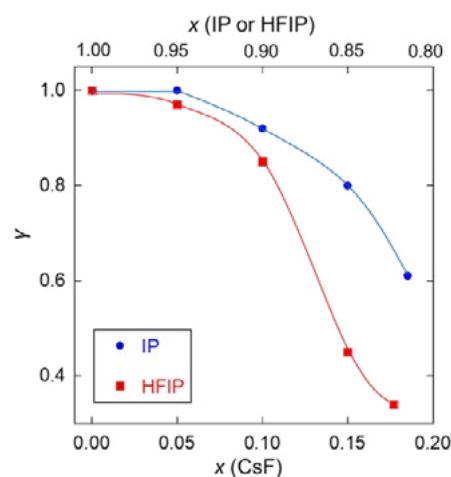Figure 1. Comparison between interaction energies of HFIP---F⁻ and IP---F⁻.[5]

Figure 2. Activity coefficients of alcohols for the CsF−IP and CsF−HFIP systems at 25 °C[5]

References
[1] J. W. Lee, M. T. Oliveira, H. B. Jang, S. Lee, D. Y. Chi, D. W. Kim, C. E. Song, *Chem. Soc. Rev. 45*, 4638-4650, 2016.
[2] K. M. Engle, L. Pfeifer, G. W. Pidgeon, G. T. Giuffredi, A. L. Thompson, R. S. Paton, J. M. Brown, V. Gouverneur, *Chem. Sci.* 6, 5293-5302, 2015.
[3] R. Francke, D. Cericola, R. Kötz, D. Weingarth, S. R. Waldvogel, *Electrochim. Acta* 62, 372-380, 2012.
[4] N. Shida, H. Takenaka, A. Gotou, T. Isogai, A. Yamauchi, Y. Kishikawa, Y. Nagata, I. Tomita, T. Fuchigami, S. Inagi, *J. Org. Chem.* 86, 16128-16133, 2021.
[5] N. Yoneda, H. Iyama, T. Nagata, M. Katahira, Y. Ishii, K. Tada, K. Matsumoto, R. Hagiwara *J. Phys. Chem. Lett.* 15, 1677-1685, 2024.

My Fluorine Chemistry and Ljubljana

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The accidental isolation of the pentafluoro-selenic acid $HOSeF_5$ in 1972 has been our starting point of more than 50 years of our fluorine chemistry [1]. I had the honor to present my work at the first European Symposium on Fluorine chemistry in Ljubljana the same year. I also participated in the Symposia on Fluorine chemistry in Bled and again Ljubljana, which had been organized by Boris Zemva.

Our work advanced with the worldwide advance in fluorine chemistry.

We have tried to focus as much as possible on fundamental problems in the field. The experimental work ended 50 years later with investigations on BrO_2F [2].

References
[1] K. Seppelt, *Angew. Chem. Int. Ed.* 11, 630, 1972
[2] K. Seppelt, *Angew. Chem. Int. Ed.* 58, 189286, 2019

Fluorine-Forged Friendship

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The author's collaboration with Boris Zemva has started at the pivotal period of her research of the new class of fluorinated carbon compounds – fluorofullerenes, following her serendipitous discovery of the selective fullerene fluorination with transition metal fluorides as mild fluorinating reagents. At that time, all the local resources of fluorinating reagents that the author's team could make or receive from collaborators in Russian institutions have been exhausted, while many unanswered fundamental questions regarding the reactivity of fullerenes and the mechanisms of their fluorination remained. As often happens in the fluorine community, it was at the 11th ESFC in Slovenia that Boris and I met and I asked him if he would be interested in collaborating. His answer was swift and positive and in no time we started receiving unique samples of various metal fluorides that we used in our lab to continue the quest for the best fluorinating agents for the fluorination of C_{60}. This collaboration yielded several publications, conference presentations and lab visits.[1-4] The highlights of this research will be presented in this lecture.

In the second part of the lecture, the current results of our synthetic efforts towards fluorinated carbon-rich materials for organic optoelectronics will be presented. Recently, a drastic turn from gas/solid, solvent-free, high-temperature, and hence - thermodynamically controlled fluorinations and perfluoroalkylations, that we were mastering in our labs for years, has been made. This new direction involves light-induced room-temperature perfluoroalkylations of polycyclic (hetero)-aromatic substrates in organic solvents. In the past few years, photochemical perfluoroalkylations have become one of the most intensely studied reactions among synthetic fluoroorganic chemists.[5,6] Initial results involving an array of PAH substrates, perfluoroalkylating reagents and photocatalysts under varying experimental conditions will be discussed, with the focus on intramolecular fluorocyclizations.

References
 [1]   N. I. Denisenko, S. I. Troyanov, A. A. Popov, I. V. Kuvychko, B. Zemva, E. Kemnitz, S. H. Strauss, O. V. Boltalina, *J. Am. Chem. Soc. 126*, 1618-1619, **2004**.
[2]   A. A. Goryunkov, I. E. Kareev, I. N. Ioffe, A. A. Popov, I. V. Kuvychko, V. Y. Markov, I. V. Goldt, A. S. Pimenova, M. G. Serov, S. M. Avdoshenko, P. A. Khavrel, L. N. Sidorov, S. F. Lebedkin, Z. Mazej, B. Zemva, S. H. Strauss, O. V. Boltalina, *J. Fluorine Chem. 127*, 1423-1435, **2006.**
[3]   A. A. Goryunkov, V. Y. Markov, O. V. Boltalina, B. Zemva, A. K. Abdul-Sada, R. Taylor, *J. Fluorine Chem. 112*, 191-196, **2001**.
[4]   A. A. Goryunkov, Z. Mazej, B. Zemva, S. H. Strauss, O. V. Boltalina, *Mendeleev Commun. 16*, 159-161, **2006**.
[5]   N. J. Straathof, D. J. van Osch, A. Schouten, X. Wang, J. C. Schouten, V. Hessel, T. Noël, *J. Flow Chem. 4*, 12-17, **2014**.
[6]   T. Liu, J. Liu, J. He, Y. Hong, H. Zhou, Y.-L. Liu, S. Tang, *Synthesis 54*, 1919-1938, **2022**.

Nucleophilic Fluorination Reagents Based on Difluorosilicates and Difluoroimidazoles

Jaroslav Kvíčala,[1*] Markéta Rybáčková,[1] Šárka Bouzková,[1] Adam Hroch,[1] Michal Trojan,[1] G. Tavčar[2]

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Fluorination of secondary and phenolic substrates belongs to the most tedious processes of organofluorine chemistry. We studied fluorination of secondary substrates, especialy bromides and mesylates, with modified difluorosilicates, and fluorination of activated phenols with difluorobenzimidazole, modified with 4-tolyl groups.
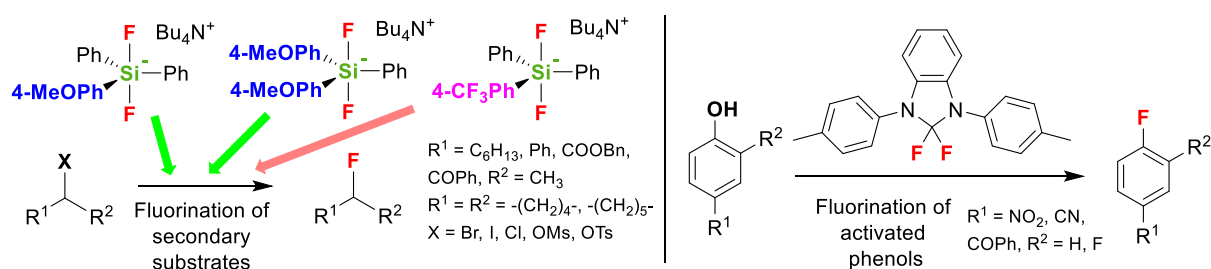

Figure 1: Fluorination of secondary substrates with modified difluorosilicates and of activated phenols with modified difluorobenzimidazole

First part dealt with modifications of the TBAT reagent, developed by Pilcher at al. [1]. We found that substitution of the tetrabutylammonium cation, prone to elimination, for other more stable quaternary ammonium cations did not improve fluorination yields [2]. On other hand, modification of the phenyl ring by electron donating methoxy group(s) improved the fluorination selectivity, while electron accepting trifluoromethyl group had adverse effect [3].

In the second part, we studied new difluoroimidazole compound, an analogue of successful Ritter's PhenoFluor[TM] reagent [4], the synthesis of which does not require intermediary NHC species. The reagent gave moderate yields of fluorobenzenes with activated phenols, while large amounts of the corresponding diphenyl ethers were formed as side products [5].

Experimental results were accompanied by DFT calculations attempting to explain the differences in reactivity compared to the commercial reagents.

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Chemical In-Depth Analysis of (Ca/Sr)F$_2$ Core-Shell Like Nanoparticles by X-Ray Photoelectron Spectroscopy with Tunable Excitation Energy

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The fluorolytic sol-gel synthesis [1] is applied with the intention to obtain two different types of core-shell nanoparticles, namely SrF$_2$-CaF$_2$ and CaF$_2$-SrF$_2$. In two separate fluorination steps for core and shell formation, the corresponding metal lactates are reacted with anhydrous HF in ethylene glycol [2]. Scanning transmission electron microscopy (STEM) and dynamic light scattering (DLS) confirm the formation of particles with mean dimensions between 6.4 and 11.5 nm.

The overall chemical composition of the particles during the different reaction steps is monitored by quantitative Al Kα excitation X-ray photoelectron spectroscopy (XPS). Here, the formation of stoichiometric metal fluorides (MF$_2$) is confirmed, both for the core and the final core-shell particles[3].

Furthermore, an in-depth analysis by synchrotron radiation XPS (SR-XPS) with tunable excitation energy is performed to confirm the core-shell character of the nanoparticles. In principle, core-shell like structures are formed, but without a sharp interface between calcium and strontium containing phases. Surprisingly, the in-depth chemical distribution of the two types of nanoparticles is equal within the error of the experiment. Both comprise a SrF$_2$-rich core domain and CaF$_2$-rich shell domain with an intermixing zone between them. Consequently, the internal structure of the final nanoparticles seems to be independent from the synthesis chronology.
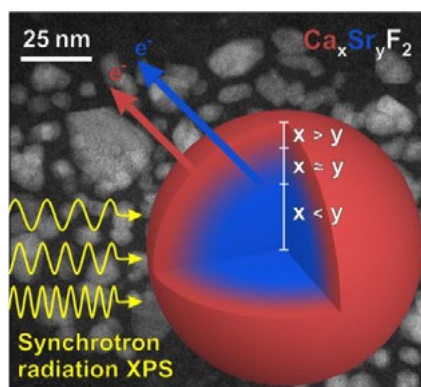
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Simplifying Fluoroalkylation Reactions with Nickel

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Simple nickel salts have been prepared that either bear only fluoroalkyl ligands or fluoroalkyl ligands with solvent a co-ligands.[1-3] These complexes were characterized by a variety of analytical techniques in order to provide insights into their electronic structures and reactivities. Trifluoromethyl and perfluoroethyl derivatives were prepared in order to compare and contrast their reactivities and fundamental properties. Reactivities that will be discussed include catalytic C-H perfluoroalkylations of electron rich arenes, stereoselective perfluoroalkylation of natural products, and stubborn reductive eliminations involving the perfluoroalkyl groups.
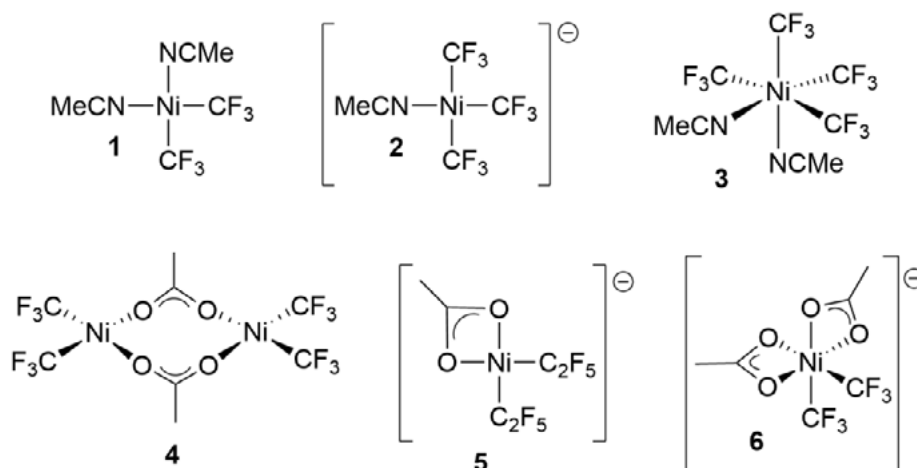
Figure 1: Trifluoromethyl and perfluoroethyl nickel complexes bearing simple supporting co-ligands.

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# RuF_6, a stronger Oxidizing Agent than PtF_6: Oxidation of Halogen Pentafluorides with RuF_6

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Platinum hexafluoride is known for its enormous oxidizing power. It gained its popularity mainly due to its ability to oxidize Xe, forming the first noble gas compound "XePtF6".[1] It was only a few years later that the actual composition of the reaction products could be determined, which was a mixture of $[XeF][PtF_6]$ and $[XeF][Pt_2F_{11}]$.[2] In addition to Xe, PtF_6 is also able to oxidize various other compounds whose oxidation seemed impossible at the time. For example, NF_3 or ClF_5 can be oxidized to the coordinatively saturated cations $[NF_4]^+$ or $[ClF_6]^+$.[3,4] However, the formation of $[BrF_6]^+$ by the reaction of BrF_5 and PtF_6 is not possible. To oxidize BrF_5, even stronger oxidizing agents such as $[KrF]^+$ or $[NiF_3]^+$ generated in situ are required.[5]

Our work shows that RuF_6 is able to oxidize all known halogen pentafluorides XF_5 (X = Cl, Br, I) at room temperature to the respective $[XF_6]^+$ salts, according to equation (1).

$$XF_5 + 2\ RuF_6 \longrightarrow [XF_6][Ru_2F_{11}] \qquad (1)$$
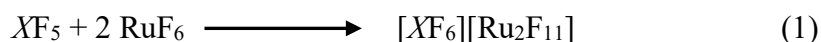
The compounds obtained were characterized using various methods, e.g. Raman spectroscopy and single-crystal X-ray structure analysis.

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Structural Peculiarities of some d-Transition Compounds in Fluorinated Environments

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This work focuses on two singular examples: [i)] the room-temperature structure of Pd(II) compounds synthesized in aHF, and [ii)] one of the very rare Jahn-Teller Cu(II) compounds in which divalent copper is located in a compressed octahedral environment, These data are based on results obtained over years in cooperative works between ICMCB and IJS.

- Palladium element is known to exhibit various oxidation states, e.g. II to IV, in fluorinated environments. In the case of $Pd^{II}F_2$, besides the rutile-type form obtained from room pressure reactions, a high-pressure (HP) form had been isolated in reactions conducted in a HP "belt" system around 50 kbar. This HP form was shown to derive from the fluorite type by a rhombohedral distortion of the cubic environment of the cation [1].
A similar structural network has been obtained via a LT route, by mixing $Pd(AsF_6)_2$ and CsF in anhydrous HF [2]. A minimum of reciprocal susceptibility occurs around 180 K, a value which is similar to the Néel temperature of HP-PdF_2 (T_N = 190 K), as determined by neutron diffraction experiments. Another Pd(II) compound: $Pd(AsF_6)_2$, can be obtained in AsF_5/aHF superacidic medium either by oxidising metallic palladium as solvated Pd^{2+} cations or by adding elemental fluorine into a suspension of PdO, from which $Pd(AsF_6)_2$ could be isolated. The crystal structure of $Pd(AsF_6)_2$ confirms the presence of highly distorted $(AsF_6)^-$ anions as predicted by vibrational spectroscopy [3]. The network is derived from the $LiSbF_6$ type (ordered ReO_3) with ordered vacancies for half of the cationic sites, i.e. $Pd_{0.5}\square_{0.5}AsF_6$. In the series of transition-metal difluorides the sequence: fluorite > LT-PdF_2 > rutile is followed, and may explain why the LT form is stabilized with respect to the rutile form via a LT process.

- In Cu(II)-based fluorides, the crystal structures and magnetic properties of $CuFAsF_6$ and $CsCuAlF_6$, prepared in aHF medium or by solid state reaction respectively, illustrate two rare examples of Cu(II) compounds with a compressed tetragonal geometry of $[CuF_6]^{4-}$ octahedra. Both structural networks are composed of 1-dimensional infinite $[CuF_5]_n^{3n-}$ chains of $[CuF_6]^{4-}$ octahedra sharing opposite corners. Their magnetic behavior can be compared to those of other 1D networks containing Cu(II) in which a non-compensation of magnetic moments occur at low temperature, as also in CrF_4 [5].

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α-Silyl Carbanions Stabilized by Pentafluoroethyl Groups

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As early as 1947, GRIGNARD reagents were used by SOMMER et al. to synthesize α-silyl carbanion-equivalent compounds [1]. Since then, various methods have been developed to generate α-silyl carbanions in situ [2][3][4][5]. Due to the instability of these compounds, it has only been possible to structurally characterize α-silyl carbanions in two cases [6][7].

In this lecture, the synthesis of isolable α-silyl carbanions stabilized by pentafluoroethyl groups on the silicon atom will be presented and their reactivity will be discussed. With regard to reactivity, particular attention will be paid to the reaction with carbonyl compounds, based on Peterson olefination.
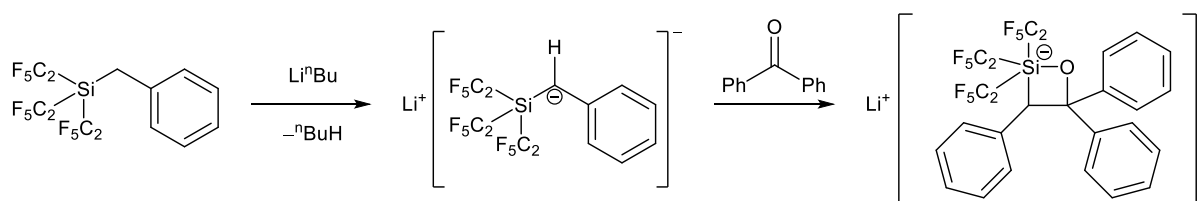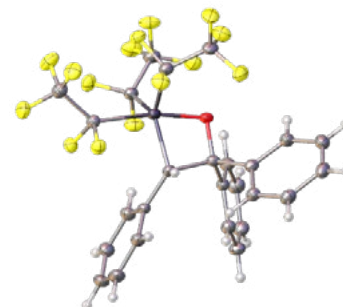

Figure 1: α-Silyl carbanions stabilized by pentafluoroethyl groups.

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Fluorochemicals with Uniquely Important Applications in Electronics

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Processing of semiconductor materials that are used in the fabrication of integrated circuits and computer chips is heavily dependent on the use of many different fluorochemical products employed at various critical stages throughout the fabrication lifecycle. For example, WF_6 is used for tungsten metal deposition; NF_3 and other fluorocarbons are used for chamber cleaning; and many different fluorocarbons, including fluoroalkanes and hydrofluorocarbons are used for various reactive-ion etching steps that collectively create the intricate electronic circuitry on a silicon wafer that results in a computer chip. And the semiconductor industry's dependence on fluorine technology has never been stronger than it is today. For example, atomic layer deposition, ALD, is a well-known and widely used technology for precision control of atomic layer by layer deposition. The complimentary process, atomic layer etching (ALE), has emerged as a critical enabling technology required for controlled and systematic layer by layer etching of device features as the required dimensions shrink to well-below 10 nm. One area of great need and especially for thermal ALE is the development of new fluorinated materials and methodologies that will improve efficiency, selectivity and self-limiting characteristics while reducing cycle times and collateral damage that is so often the result when plasma-assisted ALE processing is employed.

In addition to the "common" fluorochemicals traditionally used in semiconductor materials processing, there currently are several emerging fluorine compounds under development that provide both sustainable and environmentally friendly alternatives to the legacy materials used in semiconductor technology. An overview of fluorochemicals' importance to the electronics industry including some recent advances in technology development will be highlighted in this presentation.

Adventures in Xenon- and Mercury-Chemistry with Weakly Coordinating Perfluoroalkoxyaluminate Anions

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This lecture will honor the achievements of Boris Zemva and hence report on our own adventures in trying to prepare the seemingly simple 'naked' $Hg[WCA]_2$ salt as well as upon investigating the deelectronation capability of the mixture $XeF_2 + 2 Li[WCA]$ to formally give 2 LiF, Xe gas and two positive charges (WCA = $[pf]^-$ ($[Al(OR^F)_4]^-$) or $[alfal]^-$ ($[R^FO)_3Al$-F-$Al(OR^F)_3]^-$) and $R^F = C(CF_3)_3$).

Hence, the reaction of $XeF_2 + 2 Li^+$ in fluorobenzenes xFB (x = 1,2,3) intermediately led to radicals, from which the $[Xe((C_6F_xH_{5-x}))]^+$ salts formed and which subsequently reacted already at low temperatures (–40 °C) to the biphenyl radical cation salts shown in Figure 1. The pathway and intermediates are reported and rationalized as well as the scope of these partially extremely deelectronating cations like tetrafluorobiphenyl ($E°' = 1.80$ V vs. Fc^+/Fc) and hexafluorobiphenyl ($E°' = 2.10$ V vs. Fc^+/Fc) is delineated.

The seemingly simple 'naked' $Hg[WCA]_2$ salt should be an attractive starting material for further Hg^{2+} coordination chemistry. Yet, most of the hitherto tested routes to such salts ended up with the formation of chain-cations $[Hg_n]^{2+}$ (n = 2, 3, 4), which include two η^1-coordinated xFB solvents as ingredient. Scope and limits are explained and it is shown that xFB solutions containing the 'naked' Hg^{2+} cation react with the latter already at very low temperature under C-H bond activation to give monocations $[Hg(C_6F_xH_{5-x})]^+$ and also do activate silicon grease based on $(Me_2SiO)_n$ with formation of the $[Hg(Me)]^+$ cation salts. So, exclude silicon grease!
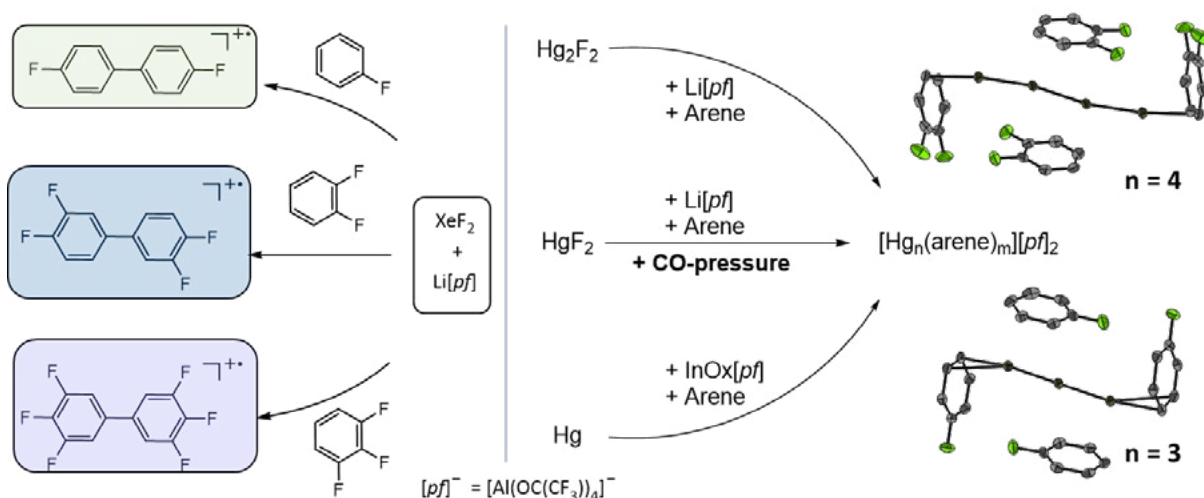

Figure 1: Final outcome of the delineated reactions. InOx = Innocent Oxidant, e.g. $[C_{10}F_8]^{+\cdot}$.

References: All of this work is hitherto unpublished and credits go to the excellent PhD student M.Sc. Chem. Konstantin Kloiber.

Novel two-dimensional quantum magnets based on Ag(II)

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There is an upsurge of interest in Ag(II)-based materials, in particular two-dimensional ones [1]. The focus is on magnetic properties of these systems as Ag(II) is a powerful spin-polarizer which often shows strong antiferromagnetic superexchange (SE) even via fluoride ligands (the least polarizable monoatomic ligands known). Superexchange between Ag(II) and other transition metal cations is also of interest but only very few cations may withstand the oxidizing power of Ag(II).

We have recently successfully prepared two novel Ag(II) based systems, $AgCoF_5$ [2] and $CuAg(SO_4)_2$ [3]. The first one is characterized by a strong Ag(II)/Co(III) SE with the SE constant of *ca.* –62 meV, which is similar to the value for pristine AgF_2 of –70 meV [1]. Our calculations predict that similar isostructural monoclinic $AgAgF_5$ featuring high-spin Ag(III) could also be prepared and it should host even stronger SE interactions (-100 meV for Ag(II)/Ag(III) and -93 meV for Ag(III)/Ag(III)) [2]. On the other hand, $CuAg(SO_4)_2$ shows a two-dimensional $[Ag(SO_4)_2^{2-}]$ sublattice (Figure 1) with SE constant of ca. -11.1 meV; here, SE is transmitted via a larger sulphate ligand, just like for $AgSO_4$ [4]. Despite that, SE could be quite strong for some as yet hypothetical members of the $M(II)Ag(SO_4)_2$ family (for example ca. -49 meV for M=Ba [3]).

While predominant magnetic SE interactions are antiferromagnetic in these compounds, their magnetic properties may be quite complex. $CuAg(SO_4)_2$ has recently been postulated to be one of very few systems which host a new form of magnetism called altermagnetism [5].
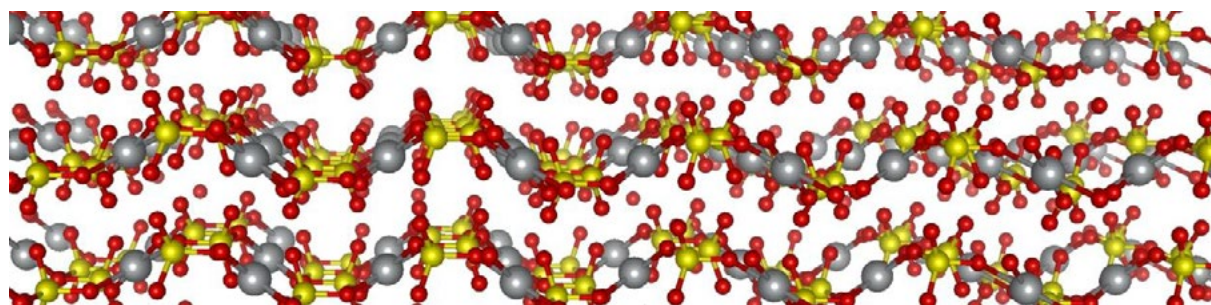

Figure 1: The two-dimensional $[Ag(SO_4)_2^{2-}]$ sublattice of $CuAg(SO_4)_2$.

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Tris(pentafluoroethyl)difluorophosphorane:
A Versatile Fluoride Acceptor for Transition Metal Chemistry

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Fluoride abstraction reactions from different types of transition metal fluoride complexes [L_nM-F] using the *Lewis* acid tris(pentafluoroethyl)difluorophosphorane $(C_2F_5)_3PF_2$[1] to yield cationic transition metal complexes with the weakly coordinating tris(pentafluoroethyl)trifluorophosphate counterion (**FAP** anion, $[(C_2F_5)_3PF_3]^-$) are presented (see Figure 1).[2] Some basic (stereo-electonic) properties of the phosphorane will be discussed as well as NHC adducts of this phosphorane.[3] $(C_2F_5)_3PF_2$ reacts with NHC (= *N*-Heterocyclic Carbene) nickel fluorides, with titanocene difluoride, and with NHC copper fluorides to yield cationic organometallic complexes with the **FAP** counterion.[2] First investigations concerning the reactivity of these salts and their application in catalysis will be presented.
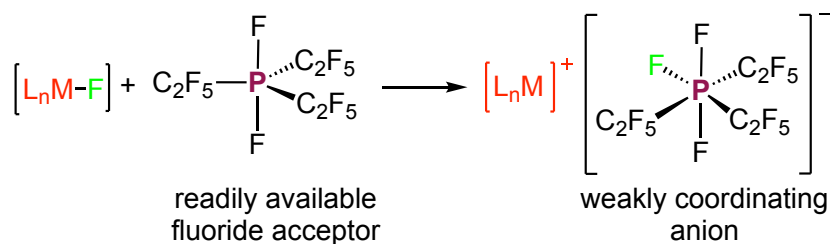

Figure 1: Fluoride abstraction from transition metal fluorides with the *Lewis* acid tris(pentafluoroethyl)difluorophosphorane.

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Unusual Fluorine Containing Compounds:
from Oxyfluorides and High Potential Oxidizers

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In recent years, several unusual fluorinated compounds have been investigated under cryogenic conditions using matrix-isolation spectroscopy in conjunction with quantum-chemical calculations, confirming experimental assignments and providing fruitful information on the stability and properties of such species. Here we will provide new insights into the formation of single oxygen atom coordination by Lewis-acids as well as hypervalent coordinated oxygen atoms. Furthermore, we will show that fluorine atoms are able to undergo heavy atom tunneling processes.
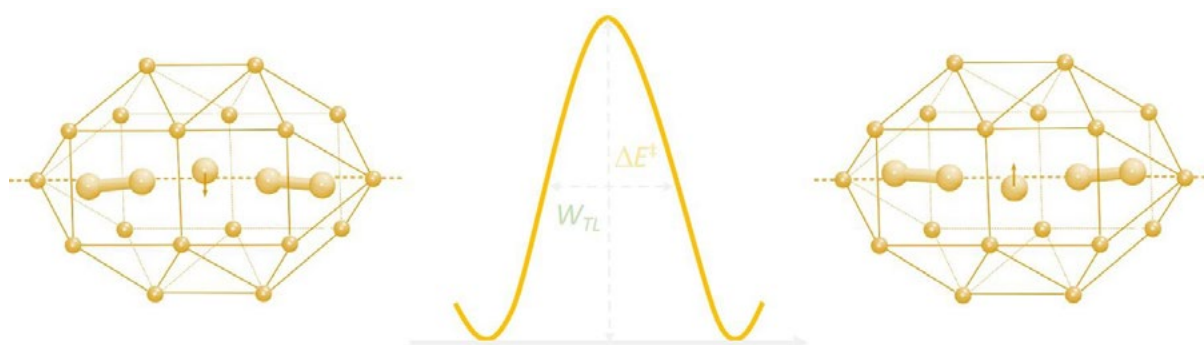

Figure 1: Heavy atom tunneling in polyfluorides

Fluorinated aminophospohonates and amino acids with olefinic motif – versatile peptidomimetics

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Aminophosphonates are compounds showing pronounced and interesting biological activity (e.g. are potent drugs against osteoporosis). Especially, considering the acidity and a steric impact, fluorinated phosphonates are frequently used as the non-hydrolysable and stable mimics of naturally occurring phosphates. Similarly fluorine modified carbohydrates (e.g. hyaluronic acid monomers) display interesting biological activity. The search for a new strategies of the synthesis of these compounds is a consequence of the previous studies in our group. Our research has been focused on new approach to a stereocontrolled synthesis of several mono and difluorinated aminophosphonates and later their dipeptides analogues. As a key strategic intermediates for a stereoselective synthesis, aziridine, oxirane or imine derivatives of fluorophosphonates were prepared and their transformations had been studied.

Peptidomimetics are compounds derived from peptides obtained by structure modification using unnatural amino acids and/or conformational restraints. Modified fluorinated amino acids are of great interest as the building blocks for the preparation of peptidomimetics. Herein we would like to report the synthesis of fluorinated analogues of amino acids bearing olefinic moiety with the use of the synthetic sequence with Horner-Wadsworth-Emmons reaction as a key reaction.
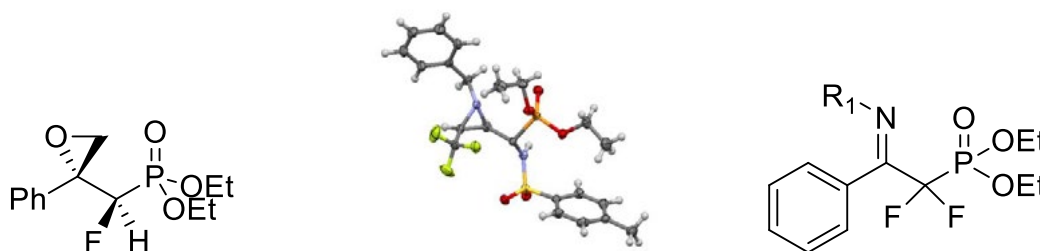

Figure 1. Examples of some intermediates used in the fluorophosphonates preparation

34

One Of The Smallest Elements Of
The Periodic Table, But The Diamond Of Our Life, Element F2

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The occurrence, discovery, isolation of element fluorine and its contributions to the field of space exploration, refrigeration, surface treatment, dental hygiene, health, agriculture and high-energy density lithium and lithium ion batteries, lubrication etc. will be discussed in this presentation.

Rhodium-Mediated C-H and C-F Bond Activation to Access Fluorinated Alkene Derivatives

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Useful methods for a metal-mediated derivatization of fluorinated molecules are often based on C−H or C−F bond activation reactions.[1] In order to make C−F bond cleavage steps feasible, other strong element−fluorine bonds such as H−F or Si−F bonds have to be formed. Thus, at rhodium, highly reactive Rh(I) species such as $[Rh(H)(PEt_3)_3]$, $[Rh\{Si(OEt)_3\}(PEt_3)_3]$ or $[Rh(GePh_3)(PEt_3)_3]$ can serve as suitable tools to induce a C−F bond activation step, but also C−H bond activation reactions.[2] Stoichiometric studies at the rhodium complexes as well as initial catalytic reactions for the hydrodefluorination, silylation or germylation of olefinic precursors will be described (Figure). In another spin-off catalytic cross-coupling reactions were developed, which are characterized by an outer-sphere C-C coupling step.
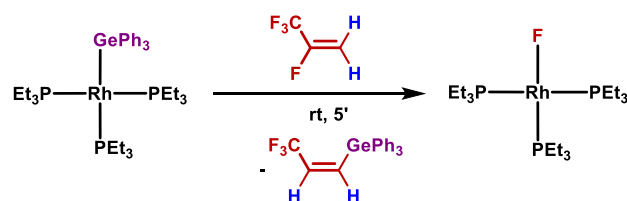

Figure: A Rh germyl complex for the germylation of a fluorinated olefin.

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Unusual Reactivity Triggered By Fluorine – From Exotic Complexes To Novel Reaction Mechanisms

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One of the peculiarities of fluorine is that on one hand it is the most reactive element, but on the other, its compounds are often ranked as the most inert. This feature is used to form so-called weakly coordinating anions (WCAs), which are typically perfluorinated species.[1] Their properties render typical cations extraordinarily reactive which opens new possibilities in chemistry.

The presentation shows our recent advancements enabled by pairing simple metal cations with the most advanced WCAs. This includes the synthesis of novel, otherwise unstable metal complexes containing exotic ligands like N_2 (Fig. 1a)[2] but also noble gas atoms. But salts of WCAs, even those containing simple metal cations can also efficiently catalyze organic reactions, at times according to novel mechanisms (Fig. 1b).[3]
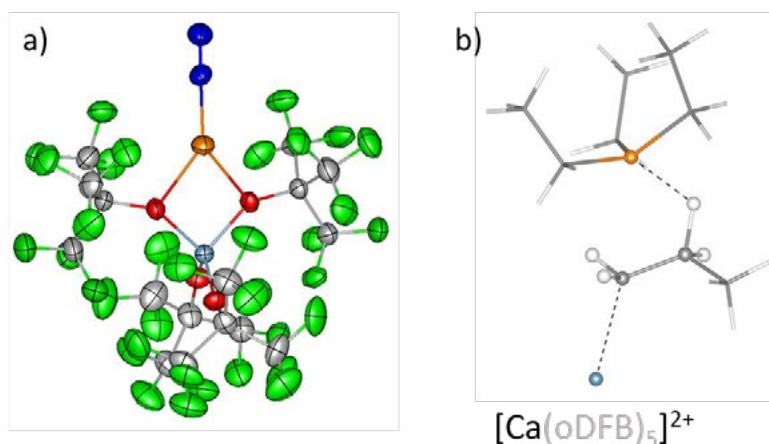

Figure 1: a) Crystal structure of Cu^+-N_2 complex stabilized with perfluorinated alkoxyaluminate; b) Transition state structure of reaction of olefin hydrosilylation catalyzed by Ca^{2+} cation.

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Theranostic Applications of Fluorinated Dendrimers

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Janus-type dendrimers (JDs) are dendritic macromolecules bearing two domains of different polarity. A tailored balance between the two portions allows to control their physico-chemical properties, and therefore their functions. The use of fluorinated chains is a powerful tool to increase JDs colloidal stability and influence their self-assembling properties [1]. Moreover, the use of branched fluorinated moieties can be exploited for non-invasive *in vivo* monitoring by ^{19}F-MRI to develop new theranostic nanosystems [2].

In this lecture, I will show how the balance between a perfluoro-*tert*-butyl moiety and polyester dendrons of generations 1-3 can strongly affect self-assembling behavior of a family of Fluorinated JDs (FJDs) [3], see Figure 1, and how the final physico-chemical properties can be exploited to synthesize an ionizable fluorinated JD for gene delivery applications [4].
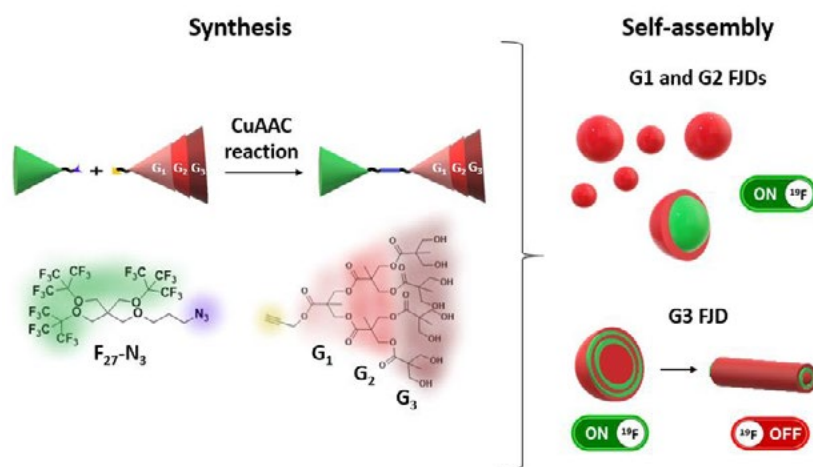

Figure 1: The three fluorinated JDs (Gen. 1 to 3) showed different magnetic properties at ^{19}F-NMR depending on their self-assembly in water media.

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Electrochemical Fluorination:
Synthesis of Fluorine-Containing Building Blocks

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The incorporation of fluorine into molecules and materials typically results in unique properties, which are relevant for applications, e.g. pharmaceuticals, agrochemicals, and energy-related materials [1]. The electrochemical fluorination (ECF, Simons process) is an efficient process for the synthesis of fluorinated molecules [2,3]. Per- and polyfluorinated compounds that are accessible via ECF include $CF_3SO_2N(CF_3)_2$ and $CF_3SO_2N(CF_2H)_2$ [4], $FSO_2(CF_2)_nSO_2F$ (n = 1–3) [5], and $(C_2F_5)_3PF_2$ [6]. Recently, we have adopted the ECF for the preparation of partially fluorinated alkyl triflates, e.g. $CF_3SO_2OCH_2F$ and $CF_3SO_2OCHF_2$ [7]. The aforementioned fluorinated molecules are versatile building blocks for organic, coordination, and materials chemistry. For example, copper and silver complexes with the bis(trifluoromethyl)amido ligand were established as $N(CF_3)_2$-transfer reagents [8] and ionic liquids (ILs) with the $[(C_2F_5)_3PF_3]^-$ (FAP) anion [2,3,9] or cyclic perfluoroalkylsulfonylimide anions [10] have been developed.

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High-pressure chemistry and physics of fluorides

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Current diamond anvil cell (DAC) techniques enable performing routine measurements on solids compressed to 100 GPa (million atmospheres). At such conditions the pressure-volume work term (pV) becomes comparable to covalent bond energies therefore considerably affecting the chemistry, structure, and properties of compounds that are otherwise well known and characterized under ambient conditions. In addition, species that are hard to attain or even yet unknown can be stabilized by high pressure. [1,2] Theoretical studies hint at the increased electronegativity and reactivity of fluorine at high pressure (p > 1GPa), and hence the possibility of formation of exotic species, such as NF_5, [3] AuF_6, [4] or IF_8. [5] On the other hand, well known fluorides (e.g. $NaMgF_3$) have been shown to be excellent low-pressure analogues (LPAs) of silicates, which are the major component of rocky planets. [6]

In an attempt to better understand the high-pressure reactivity and properties of halogen fluorides, which are archetypical compounds used for testing fundamental chemical concepts (e.g. molecular orbital theory or the VSEPR model) we performed a computational study on the high-pressure behavior of bromine fluorides. [7] We found that at a moderately high pressure of 15 GPa, the bonding preference in the Br/F system should change considerably with BrF_3 becoming thermodynamically unstable and two novel compounds emerging as stable species: BrF_2 and BrF_6.

In another study, combining both experiment and calculations, we show that above 30 GPa Na_2CuF_4 adopts a Th_3P_4-like structure, and that the high-pressure properties of this polymorph closely mimic those of an analogous structure of Mg_2SiO_4 – a compound that is predicted to form in the mantle of rocky planets under sub-TPa conditions. [8]

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Chloroimidazolium Deoxyfluorination Reagent with $H_2F_3^-$ Anion as a Sole Fluoride Source

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The selective and efficient introduction of fluorine is still an unresolved challenge. Direct fluorination via the "electrophilic" route has problems with selectivity, as there are usually several reaction sites available. On the other hand, the nucleophilic pathway is a selective process as the reaction site is defined by a substituent. However, the fluoride anion is a difficult nucleophile, and several approaches have recently been developed to overcome the disadvantage of nucleophilic fluorination and provide a general and cost-effective method [1] Fluorination with imidazolium-based fluoride reagents has evolved since the 2000s. The best known members of this reagent family include PhenoFluor [2] and its air-stable successor AlkylFluor, [3] which appear to be the favoured reagents for the deoxyfluorination of phenols and aliphatic alcohols, respectively. The use of dihidrotrifluoride anions as a source of fluorine atoms in NHC-based reagents has been developed as a shelf-stable fluoride source with the properties of a free fluorine reagent. [4] It has been further developed into a renewable fluorinating reagent for the fluorination of various organic substrates (benzyl halides, aliphatic halides, tosylates, mesylates, α-haloketones, a silyl chloride, acyl and sulfuryl chlorides, and a nitroarene).[5]

We discuss the use of imidazolium-based reagent **1** for fluorination of substrates containing –OH or P(V)OH groups, such as alcohols, carboxylic acids and phosphates, to convert them to their respective fluorides without additional fluoride sources. We also investigated the mechanism of oxygen transfer to form imidazolone 2.
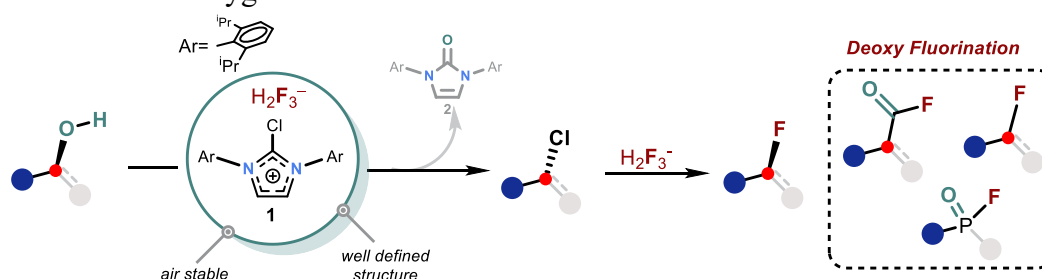

Figure 1. Deoxyfluorination with chloroimidazolium $H_2F_3^-$ reagent

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Do We Still Need To Determine Crystal Structures Experimentally?

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First structural information on $LiAuF_4$ was derived from X-ray powder diffraction data in 1970 [1]. A tentative model in monoclinic space group C/c was suggested and compared to tetragonal $KBrF_4$-type structure. Symmetry of the monoclinic model was further reduced in 1991 based on single crystal data [2]. However, in a footnote in 1998 Neil Bartlett and coworkers mentioned the model in $C2/c$ being the correct one [3]. A single crystal selected from this very sample was used to evaluate single crystal diffractometers suitable for K1 at IJS in 1996. This obviously simple crystal structure proved very challenging for the application labs of all major vendors involved. The fact that both monoclinic models are still present in major data bases calls for some clarification. Even more as this confusing information is being incorporated in newer types of data compilations like Materials Project [4].

Clearly a deeper understanding of specific experimental details for this peculiar structure very likely will help to deal with any challenging case. A quite recent example is demonstrated for the metallic delafossite $PdRhO_2$ [5].

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ABSTRACTS

Student session

Phase Transitions in Compressed Palladium Trifluoride

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Fluorides are model systems for the study of pressure-indcued structural transitions, as well as compression-induced reactivity. [1,2] In particular, transition metal fluorides can exhibit high-pressure transformations involving both electronic and magnetic degrees of freedom. [3]

Palladium trifluoride adopts at ambient conditions a distorted ReO_3-type structure with two inequivalent Pd sites exhibiting II and IV valency. [4] This charge ordering leads to different electron counts and spin population at both sites – Pd^{2+} with a d^8 count has two unpaired electrons, while Pd^{4+} (d^6) has no unpaired electrons. Recent theoretical investigation suggest that this compound should undergo two consecutive phase transitions at 19 and 57 GPa, [5] a prediction yet to be verified. Moreover, the question whether large compression will force $Pd^{(II)}Pd^{(IV)}F_6$ into a metallic state, or rather a spin-1/2 semiconductor state with genuine Pd^{3+} cations, is still open.

Our Raman measurements indicate that palladium trifluoride retains the ambient pressure $R-3$ structure up to 41 GPa. Above this pressure a transformation occurs into new phases containing Pd^{3+} cations therefore exhibiting a crossover from mixed valency (II and IV) to single valency (III).

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Preparation and Structural Characterisation of Salts Containing the Unique [MF$_3$(XeF$_2$)$_3$]$^+$ (M = Pd, Pt) Adduct Cations

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The reactions of XeF_2 with Lewis acidic tetra- and pentafluorides has been a subject of interest since the discovery of noble-gas reactivity, where the interaction of Xe with PtF_6 resulted in the formation of compounds of XeF_2 with platinum in either +4 or +5 oxidation states [1,2]. Investigations of XeF_2–MF_5 systems have revealed a plethora of compounds with 2:1, 1:1 and 1:2 stoichiometries, which were shown to be ionic species with discrete structures [3,4]. Conversely, crystallographically characterised XeF_2–MF_4 (M = Ti, Cr, Mn) adducts display considerably greater structural diversity, exhibiting either oligo- or polymeric structures [5–8]. In the present work, we report on the synthesis and structural characterisation of $[Xe_2F_3][MF_3(XeF_2)_3][AsF_6]_2$ (M = Pd, Pt). The $[MF_3(XeF_2)_3]^+$ adduct cations are composed of octahedrally coordinated M^{IV} centres, with three of the coordinating F atoms provided by *fac*-coordinated XeF_2 ligands (Figure 1). These unique compounds represent the first example of multiple XeF_2 molecules bonded to a single M^{IV} centre as well as the only example where coordination of XeF_2 to M^{IV} results in a mononuclear species. Moreover, the $[PtF_3(XeF_2)_3]^+$ adduct cation is the first crystallographically characterised case of XeF_2 coordination to Pt^{IV}.
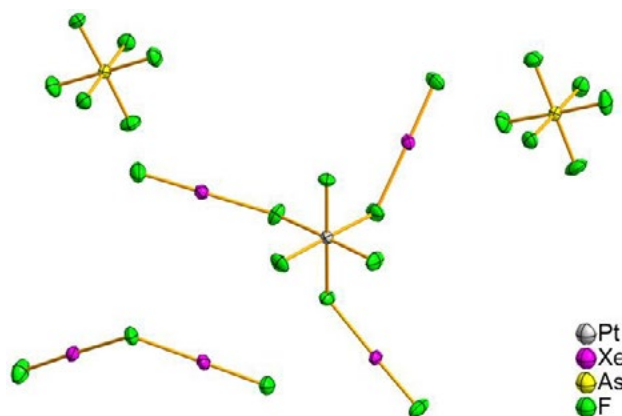

Figure 1: Crystal structure of $[Xe_2F_3][PtF_3(XeF_2)_3][AsF_6]_2$ (50% probability ellipsoids).

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Pyridine and pentafluoropyridine as ligands in transition metal complexes

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Pyridine is a commonly used basic solvent in organic chemistry that can donate coordination bonds via its nitrogen atom. Transition metal complexes with pyridine have been studied for decades. [1] Replacing hydrogen atoms with five fluorine atoms in pyridine increases steric hindrance and significantly reduces electron density at the nitrogen atom, weakening its Lewis base properties. Consequently, complexes with pentafluoropyridine (PFP) are rare, with only a few known platinum complexes [2-5], which may act as efficient oligomerization catalysts [5].

In our research, we successfully synthesized $Ag(C_5F_5N)_4^+$ and $Ag(C_5F_5N)_3^+$ cations supported by weakly coordinating alkoxyaluminate anion – $[Al(OC(CF_3)_3)_4]^-$. [6] We extended this research to attempt the synthesis of divalent cation salts containing pentafluoropyridine. Although most attempts were futile, we successfully obtained a Fe salt (Figure 1). We also synthesized the corresponding pyridine complexes, and all compounds were analyzed using DFT calculations to determine their Lewis acidity (fluorine ion affinity, FIA) and enthalpy of formation. These findings highlight the challenges and potential of pentafluoropyridine in coordination chemistry, paving the way for further exploration of its applications in catalysis and material science.
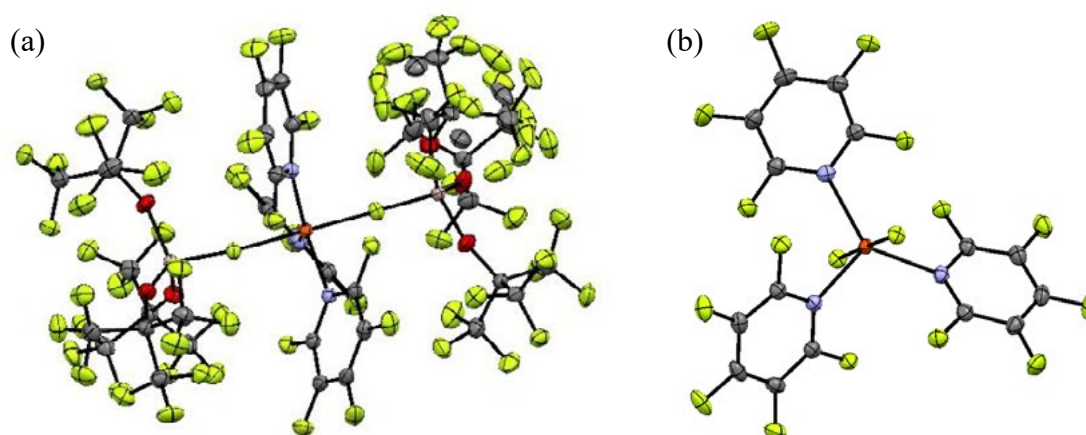

Figure 1: Obtained molecular compound containing Fe(II) cation and 3 pentafluoropyridine molecules: whole molecule (a) and highlighted metal coordination sphere (b)

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Protective Role of Aluminium Against Fluoride Toxicity in THP-1 Monocytes

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Monocytes are ideal targets for the assessment of chemical toxicity due to their crucial role in the immune system, sensitivity to environmental stressors and ability to reveal systemic toxicological effects. As precursors of macrophages and dendritic cells, monocytes circulate in the bloodstream and can respond rapidly to toxic exposures, providing early indicators of immune activation and damage. When exposed to toxic substances such as fluoride (F^-) and aluminium (Al), monocytes show changes in viability, cytokine production and oxidative stress markers [1,2]. These responses can be measured quantitatively to assess the extent of toxicity. There are few studies investigating the toxicity of F^- and Al on monocytes/macrophages, but the toxicity of aluminium-fluoride complexes (AlF_x) formed in aqueous solutions remains largely unexplored.

To fill this gap, we investigated and compared the toxicity of F^-, Al and AlF_x using THP-1 monocytes *in vitro*. The cells were treated for 48 hours with standard solutions of F^-, Al and AlF_x at concentrations ranging from 2 to 2000 μM. Flow cytometric analyses and annexin V/propidium iodide (PI) assays were used to determine the early and late stages of apoptosis and necrosis. The greatest differences in toxicity were observed a 2000 μM concentration (Figure 1). F^- showed the highest toxicity, while Al showed the lowest toxicity. The presence of Al appears to attenuate the toxicity of F^- due to the formation of AlF_x.
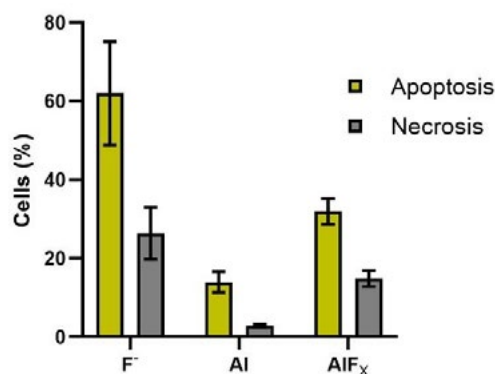
Figure 1: Percentage (%) of apoptotic and necrotic cells after 48 h stimulation with 2000 μM F^-, Al and AlF_x standards. The values are given as mean ± SD.

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Hydrosilylation of olefins on highly reactive calcium cation

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Olefin hydrosilylation is a process, in which an addition of the Si-H bond to the multiple C=C bond takes place. The organosilicon compounds, which are formed afterward, can be found in a wide range of substances, such as adhesives, coatings, and antifoams, to name just a few. Hydrosilylations that are performed at a commercial scale usually rely on precious metal catalysts, which can boost their final price by as much as 30%.[1] Therefore, there are ongoing efforts towards designing a new class of catalysts, that would be cheap and efficient, but also as versatile as possible, hopefully with a low toxicity profile.

The pseudobinary calcium salt of a Weakly Coordinating Anion (WCAs), $Ca[Al[OC(CF_3)_3]_4]_2$ **(1)** seems to fulfill these criteria. Upon dissolution in 1,2-difluorobenzene, it forms a highly acidic $Ca(C_6H_4F_2)_6{}^{2+}$ complex, with the FIA value comparable to SbF_5. Thanks to the totally perfluorinated surface and in the presence of weakly solvating solvents, the salt has proved to catalyze often demanding hydrosilylations, with sterically-hindered substrates. The key stage, as confirmed by both ^1H NMR monitoring and DFT calculations, is the olefin coordination to the calcium cation, which leads to C=C bond polarization, which ensues with the subsequent H^- abstraction from the silane molecule and its coordination to the olefin-Ca^{2+} complex (**Figure 1**). Quantitative NMR studies, carried out for several hydrosilylation systems give hope for developing a new class of catalysts, which can exhibit unique properties in a weakly solvating environment. [2]
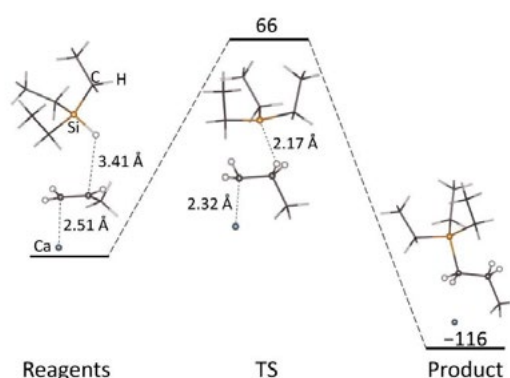

Figure 1: Hydrosilylation pathway for a propene/triethylsilane model system catalyzed by **(1)**. TS denotes the transition state, in which alkyl anion is formed, binding eventually to the olefin-Ca^{2+} complex.

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Novel Xe^{II}−N-bonded compounds derived from cyanogen

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Compounds containing Xe^{II}−N bond can be synthesized by reactions of Lewis acidic xenon(II) derivatives such as $[XeF]^+$ and $[XeOTeF_5]^+$ with oxidatively resistant nitrogen bases [1–6]. However, only one xenon(II) moiety could be coordinated to the corresponding Lewis base.

To investigate the possibility of bonding multiple xenon(II)-based moieties to a polytopic nitrogen Lewis base, the reaction between the simplest ditopic nitrogen base cyanogen and $[XeF][AsF_6]$ was carried out at low temperatures. This led to the isolation of $[FXeNCCNXeF][AsF_6]_2$ in which a nearly linear cation $[FXeNCCNXeF]^{2+}$ (Figure 1a) has the longest Xe−N and the shortest Xe−F bonds in the series of crystallographically characterized $[R{\equiv}NXeF]^+$ adduct cations [4,5]. The $[FXeNCCNXeF][AsF_6]_2$ compound undergoes a formal fluoride rearrangement, similar to the one observed in $[F_3SNXeF][AsF_6]$ [7], yielding $[XeNC(F)C(F)NXe][AsF_6]_2$ (Figure 1b), which features a unique C=N−Xe bonding modality. This compound is remarkably stable at room temperature and could be used as a suitable starting material for further studies of xenon–nitrogen chemistry due to the presence of σ-holes on the Xe^{II} atoms. This was demonstrated by the low-temperature synthesis of its acetonitrile adduct, $[CH_3CN{\cdots}XeNC(F)C(F)NXe{\cdots}NCCH_3][AsF_6]_2$ (Figure 1c), which is, in addition to $[F_4SXe{\cdots}NSF_3][AsF_6]$ [8], the only other crystallographically characterized example of an N−Xe−N linkage.
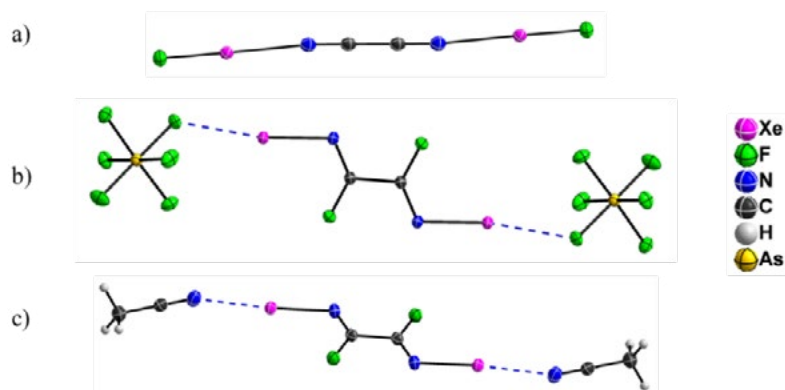
Figure 1: Compounds isolated from NCCN–$[XeF][AsF_6]$ system. In a) and c) the anions are omitted for clarity.

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Trifluoromethylthiolation: A Strategy for Hydrophobic Peptide Development

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The incorporation of fluorinated motifs has become an essential strategy in the pharmaceutical and agrochemical industries in recent decades. In addition, the integration of fluorine atoms into peptides often leads to improved metabolic stability, increased side-chain hydrophobicity and membrane permeability, as well as stabilization of the desired secondary structures [1]. Due to the rapidly growing significance of peptide therapeutics, the synthesis of diverse fluorinated amino acids (F-AAs) in enantiomerically pure form and their selective incorporation into peptides represents an important area of innovation.

Most reported F-AAs are either monofluorinated or consist of the trifluoromethyl group [2]. However, other fluorinated groups, especially in combination with chalcogen atoms, are still largely unexplored in the peptide arena. The trifluoromethylthio group ($CF_3S–$) is particularly intriguing due to its high lipophilicity parameter, a strong electron-withdrawing effect and a favorable pharmacological profile [3]. Therefore, the synthesis of trifluoromethylthiolated amino acids and their incorporation into peptides is a promising strategy to improve the bioavailability of peptide-based drugs.

We will highlight the development of a method for direct trifluoromethylthiolation of aromatic AAs such as tyrosine (Tyr) and tryptophan (Trp) and their related monoamine derivatives (Scheme 1). This strategy has also been applied for the selective late-stage functionalization of Trp-containing peptides and the trifluoromethylthiolated building blocks have been successfully used in the solid-phase peptide synthesis of endomorphin-based neuropeptides.
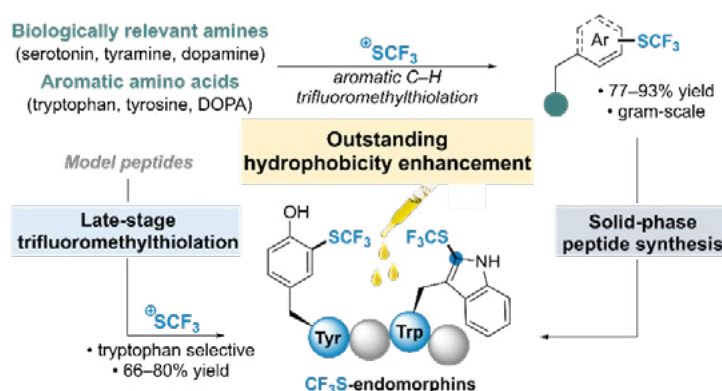
Scheme 1: Direct trifluoromethylthiolation of aromatic AA residues.

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Carboxylic Acids to Acyl Fluorides: An Easy Access for Amides and Esters

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Fluorine plays a detrimental role in organic chemistry as it imparts unique properties to organic compounds. Not only is it a key component in modern pharmaceuticals and drug design, fluorine also finds application among synthetic chemistry. Acyl fluorides, a carboxylic acid derivatives, are prominent stable synthetic intermediates due to their superior reactivity/stability profile compared to other acid derivatives such as acyl chlorides. Accordingly, they are regarded as easy-to-handle and valuable reagents used as acyl sources. Acyl fluorides have been successfully employed in synthesis of amides, esters, and even in solid-phase peptide synthesis [1,2]. Amides and esters, commonly present motifs in biologically-active compounds, are accessed from carboxylic acids by use of traditional coupling methods that often suffer from limited applicability, high reagent prices, use of toxic chemicals, poor atom economy and impractical procedures. Our research focuses on the development of carboxylic acid deoxyfluorination protocol for acyl fluoride synthesis with an easy-to-handle, cost-effective reagent previously reported by our group [3]. Furthermore, this will provide a new, simple method for accessing amides and esters (Figure 1).
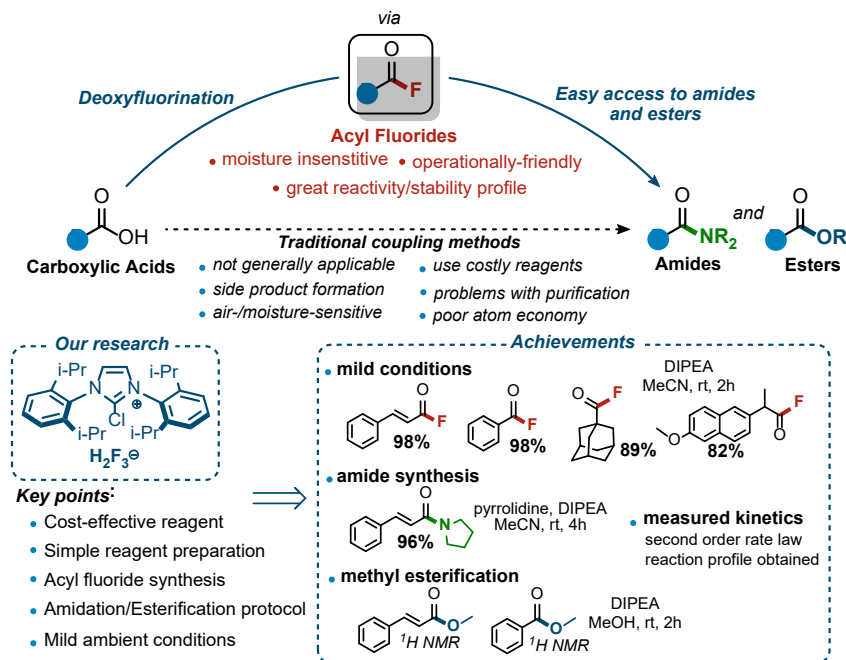

Figure 1: Deoxyfluorination of carboxylic acids to acyl fluorides for access of amides/esters.

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