

Stabilization and Reactivity of Soluble Trifluoridogold Complexes

Inaugural-Dissertation
to obtain the academic degree
Doctor rerum naturalium (Dr. rer. nat.)

by

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2018

The present thesis is based on work carried out from March 2015 until December 2018 at the Institut für Chemie und Biochemie of the Freie Universität Berlin under the supervision of Prof. Dr. Sebastian Hasenstab-Riedel.

First Referee: Prof. Dr. Sebastian Hasenstab-Riedel

Second Referee: Prof. Dr. Thomas Braun (Humboldt-Universität zu Berlin)

Date of Defense: March 21st, 2019

Acknowledgement

First of all, I want to thank my doctoral supervisor **Prof. Dr. Sebastian Riedel** for his trust to do my PhD thesis in his group. He has been very helpful and supporting in all events concerning my thesis including the opportunity to visit various conferences, but also off-topic in support of our relay marathon, barbecue events, and group trips.

I want to thank **Prof. Dr. Thomas Braun** for his always supportive and inspiring discussions, his very helpful revised manuscript comments, and that he challenged us on the relay marathon twice.

Many thanks to **Dr. Simon Steinhauer** who supported with many advices in NMR spectroscopy, in measuring crystals, his fast revisions on many manuscripts and many fruitful discussions on my topic and on others.

I want to thank **Dr. habil. Helmut Beckers** for his always open ears, quick and helpful support, the wording of several manuscripts, and many things in the setup of the fluorine lab.

I want to thank my Bachelor students: **Benjamin Schröder** helped to build up the fluorine line, **Noah Subat** stayed highly motivated all the time despite all the negative results during his thesis. **Paul Golz** finally succeeded with $\text{Cs}[\text{AuF}_4]$ and the first spark in the dark. I also want to thank **Yunfei Zhou** who has done an internship with me.

Many, many thanks to **Clara von Randow** who has done her internship of 4 weeks with me but spend in the end more than 10 weeks because she was so interested in the topic. I hope you stay so inspired all the time Clara!

I want to thank my lab mate **Anja Wiesner** who also conducted some of the crystal measurements. Thank you for the good and neat lab atmosphere, for being supportive with many things, the good discussions and for being my faithful lab mate.

Thanks to **Stefan Scheifler** who prepared many times the SIMes ligand precursor.

Thank you **Simon Rucher**, for revising my introduction and for fruitful discussion.

I want to thank the many members of the AG Riedel starting from **Dr. Heike Haller**, **Dr. Alexander Higelin**, **Dr. Felix Brosi**, **Dr. Robin Brückner**, and **Dr. Lisa Mann** who had been here at the beginning. Also thanks to **Thomas Drews** for support mainly connected to the fluorine lab with his decades-long experience and **Maximilian Stahnke** for being helpful any time needed. Thanks to all the other PhD students that started in the order

Dr. Karsten Sonnenberg, Jan Hendrick Nissen, Sebastian Hämmerling, Tony Stüker, Frenio Redeker, Lin Li, Benjamin Schmidt, Patrick Pröhm, Kurt Hoffmann, Tyler Gully, Gene Senges, Marlon Winter, and Patrick Voßnacker for a great time!

I want to thank all members, visitors, and speakers of the research training network GRK 1582 "**Fluorine as a Key Element**" for a productive atmosphere and fruitful discussions. I want to especially thank **Prof. Dr. Florian Kraus** for very supportive advices. Thanks to **Dr. Carsten Müller** for coordinating everything concerning the GRK.

I also want to thank the radiochemistry crew for the good hours during the lab courses, **Prof. Dr. Ulrich Abram, Dr. Adelheid Hagenbach, Jacqueline Grewe, Dr. Janine Ackermann, Dr. Sarah Hildebrand, Abdullah Abdulkader, Anna Grunwald, and Dominik Nowak.**

Thanks to **Dirk Hauenstein** and the whole team from the Materialverwaltung.

Thanks to our technical staff, the glass-blower team with **Dirk Busold, Jesse Holloway,** and **Stefanie Seelbinder,** the workshops with **Peter Scharmberg, Horst Binkowski,** and the workshop in the physical department. Further thanks to the caretakers **Jürgen-Peter Böttcher** and **Sven Sasse.**

Thanks to all people from the inorganic department with the work groups **Prof. Ulrich Abram, Prof. Dieter Lentz, Prof. Biprajit Sarkar, Prof. Christian Müller, Prof. Nora Kulak, Dr. Günther Thiele, Dr. Moritz Malischewski,** and **Dr. Johann Spandl.**

Thanks to **Prof. Dr. Konrad Seppelt,** who always had a good idea or explanation.

Thanks to my **family** and **friends** to support me ever since.

Finally, I want to thank my brightest star and biggest support, **Sofiya.**

List of Abbreviations

aHF	anhydrous hydrogenfluoride
BDE	bond dissociation energy
Δ BDE	difference in bond dissociation energies
DNA	desoxyribonuclein acid
dcm	dichloromethane
Et	ethyl
ΔG_f^0	standard Gibbs free energies of formation
ΔH_f^0	standard enthalpies of formation
HIV	human immunodeficiency virus
HSAB	hard and soft acids and bases
im	imidazole
IPr	1,3-Bis(2,6-diisopropylphenyl)-imidazol-2-ylidene
Me	methyl
MeCN	acetonitrile
NHC	N-heterocyclic carbene
oDFB	<i>ortho</i> -difluorobenzene
Pr	propyl
py	pyridine
SIMes	1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene
SIPr	1,3-Bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene
teflate	pentafluoro-orthotellurate
teflato	pentafluoro-orthotellurato
teflic	pentafluoro-orthotelluric
THF	tetrahydrofuran
UV	ultraviolet

Abstract

A facile synthesis for $\text{Cs}[\text{AuF}_4]$, AuF_3 and the new salts $[\text{NMe}_4][\text{AuF}_4]$, $[\text{NEt}_4][\text{AuF}_4]$ from elemental gold or AuF_3 is described. The latter salts are stable and well dissolvable in solvents such as acetonitrile. The direct use of these gold(III) fluorides as precursor compounds in metal organic chemistry is reported for the first time. The molecular AuF_3 unit can be stabilized with a MeCN or a pyridine ligand. The complex $[\text{AuF}_3(\text{MeCN})]$ is only stable at low temperatures and the more stable $[\text{AuF}_3(\text{py})]$ shows the formation of complex equilibria with other fluoro pyridine gold(III) species. Synthesis and characterization of the room temperature stable compound $[\text{AuF}_3(\text{SIMes})]$ bearing the N-heterocyclic carbene SIMes is shown to be the first isolated trifluorido organo gold compound. Reactivity studies on $[\text{AuF}_3(\text{SIMes})]$ identified the *trans*-fluorido ligand to be easily substituted by nucleophiles, strong acids or in a metathesis reaction with Me_3SiCl or $\text{Me}_3\text{SiOTeF}_5$. Thus, synthesis of the unprecedented $[\text{AuClF}_2(\text{SIMes})]$ as the first isolated chlorido fluoro gold(III) species and, secondly, $[\text{AuF}_2(\text{OTeF}_5)(\text{SIMes})]$ as the most Lewis acidic gold center that could be stabilized by an organic ligand was possible. The Lewis acidity of the metal center of those compounds can be described with a new SIMes affinity scale that characterizes similar compounds by the ^{13}C NMR chemical shift of the carbene carbon atom and the reaction energy of the Au–C bond dissociation.

Zusammenfassung

Es wird eine einfache Synthese der bekannten Goldfluoride AuF_3 und $\text{Cs}[\text{AuF}_4]$ sowie der neuen Salze $[\text{NMe}_4][\text{AuF}_4]$ und $[\text{NEt}_4][\text{AuF}_4]$ ausgehend von elementarem Gold oder AuF_3 beschrieben. Die beiden zuletzt genannten Verbindungen sind in Lösungsmitteln wie Acetonitril stabil und gut löslich. Es wird erstmalig gezeigt, dass alle aufgezählten Goldfluoride als Edukt in der metallorganischen Chemie eingesetzt werden können. Goldtrifluorid kann als molekulare AuF_3 -Einheit mit einem MeCN oder Pyridin-Liganden stabilisiert werden. Der Komplex $[\text{AuF}_3(\text{MeCN})]$ ist jedoch nur bei tiefen Temperaturen stabil, während $[\text{AuF}_3(\text{py})]$ komplexe Gleichgewichte mit weiteren Fluoridopyridingold(III)-Komplexen ausbildet. Über die Synthese und Charakterisierung des raumtemperaturstabilen $[\text{AuF}_3(\text{SIMes})]$, als erste in Reinform isolierte Trifluoridoorganogold-Verbindung, wird berichtet. In Reaktivitätsstudien mit $[\text{AuF}_3(\text{SIMes})]$ zeigte sich, dass der *trans*-Fluoridoligand leicht durch Nukleophile, starke Säuren oder in einer Metathesereaktion mit Me_3SiCl oder $\text{Me}_3\text{SiOTeF}_5$, substituiert werden kann. Hierdurch wurde die Synthese der einzigartigen Komplexe $[\text{AuClF}_2(\text{SIMes})]$, als erster isolierter Chloridfluoridogold-Komplex, und zweitens $[\text{AuF}_2(\text{OTeF}_5)(\text{SIMes})]$ mit dem Lewis-azidesten Goldzentrum das durch einen organischen Liganden stabilisiert werden konnte, möglich. Die Lewis-Azidität solcher Komplexe kann mit einer neuen SIMes-Affinitätsskala beschrieben werden, welche die Verbindung anhand der ^{13}C NMR chemischen Verschiebung des Carbenkohlenstoffatoms sowie der Reaktionsenthalpie der Au–C Bindungsdissoziation charakterisiert.

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A Introduction

In the behavior of the late transition metals relativistic effects play a substantial role, leading to shrinkage of the s orbitals and, subsequently, enlargement of the d orbitals. The energy gap between the 6s and the 5d orbitals is smaller which makes the metal nobler, because the first oxidation state is harder to access but at the same time higher oxidation states are also easier accessible. In gold this reaches a summit giving it a unique set of properties which attracted its attention all through history.^[1]

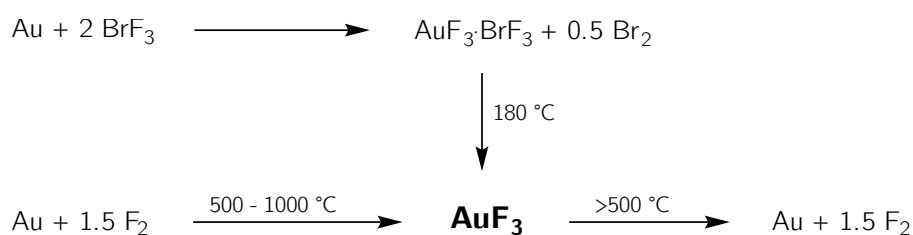
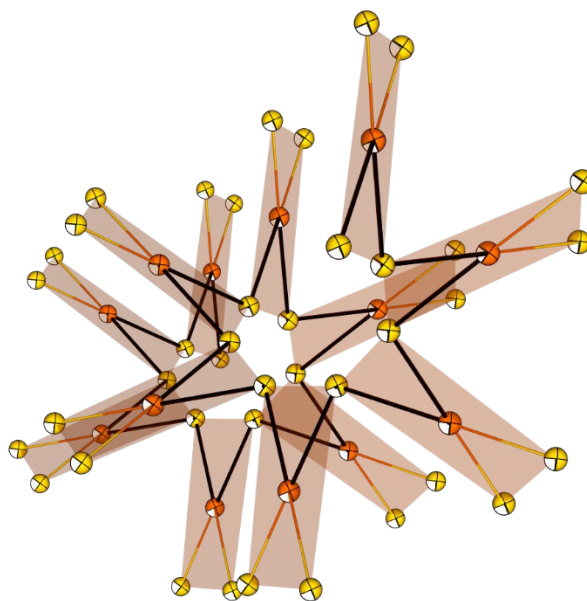
These specialties are the reason why mankind was using gold already in the Chalcolithic Age – the transition time from the Stone Age to the Bronze Age where metallurgy was developed. The oldest jewelry containing processed gold dates back to around 4500 BC and it certainly was one of the first metals used by humans.^[2] Gold is also prominent in its oxidized form such as $[\text{Au}(\text{CN})_2]^-$ that is well known from gold mining,^[3] and $[\text{AuCl}_4]^-$ which is formed by dissolution of elemental gold in aqua regia.^[4]

The halides of gold are versatile in their behavior and often are used in at least one synthetic step when gold is present. Most of the chlorides are stable under ambient conditions and compounds like the dimeric gold trichloride Au_2Cl_6 are readily used as a homogeneous catalyst in organic reactions – in this case because of its exceptional alkynophilicity.^[5] Where the chlorides have been used widely including medical applications already in the 19th century,^[6] the scope for gold fluorides has been limited to a few chemists hands.

A.1 The Fluorides of Gold

Henry Moissan prepared AuF_3 in 1889 as first of such compounds by heating Au to 500 - 600 °C under a flow of fluorine gas. He described it as dark colored and very hygroscopic compound that decomposes at higher temperatures.^[7] Other attempts by Lenher^[8] and Ruff^[9] with less reactive compounds than elemental fluorine failed and only six decades later Sharpe reported on the synthesis of AuF_3 by using BrF_3 as fluorination reagent which is liquid at room temperature.^[10] In this reaction, first the mixed gold bromine fluoride $\text{AuF}_3 \cdot \text{BrF}_3$ is formed which is also described as $[\text{BrF}_2]^+[\text{AuF}_4]^-$ and can be thermolysed at 120 - 180 °C to yield pure AuF_3 (Scheme 1).^[10] The structure of AuF_3 in the solid state consists of polymeric chains that contain planar AuF_4 units in a helical arrangement (Figure 1).^[11,12] Note, that the structure of $\text{AuF}_3 \cdot \text{BrF}_3$ is similar, having

Figure 1. Crystal structure of AuF₃ (reported by Bartlett et al. 1967).^[11] Square planar AuF₄ units are highlighted with planar surfaces (orange). Au–F bonds to bridging fluorine atoms are colored black.



Scheme 1. Synthetic routes to AuF₃ reported by Sharpe (top),^[10] Moissan,^[7] and others^[14] (bottom) including its decomposition above 500 °C.

alternating planar AuF₄ and BrF₄ units that are connected by fluorine atoms.^[13] Beginning at around 500 °C AuF₃ liberates elemental fluorine under reduction back to Au⁰. Yet, this reductive elimination must be slow because AuF₃ can be prepared from Au at 1000 °C with pressurized fluorine.^[14] Sharpe also reported on the instability of AuF₃ with CCl₄ to yield chlorofluorocarbons and on a violent reaction with benzene and alcohol.^[10]

The anionic [AuF₄][−] is significantly more stable than the Lewis acid AuF₃ which is also seen in the solid state structure where the bridging fluoride ligands of neighbored gold centers fill the fourth coordination side. Tetrafluoridoaurate salts like M[AuF₄] are known for many mono-cationic metals where M^[15–17] = Li⁺,^[18] Na⁺, K⁺,^[18] Rb⁺, Cs⁺,^[19] and Ag⁺^[10] but also for more complex mono-cations where M = AgF⁺,^[20] NO⁺,^[21] XeF₅⁺^[22] as well as many di-cations in the composition M[AuF₄]₂ with M^[16,23] = Mg²⁺, Ba²⁺, Ni²⁺, Zn²⁺, Cd²⁺, Pd²⁺, Hg²⁺ among many others.^[24] Most mentioned [AuF₄][−] salts have been prepared either by

direct fluorination of the corresponding $[\text{AuCl}_4]^-$ salt at 200 - 300 °C,^[15] or by a solid state reaction between AuF_3 and $\text{MSO}_4 \cdot n\text{H}_2\text{O}$ (M = Mg, Zn, Ni, Cd; n = 6-8) with N_2/F_2 at 280 - 330 °C^[23] or instead the metal fluoride salt.^[19,25]

The neutral AuF_2 was up-to-date only characterized in noble gas matrices under cryogenic conditions at 4K.^[26,27] Gold(II) fluorides in bulk are only known in combination with a stabilizing anionic species such as the hexafluoride antimonate^[28] in $\text{Au}(\text{SbF}_6)_2$ or the related $\text{Au}(\text{SO}_3\text{F})_2$ ^[29] but also as the binary phase $\text{Au}[\text{AuF}_4]_2$, short Au_3F_8 ,^[28] and combinations of both in $[\text{Au}_3\text{F}_8(\text{SbF}_5)_2]$ as well as $[\text{Au}_3\text{F}_7(\text{SbF}_5)_2]$.^[30] Note, the mixed valent $\text{Au}[\text{AuF}_4]_2$ was prepared from an aHF (anhydrous HF) solution that was acidified with SbF_5 leading to stabilization of the lower oxidation state Au^{2+} .^[28,30,31] In such an acidic aHF/ SbF_5 system AuF_3 can be reduced in the presence of xenon to an Au^{2+} species that can then complex xenon atoms to give the unprecedented $[\text{AuXe}_4]^{2+}$ cation plus the oxidized Xe_2^+ .^[32]

Similar to AuF_2 the AuF molecule has only been observed at extreme conditions in mass spectrometric measurements^[33] and with microwave spectroscopy.^[34] Even in a noble gas matrix a free AuF could not be observed but instead complexes with a noble gas atom $[\text{NgAuF}]$ (Ng = Ne, Ar) were found - pointing out its instability and high reactivity towards any kind of base.^[26,27] Theoretical investigations predicted the formation of AuF in the gas phase,^[35] however they also showed that the disproportionation reaction to form AuF_3 and Au^0 is exothermic^[36] making it very challenging to isolate AuF as pure substance. The anion $[\text{AuF}_2]^-$ would be a more stable version of a gold(I) fluoride and has been predicted by theoretical studies^[37] but, nevertheless, it was up-to-date only observed in mass spectra.^[38]

Gold(V) fluorides can be prepared as $[\text{AuF}_6]^-$ salts and are known with group 1^[39-41] and group 2^[42] element cations but can also be used to stabilize highly reactive electrophilic species such as NO^+ ,^[43] O_2^+ ,^[39,40,43-45] ClF_6^+ ,^[46] BrF_6^+ ,^[40] ReF_6^+ ,^[47] XeF_5^+ ,^[22,40] KrF^+ ^[40,43,44] just to mention some.^[48] The hexafluoro aurate(V) anion can be prepared in aHF by oxidation of the tetrafluoro aurate(III) with F_2 and UV light or directly with KrF_2 from elemental Au.^[39,43] The neutral gold(V) fluoride AuF_5 cannot be prepared in aHF because it decomposes under liberation of F_2 similar to the decomposition of AuF_3 in the aHF/ SbF_5 system,^[49] instead it is obtained by thermolysis of either $\text{KrF}[\text{AuF}_6]$ at around 60 °C or $\text{O}_2[\text{AuF}_6]$ around 160 °C.^[43,50] Pure AuF_5 exists as the dimer Au_2F_{10} because of its high Lewis acidity.^[49] Its extreme Lewis acidity makes it the only molecule that has been predicted to form a stable end-on complex with F_2 where fluorine acts as a base.^[51,52]

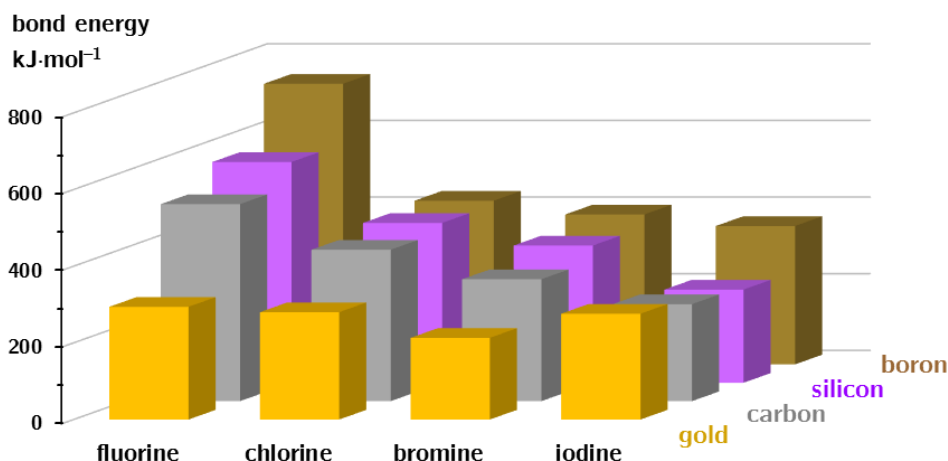


Figure 2. Experimental bond energies of the diatomic molecules E–X (E = Au, C, Si, B; X = F, Cl, Br, I). Exact values are given in the appendix.^[53]

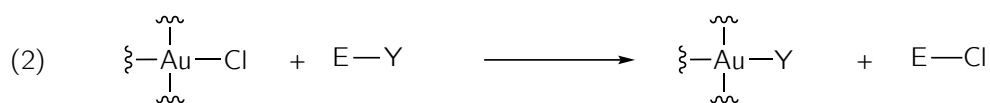
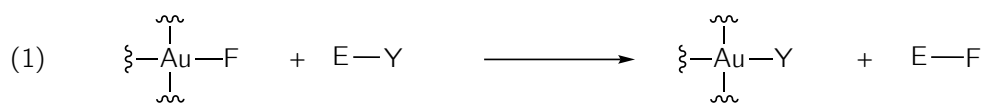
Gold(IV) and gold(VI) fluorides have only been investigated theoretically and are probably only stable under high pressure in bulk.^[53] However, the so far hypothetical AuF₆ would be an extreme strong oxidizer exceeding the oxidizing strength of all other known metal fluorides, based on quantum-chemical calculations.^[52,54]

It is evident that gold fluorides are all very reactive and, thus, need full moisture and air free conditions at all times. Comparison with their chloride, bromide, and iodide analogues that can be stored under air and are regularly used for many reactions,^[5,59] raises the question where this significant difference in reactivity originates. Here, a good insight is given by the experimental bond dissociation energies (BDE) of the diatomic species Au–X with X = F, Cl, Br, I where the values for the AuX molecules are very similar and the BDEs for AuF and AuCl only differ by 14 kJ·mol⁻¹ (Figure 2).^[60] In comparison the corresponding

Table 1. Experimental enthalpies of formation ΔH_f^0 taken from the CRC handbook, if no other reference is provided.^[55]

		AuX ₃	CX ₄	SiX ₄	BX ₃
$\Delta H_f^0 / \text{kJ}\cdot\text{mol}^{-1}$	X = F	-349 ^a	-934	-1615	-1136
	X = Cl	-118 ^b	-96	-662	-403 ^c

a: from reference,^[36,56] values at 298K and 1 atm. b: from reference,^[57] values at 416K and 1 atm. c: from reference.^[58]



E: B, Si, C, ...

Y: Cl, Br, CR₃, NR₂, OR, ...

Scheme 2. General scheme for the reaction of a fluoro gold complex (1) and a chlorido gold complex (2) with the exemplary molecule E–Y for a Y-group transfer reaction. The free reaction energies of (1) and (2) are strongly influenced by the E–F and E–Cl bond energies. For most elements the element-fluorine bond is significantly more stable than the element chlorine bond. Therefore, the usual order is: $\Delta_r G^0$ of (1) > $\Delta_r G^0$ of (2)

element-halogen BDEs show a much larger difference as nicely seen for the pairs of the diatomic molecules CF/CCl ($\Delta \text{BDE} = 119 \text{ kJ}\cdot\text{mol}^{-1}$) and SiF/SiCl ($\Delta \text{BDE} = 159 \text{ kJ}\cdot\text{mol}^{-1}$).

A similar trend is found in the enthalpies of formation ΔH_f^0 for the larger molecules as can be seen in the pairs AuF₃/AuCl₃, CF₄/CCl₄, SiF₄/SiCl₄, and BF₃/BCl₃, see Table 1. Consecutively, the reaction of a usual gold fluoride (Scheme 2, equation 1) with an exemplary molecule E–Y (E: element that forms an E–F or E–Cl bond; Y: any group that is stable at a gold central atom) is more exothermic and thermodynamically favored in comparison to the reaction with the corresponding gold chloride (Scheme 2, equation 2). Therefore, the reactivity of any fluoro gold compound is expected to be higher than their corresponding chlorido gold compounds.

Surprisingly gold fluorides have mainly been in focus of structural studies but were rarely investigated in order to pursue their extraordinary reactivity. This is also seen in the number of publications listed for AuF₃ (79 results on scifinder.cas.org) that outreaches those for [AuF₄][−] (21 results on scifinder.cas.org) and which would be seen the most promising candidate for further application as the most stable binary gold fluoride.^[61]

A.2 Bonding Characteristics of Gold Complexes

The unique bonding situation in gold complexes arises from its nature as most electronegative metal that rather fits into the light main group elements, but is found at the central bottom of the periodic table. Due to the strong relativistic effects its

Table 2. Values for the electronegativity of selected elements in the Pauling scale.^[55,68]

	H	C	P	S	Br	I	Au	Te
Pauling electronegativities	2.2	2.55	2.19	2.58	2.96	2.66	2.4	2.1

electronegativity is close to that of carbon, iodine, and sulfur (see Table 2). Through the high nuclear charge of the gold nucleus the speed of the electrons in the s orbitals correspond to a significant fraction of the speed of light, resulting in an increase of the electrons' mass and a contraction and stabilization of the s orbitals (direct relativistic effect). The direct relativistic effects in the periodic table reach a maximum at gold which can be seen by comparing the calculated radii of the 6s orbitals with and without accounting for the relativistic effects.^[37,62–67] The stabilization of the s orbitals lead to a better shielding of the effective nuclear charge and, thus, a destabilization of the d orbitals (indirect relativistic effect). Hence, gold has a high 1st ionization energy (9.23 eV) and at the same time a high electron affinity (2.31 eV).^[55] As a result the gap between the 6s and the 5d orbitals is small enough to absorb blue light (not only UV light as in case of most other metals) which results in the characteristic golden color.^[64,65] The indirect relativistic effect makes the oxidation state +III easier accessible to gold than to silver. In general, gold reaches the highest oxidations states within the coinage metals.

Gold(0) has one unpaired electron ($[\text{Xe}]5s^15d^{10}$) and can form diatomic molecules Au_2 in the gas phase like the halogens. It can also readily be reduced to cesium auride CsAu ,^[69] LiAu_3 , LiAu , Li_2Au and others^[70] such as $[\text{NMe}_4]\text{Au}$.^[71] In this regard it is confusing that in literature gold is often treated as a usual metal to which a positive oxidation state is assigned, even though it is the more electronegative atom following the Pauling scale of electronegativities. Following Pauling's assignment, gold hydrides formally should be called hydrogen aurides instead.

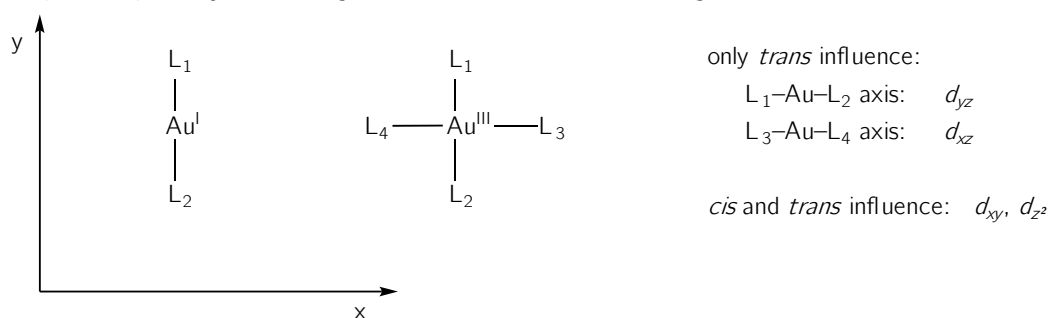
In case of a gold carbon bond the $\Delta\text{EN} = 0.15$ is smaller than between hydrogen and carbon ($\Delta\text{EN} = 0.35$) with the result that the Au–C bond is less polar than the C–H bond and predominantly covalent. Beside this questionable description of the oxidation state of gold, it usually describes the geometry of the coordination sphere in gold complexes very well where Au^{I} complexes (d^{10}) are mostly linear and Au^{III} complexes (d^8) are mostly square

planar. Note, also square planar group 11 complexes with a d^{10} configuration have been reported, due to an inversion of the ligand field.^[72]

Gold(I) complexes are closed shell d^{10} compounds. Despite the partial positive charge on the Au^+ centers they have the tendency to interact between each other and favor dimeric or oligomeric structures that can form clusters, chains, and two dimensional planes. This so called aurophilicity is within the energy range of a hydrogen bond and explains the easy formation of gold clusters in any size between a few atoms up to nanoparticles that have an average oxidation state between +1 and 0. The true nature of aurophilicity has not yet been fully understood, but it is known that relativity plays a major role.^[73,74] It has been described as “super van-der-Waals bonding”, though, it has dispersive and non-dispersive components.^[75] The aurophilicity in gold(III) complexes is definitely less profound than for gold(I) compounds but its presence and nature is still under debate.^[73,74,76]

For transition metal complexes the *trans* influence plays a substantial role in the stability of complexes.^[77–79] This bonding interaction arises for ligands bound to the same orbitals of the metal center. The strength of a ligand-metal bond (L_1-Au) influences the bond strength of the *trans* ligand (L_2), when they share the same set of orbitals at the metal center. Ligands in a *cis* position to L_1 and L_2 have a different bond axis and, thus, different overlap with these metal orbitals.^[79]

The *trans* influence describes the relative bond stabilities whereas *trans* effect is used to describe the bond reactivity, but usually they affect each other. The strength of the ligand-metal bond and, thus, the strength of the *trans* influence is determined by the σ -donor and π -acceptor capability of the ligands.^[78,79] Probes for the ligand influence can be the NMR



Scheme 3. Coordination sphere of gold complexes in the oxidation states +I (mostly linear) and +III (mostly square planar). The ligands L_1 & L_2 (also L_3 & L_4) form ligand-metal bonds to the same d orbitals and affect each other, therefore, more strongly (*trans* influence). Ligands in *cis* position, L_3 and L_4 , are additionally bound to other orbitals (d_{xz}) and only influence L_1 and L_2 by sharing interactions with the d_{xy} and d_{z^2} orbitals.

chemical shifts, bond lengths, and quantum-chemical methods such as the description of the bond critical point.^[80,81,82] Recently, a detailed study on the bonding situation in gold(III) hydrides reported the influence of different ligands and substitution patterns on the ¹H NMR chemical shift of the hydride atom. The ¹H NMR chemical shift of the gold hydride compounds ranges from +6.5 to -9.0 ppm which already shows the extend of this influence. It was found that the *cis* influence is 3 to 4 times weaker than the *trans* influence of the ligand.^[82] The ¹³C NMR chemical shift of a carbon atom directly bonded to the gold center spreads over a region of more than 200 ppm and shows a strong *trans* influence.^[81] A stronger ligand-metal bond can also be described as a change in the Lewis acidity of the metal center and *vice versa*. This can be used to increase the reactivity of gold(III) hydride complexes by a *trans*-carbon donor in order to facilitates β-hydride elimination in gold(III) alkyl and formate compounds.^[83]

A.3 An Introduction to Organo Gold Chemistry

In organo gold chemistry there is a large interest in medicinal chemistry,^[84,85] heterogeneous catalysis,^[86] which was strongly driven by the gold nanoparticle rush of the last decade,^[87] and in homogeneous catalysis.^[87]

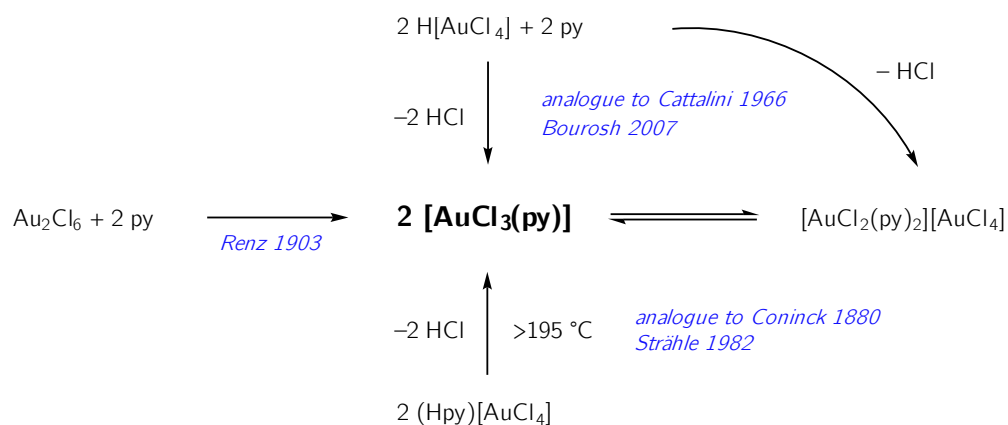
In medicinal chemistry gold compounds have been used since their discovery to treat various diseases but also addictions like alcoholism. Here often chlorido gold compounds were used.^[6,85] The discovery of the antibacterial activity of $[\text{Au}(\text{CN})_2]^-$ in even low concentrations by Robert Koch initiated the development of modern medicinal chemistry.^[85,88] Today especially gold(III) compounds are investigated for their antitumor activity, their antibacterial and antiviral behavior, as drug against parasitic diseases, and as potential radiotherapeutic agent where the β⁻-emission of the non-abundant isotopes ¹⁹⁸Au and ¹⁹⁹Au is used.^[84,89] Such compounds usually are organo gold compounds and often show selective cytotoxic and also antiviral activity. In fact, some complexes inhibited the replication of HIV.^[84,90]

In heterogeneous catalysis the reactions happen on the surface of a solid Au⁰ precursor as in case of the recently commercialized hydrochlorination of acetylene.^[86,91] Such solid precursors can be gold coated surfaces, deposited gold particles on a suitable material or gold nanoparticles all of which are additionally investigated far outside of organo gold chemistry due to their easy preparation and special physical properties.^[86,87,92]

The “homogeneous” organo gold chemistry usually involves the use of gold chlorides as convenient molecular source of oxidized gold precursors that are prepared by dissolving gold in aqua regia since the 13th century.^[93] In the HSAB concept gold is considered as “soft” metal in case of the oxidation states 0 and +I, and “soft to hard” in case of the oxidation state +III.^[84,94,95] This matches that of chlorine, but also that of sulfur and phosphorous which explains the high stability of gold chlorides and the affinity of gold towards sulfur and phosphorous ligands.^[96,97] Moreover, gold readily forms complexes with C–C double and even better with C–C triple bonds acting as a π -Lewis acid and, thus, can be used to activate such bonds.^[98] In many cases the construction of a catalytic cycle has been possible.^[99–101] However, a change of the oxidation state at the gold center from +I to +III is often questionable because of the high standard potential of the Au^I/Au^{III} redox couple (1.40 V).^[102] The noble prize in 2010 for C–C coupling reactions with the redox couple Pd⁰ / Pd^{II} for Heck, Negishi, and Suzuki underlined the importance for selective coupling reactions. Development of a homogeneous catalytic cycle with gold requires to understand its coordination chemistry. Chlorido gold complexes play a major role everywhere in organo gold chemistry and some of the important developments in chlorido gold chemistry will be discussed in the following chapter as the most important analogues to the fluorido gold compounds.

A.4 Organometallic Chlorido Gold Compounds

One of the first examples of a chlorido gold complex with an organic ligand was reported in 1880 by Coninck who prepared a red crystalline powder fitting to the formula [AuCl₂(lutidine)₂]Cl (lutidine: 2,6-dimethyl pyridine).^[103] Neutral analogues followed in 1903 by Carl Renz who isolated yellow crystalline [AuCl₃(py)] together with [AuCl₃(quinoline)] after an equimolar reaction between an AuCl₃ solution and pyridine or quinoline.^[104] It can also be synthesized starting from an [AuCl₄][−] source. In some cases the formation of the autoionization product [AuCl₂(py)₂][AuCl₄] is found and likely forms an equilibrium with [AuCl₃(py)] which is nicely seen in molecular structure in the solid state of [AuCl₂(py)₂][AuCl₄]·[AuCl₃(py)]₂ (Scheme 4).^[105] The [AuCl₃(py)] can also be prepared by ligand exchange of a weaker ligand as it was found for the trichlorido nitrile gold complexes.^[106]

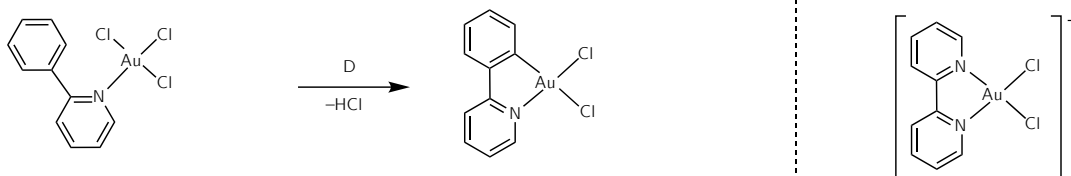


Scheme 4. Synthesis of $[\text{AuCl}_3(\text{py})]$ on different routes by Renz,^[102] Coninck,^[101] Strähle,^[105] Cattalini,^[106] and lately Bourosh.^[103] The structure in the solid state for the neat $[\text{AuCl}_3(\text{py})]$ was reported by Strähle^[105] and for a mixed crystal containing $[\text{AuCl}_2(\text{py})_2][\text{AuCl}_4] \cdot [\text{AuCl}_3(\text{py})]_2$ by Bourosh.^[103]

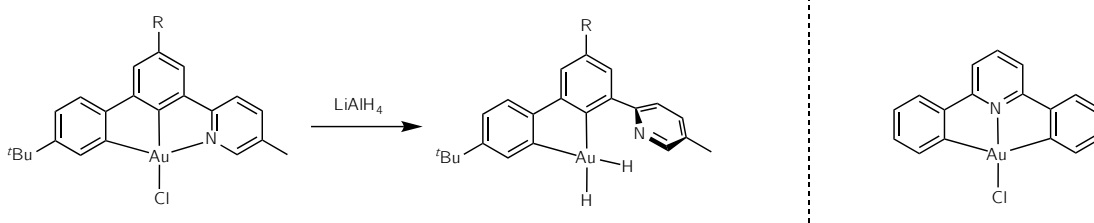
Interestingly, the studies on this system are spread over a timeline of more than a century since its first preparation in 1903 and new studies every once in a decade.^[104,107] In fact, complexes of gold trichloride with nitrogen- or oxygen-containing ligands usually react similar to AuCl_3 but often perform faster and better. Gold trichloride is known to catalyze several reactions for a long time.^[5,101,108] Since the early 2000s, $[\text{AuCl}_3(\text{py})]$ has been reported as potent catalyst in the activation of alkynes^[100] that can be reacted selectively in multicomponent reactions,^[109] as well as for the carbonylation of alkyl nitrate^[110] or as precursor in the synthesis of di- and trinuclear gold complexes^[111] and the activation of iodine in order to synthesize $[\text{C}_5\text{H}_6\text{N}][\text{ICl}_2]$.^[112]

Other chlorido gold complexes with N-containing ligands usually contain structural motifs derived from pyridine. Today, mainly bidentate or tridentate ligands are used to create controlled substitution patterns in order to achieve a selective reactivity.^[94,113,114] Pincer type ligands often consist of a pyridine unit that has in *ortho* position one or two more pyridine units or phenyl rings. The dichlorido κ^2 -(2-phenylpyridine) gold(III) complex is prepared by coordination of the pyridine moiety to the gold center in the first step and elimination of HCl under formation of an Au–C bond by thermal activation.^[115] The use of the 2,2'-bipyridine ligand leads to the cationic dichloride complex and a tridentate chlorido 2,6-biphenylpyridine complex is a stable gold(III) complex that can react either at one or two positions dependent on the substrate.^[97,114,116] For such ligand systems it has been shown that the pyridine moiety has the ability to temporarily dissociate to offers a vacant position for substrates without losing the ligand (Scheme 5).^[82]

bidentate ligands



tridentate ligands



Scheme 5. Top: bidentate gold(III) complexes. Synthesis of the κ^2 -(2-phenylpyridine) dichlorido gold(III) complex starting from Au_2Cl_6 and coordination of the pyridine moiety the gold center followed by thermal activation in a microwave of the HCl elimination to form the Au–C bond (top left).^[117] Dichlorido 2,2'-bipyridine gold(III) cation (top right). Bottom: tridentate gold(III) complexes. Chlorido κ^3 -(2,3'-biphenylpyridine) gold(III) derivative that can be reacted with LiAlH_4 under dissociation of the pyridine unit (bottom left) and a chlorido κ^3 -(2,6-biphenylpyridine) gold(III) complex (bottom right).^[80]

The gold rush of chemistry in the most recent decades was made possible by development of free stable carbenes. In 1991 Arduengo et al. reported on the first free crystalline carbene the bis-*N,N*-(adamantly)imidazol-2-ylidene.^[117] As strong σ -donor ligand with flexible π -acceptor capabilities they are ideal ligands for stabilization of a large variety of metal complexes. Substitution in the backbone of the imidazole ring by electronegative substituents increases the π -acceptor abilities and the substitution of the moiety connected to the nitrogen atom allows to change the steric surrounding that is present at the metal center.^[118] Though, the first gold carbene complexes were reported in 1974^[119,120] only these convenient to handle Arduengo carbenes – namely the N-heterocyclic carbenes (NHC) – brought frequent research to gold compounds reaching from Au^0 to Au^{III} .^[121] The carbene ligand can be transferred via a transmetallation reaction from other transition metal complexes such as $[(\text{CO})_5\text{Cr}(\text{NHC})]$,^[122] $[(\text{CO})_5\text{W}(\text{NHC})]$,^[123] $[\text{Ag}(\text{NHC})_2][\text{PF}_6]$ ^[124] but also from $\text{P}(\text{NHC})_3$ ^[125] or *in situ* be generated by reaction with a base.^[126]

Interestingly, the direct reaction of a gold(III) trihalide with the free carbene usually is not used because of the need of moisture free conditions.^[121] Any convenient $\text{Cat}[\text{AuCl}_4]$ (Cat: H^+ , Na^+ , K^+) is suitable as gold(III) precursor or $\text{AuCl}(\text{SMe}_2)$ with dimethylsulfide as a

good-to-be-substituted group. Some gold carbene compounds were also prepared by the direct carbene formation at the gold center with a gold monochloride isocyanide complex as precursor and reaction with a β -chloroammonium salt.^[120,127]

All these routes provide a ready access to a large variety of Au(I) complexes that usually are neutral $[\text{Au}(\text{Hal})(\text{NHC})]$ (Hal: often halide or pseudohalide but also C_6F_5 ^[128] and others) or cationic compounds $[\text{Au}(\text{NHC})(\text{L})]^+[\text{A}]^-$ (L: neutral donor ligand e.g. MeCN, py, NHC, alkyne; A: PF_6^- , BF_4^- , SbF_6^- , others) are known.^[121] Gold(III) complexes such as $[\text{AuCl}_3(\text{NHC})]$ are available starting from a $\text{Cat}[\text{AuCl}_4]$ (Cat: H^+ , Na^+ , K^+) precursor under non-reducing reaction conditions or by oxidation of the corresponding gold(I) compound. Herein, potential oxidizers are neat Hal_2 (Hal: Cl, Br, I) but also hypervalent iodine compounds such as PhICl_2 .^[129]

Gold NHC complexes have been shown to activate unsaturated molecules by coordination of the alkyne or alkene to the gold center and subsequent reaction – usually a nucleophilic attack.^[121,130] In such homogeneous catalytic reactions the gold(I) compounds play the major role.^[131] Surprisingly, the focus lied on the gold(I) species for a long time and much less is known about the reactivity of gold(III) carbene complexes.^[132] However, metalorganic gold(III) complexes seem to increasingly catch the interest of researchers and exploit new areas of reactivity.^[133] Gold NHC complexes often show photoluminescence that can be tuned with different ligands.^[134] They are also candidates for pharmaceutical applications in luminescent detection methods, their inhibitor abilities and for their cytotoxicity which partially is assigned to the strong interaction of gold(III) NHC complexes towards the DNA.^[84,135]

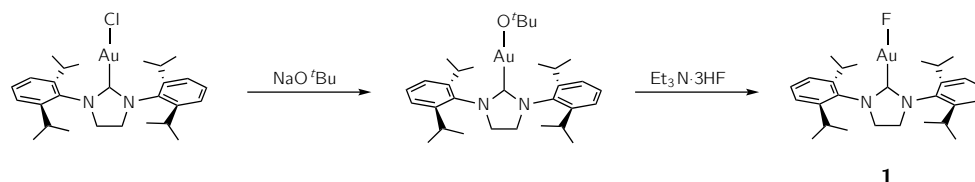
A.5 The Fluorido Ligand in Organometallic Gold Compounds

The isolated molecules AuF and AuF_3 are fairly instable because the fluorido ligand has a strong electron-withdrawing power that creates a significant increase in Lewis acidity in *trans* position to the fluorido ligand. The first monofluorido gold(I) compound has been isolated in 2005 by the group of Sadighi with an NHC ligand as strong stabilizing σ -donor.^[136] The *tert*-butoxy gold(I) precursor is reacted with a source of HF to break the Au–O bond under formation of the fluorido gold(I) complex **1** and *tert*-butanol. Hydrogenfluoride is added as Olah's reagent $\text{py}\cdot\text{HF}$ or as the related $\text{Et}_3\text{N}\cdot 3\text{HF}$ (Scheme 6). The reaction of the fluorido complex **1** with an alkyne yields the product of the insertion

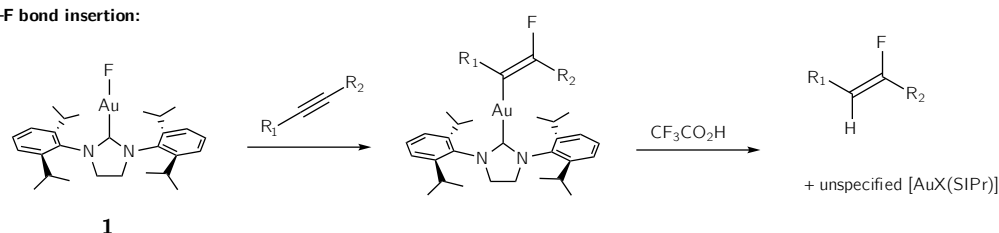
into the Au–F bond and could be isolated as pure compound.^[137] The hydrofluorination product of the alkyne is formed after a protodeauration step with triflic acid. Additionally, the reaction of the π -complex $[\text{Au}(\text{alkyne})(\text{SIPr})]^+[\text{BF}_4]^-$ with $\text{Et}_3\text{N}\cdot 3\text{HF}$ and *in situ* generation of the fluorido complex **1** followed by reaction with the alkyne is also catalytically possible (Scheme 6 bottom). In such reactions gold does not change its oxidation state and reacts as a carbophilic π -Lewis acid in order to activate carbon-carbon multiple bonds towards nucleophilic attack.^[99] In case of a fluorido ligand the Au–F bond is reactive enough to enable the insertion into of the unsaturated carbon-carbon bond.

Evaluation of possibilities to switch between the two oxidation states +I and +III is a major field of interest which is greatly motivated by the known catalytic cycles for the late transition metals. The main difficulty here is the high standard potential of the redox couple $\text{Au}^{\text{III}}/\text{Au}^{\text{I}}$ (1.40 V) which is 0.45 V higher than in case of the prominent $\text{Pd}^{\text{II}}/\text{Pd}^0$ system (0.95 V).^[55] As a consequence the oxidative addition of a carbon-halogen or carbon-carbon bonds is only in special cases favored as for biphenylene to reduce the ring strain.^[138,139] Regularly, additional oxidation reagents are used to reach the oxidation state +III. Xenon

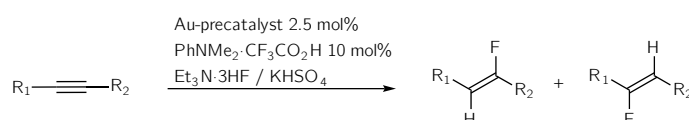
Fluorido gold complex:



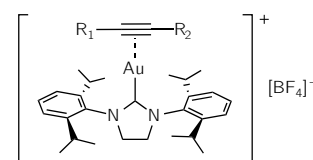
Au–F bond insertion:



Catalytic reaction:



Au-precatalyst:

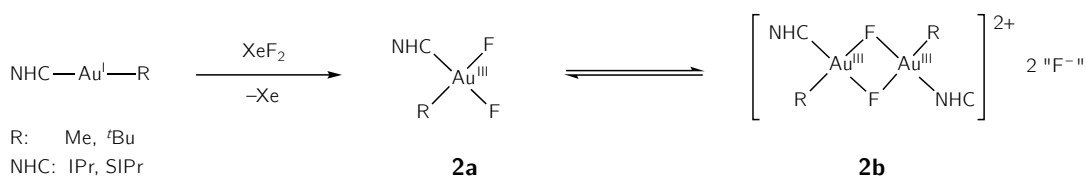


Scheme 6. Top: Sadighi's synthesis of the $[\text{AuF}(\text{SIPr})]$ complex.^[137] Middle and bottom: Reactivity of the fluorido complex towards alkynes and catalytic reaction.^[138] The Au-precatalyst is synthesized from $[\text{AuCl}(\text{SIPr})]$ and $\text{Ag}[\text{BF}_4]$ in presence of an alkyne.

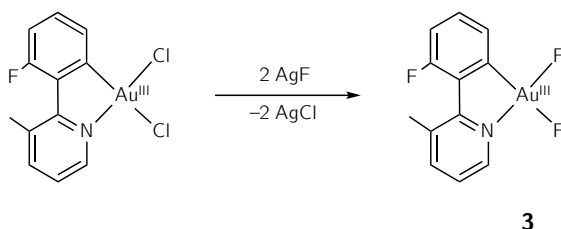
difluoride or Selectfluor and sometimes hypervalent iodine compounds such as $\text{PhI}(\text{OAc})_2$ are prominent examples for such oxidation reagents.^[99,140] Most commonly XeF_2 reacts with a gold(I) precursor compound under formation of a *cis*-difluorido gold(III) complex (**2a**, Scheme 7). The stability of the fluorido gold(III) complex is strongly influenced by the other ligands and its concentration. At low concentrations **2a** is the major compound but when increasing the concentration the dication $[\{(\text{NHC})(\text{R})\text{Au}(\mu\text{-F})\}_2]^{2+}$ (**2b**) with two bridging fluorido ligands is formed. So far, it has been impossible to get crystallographic proof of **2a**.^[141]

The synthesis of fluorido gold(III) and *cis*-difluorido gold(III) compounds from their chlorido precursor compound is also possible by a halogen exchange reaction with AgF as shown by the group of Nevado (Scheme 7).^[142,143] This procedure also works for the synthesis of other mono- and difluorido gold(III) complexes starting from the corresponding chlorido or bromido complexes.^[116] Most recent reports on the reaction of XeF_2 with the $[\text{Au}^{\text{I}}(\text{CF}_3)_2]^-$ anion^[38] and the $[\text{Au}^{\text{I}}(\text{im})_2]^+$ cation^[144] resulted in the corresponding difluorido gold(III) compounds with *trans*-arrangement (Scheme 8). The synthesis of the latter compound $[\text{Au}^{\text{III}}\text{F}_2(\text{im})_2]^+$ was motivated by results that are part of this thesis.^[145] Further, the cation $[\text{Au}^{\text{III}}\text{F}_2(\text{im})_2]^+$ can also be synthesized from KF and *trans*- $[\text{Au}^{\text{III}}(\text{im})_2(4\text{-CN-py})_2]$ by

Oxidation with XeF_2

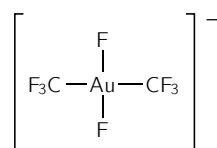


Substitution with AgF :

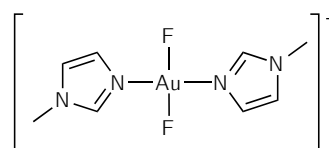


Scheme 7. Top: Synthesis of a *cis*-difluorido gold(III) complex (**2a**) by oxidation of a gold(I) precursor. The equilibrium of the *cis*-difluorido complex with the fluoride-bridged bimetallic dication (**2b**) is strongly depended on the concentration. The counter anions formally are F^- but they were not found in the reported crystal structures and the identity of the anion has not been resolved unambiguously.^[142] Bottom: Synthesis of a *cis*-difluorido gold(III) complex (**3**) by halogen exchange with AgF .^[143]

Menjón 2018:



Dutton 2018:



Scheme 8. *Trans*-difluorido gold(III) complexes reported from Menjón et al. (anion)^[38] and Dutton et al. (cation).^[145]

substitution of the 4-pyridincarbonitrile ligands.^[144] The formation of different configuration isomers after oxidation with XeF₂ is intriguing and probably strongly depending on the transition state of the fluorination reaction.

It was found that the use of Selectfluor^[146] as oxidation reagent in a proposed catalytic cycle of an Au^I/Au^{III} system as an electrophilic reacting source of fluorine works surprisingly well for C–C coupling reactions where one coupling partner is an alkyne or an alkene (Scheme 10).^[99,140,147] During the oxidation of a gold(I) compound with Selectfluor one fluorine atom is transferred to the gold center which is oxidized to gold(III) resulting in one vacant fourth coordination side at the gold atom (Scheme 9). This side is probably occupied by a donor solvent, a substrate such as alkynes or a donor atom that is part of a functionalized ligand (X) such as a ketone or ester moiety.

A C–F reductive elimination from fluorido gold(III) derivatives is not as facile as for the other halogens and instead gold-bonded carbon atoms are activated towards attack by a nucleophile under reduction of the gold.^[148,149] Generally, C–F reductive eliminations are rare for transition metals and only few reports discuss such a reactivity.^[150] A ligand assistance with C–H bond activation prior to the C–F bond formation has been reported for several complexes.^[151] In case of the *cis*-difluorido gold(III) compound a C_{sp³}–F reductive

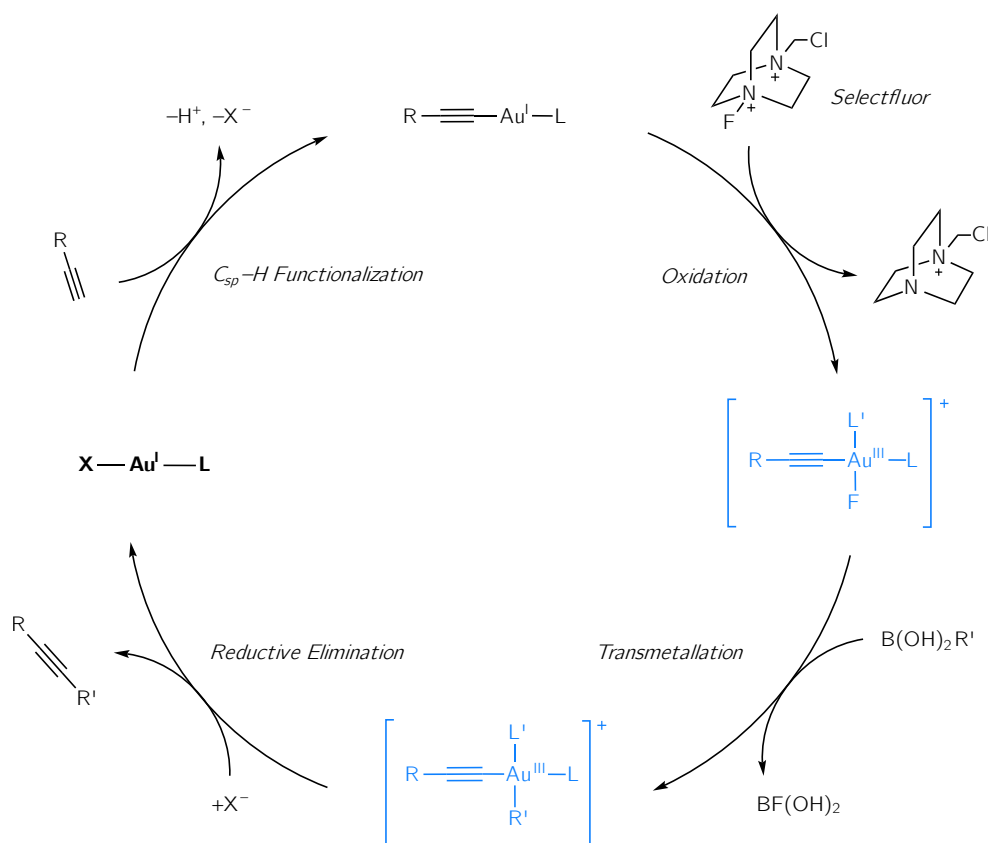


R: NHC, PPh₃

X: Cl, Br, alkene substrate

L: solvent, other present donor ligand

Scheme 9. General scheme for the proposed intermediates (denoted in blue) after reaction of Selectfluor with a gold(I) complex. The fourth ligand is most likely a solvent molecule or a different present donor ligand and is often either not specifically assigned^[149,150] or not further specified.^[141] Often an isomerization is required to enable a *cis*-reductive elimination.



L: donor ligand such as PPh_3 or NHC
 L': donor solvent or other present donor ligand

Scheme 10. Plausible mechanism as representative for a catalytic cycle of a gold(I)/Selectfluor system – here yielding a cross coupling product similar to the Sonogashira coupling reaction (modified cycle from different references^[141,149]). The steps functionalization and oxidation could happen vice versa. The blue intermediates have not been observed yet.

elimination is found but often accompanied by a β -H elimination which regularly outreaches the C–F bond formation.^[148] Interestingly, in case of a $-\text{CF}_2\text{Ph}$ substituent the potential C–F reductive elimination becomes facile and instantly appears.^[152] For fluorination reactions with Selectfluor and organometallic gold(I) compounds two reaction mechanisms are discussed – first, oxidation of the gold(I) compound followed by a C–F reductive elimination and secondly, a fluoro-demetalation where the $\text{Au}^{\text{I}}\text{--C}$ bond is directly attacked by Selectfluor without oxidation of the gold.^[140] Nevertheless, the gold complex is necessary for the fluorination reactions and usually no fluorination is found without a organometallic gold species.^[140,153]

Most investigations focus on the application as homogeneous C–C cross coupling catalyst because the fluoro ligand readily is exchanged using compounds like dihydroxy phenyl

borane and followed by a C–C reductive elimination.^[141,142] Additionally, the fluoro gold(III) compounds are significantly more stable in comparison to their other halogenido analogues which show facilitated C–Hal reductive eliminations (Hal: Cl, Br, I).^[141,154] The C–C reductive elimination is quick and facilitated in comparison to the C–F reductive elimination. The transmetalation reaction with dihydroxy phenyl borane can be either via a two-step reaction or a bimolecular transmetalation with coupled reductive elimination.^[141,142]

Stoichiometric sacrificial use of Selectfluor for catalytic C–C cross coupling reactions has been investigated by many groups (Scheme 10).^[99,153,155,156,157] Nevertheless, none of the intermediate species after reaction with Selectfluor have been observed, yet. For an expected *cis*-reductive elimination often first an isomerization is necessary (Scheme 9). Such active species might be bimetallic because the bimetallic systems can be stabilized by an Au...Au interaction that could result in a complex with two gold(II) species.^[157] Recently, a pathway to use both, NHC chlorido gold(I) complex and Selectfluor catalytically for C–C coupling reactions between alkynes and alkenes has been reported. The active catalyst is proposed to be $[\text{AuClF}(\text{NHC})]^+$ with one vacant coordination site at the gold(III) – yet, characterization of such intermediate is still pending.^[156] It is surprising that no chlorido fluoro gold compound has been reported prior to results of this work and the only characterization has been done on intermediate species or complex mixtures.^[15,158]

Fluoro gold complexes are also intermediates in hydrodefluorination reactions^[159] as well as hydrofluorination reactions.^[137,160] and attract an increasing number of researchers.^[140,141,147,161] The capabilities of gold(III) as Lewis acidic reaction center are just at the beginning of being explored and only few studies are known^[138,162] as for example the C–F bond activation and conversion to a C–O bond.^[163] Recent investigations also focused on the trifluoromethyl derivatives of gold(III) and sometimes found decomposition to the corresponding fluoro gold(III) compounds after liberation of the comparable stable difluorocarbene.^[38,164]

Quantum-chemical calculation of such intermediate species offer a similar challenge as for the preparative chemists but also a great interest due to accountability for the relativist effects and its influence on the bonding in gold complexes^[37,62–67,165] and lately also the influence on the NMR parameters.^[166]

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B Objective and Scientific Goals

Since their first preparation, fluoro organo gold compounds are synthesized from chlorido gold compounds and the fluoro ligand is introduced in the last synthetic step. Usual pathways are halogen exchange reactions with AgF, an Au–O bond cleavage with py·HF, or oxidation of the gold(I) precursor by XeF₂. Trifluoro gold compounds are unknown in metalorganic chemistry. Gold fluorides are strongly oxidizing reagents and have been considered unsuitable for synthetic chemistry.

Objective of this thesis is the investigation on the feasibility to use neat gold fluorides as precursor materials for synthesis of fluoro organo gold complexes. As first step, this includes examination on the reactivity and stability of such compounds in suitable solvents. New gold fluorides that have a good stability and solubility in usual organic solvents should be synthesized. The preparation of trifluoro gold complexes has been unsuccessful up-to-date and the use of gold fluoride precursors, if feasible, is expected to give the necessary advantage to access such species.

Trifluoro organo gold(III) complexes are promising candidates for fluorination reactions. Several fluoro organo gold(III) complexes have been proposed as intermediates in catalytic reactions. However, they were never characterized or even observed and understanding of the reactivity is urgently required to understand and further develop catalytic chemistry with the redox couple Au^I/Au^{III}. Studies on the reactivity of trifluoro gold complexes are highly interesting and certainly open new possibilities to synthesize unprecedented gold(III) complexes.

C Publications

C.1 Taming the High Reactivity of Gold(III) Fluoride: Fluorido Gold(III) Complexes with N-Based Ligands

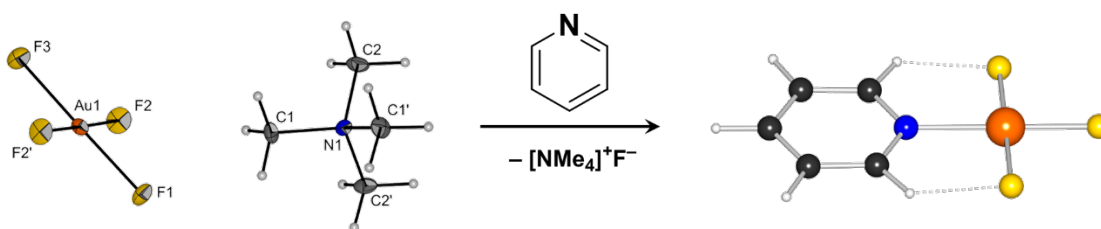


Figure 3. Graphical abstract. This figure and the following pages contain a modified reprint of the reference cited below by permission of Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Mathias A. Ellwanger, Simon Steinhauer, Paul Golz, Helmut Beckers, Anja Wiesner, Beatrice Braun-Cula, Thomas Braun, and Sebastian Riedel*

Chemistry – A European Journal **2017**, *23*, 13501 – 13509.

<https://doi.org/10.1002/chem.201702663>

Author Contribution

M. A. E. carried out most of the experiments and characterization, all of the computational studies and wrote the manuscript. S. S. and H. B. advised in spectroscopic measurements and revised the manuscript. P. G. (Bachelor thesis) carried out some of the experiments under M. A. E.'s supervision. A. W. and B. B.-C. conducted the crystallographic studies of $[\text{NMe}_4][\text{AuF}_4]$ and $[\text{NEt}_4][\text{AuF}_4]$. T. B. and S. R. managed the project and revised the manuscript.

The pages 32 – 40 contain the printed article and were removed due to the Copyright.

The article is available at

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The pages 41 – 58 contain the Supporting Information of the article
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C.2 Stabilization of Lewis Acidic AuF₃ as an N-Heterocyclic Carbene Complex: Preparation and Characterization of [AuF₃(SIMes)]

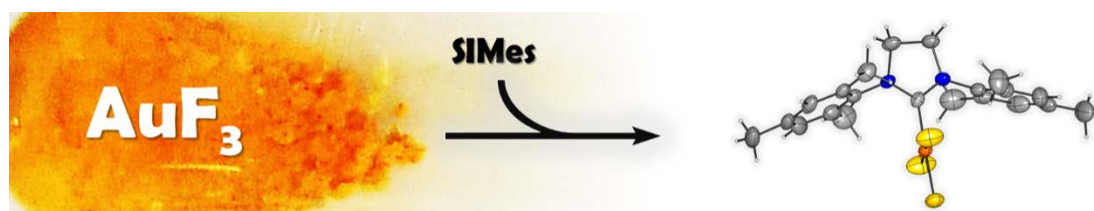


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Mathias A. Ellwanger, Simon Steinhauer, Paul Golz, Thomas Braun,* and Sebastian Riedel*

Angewandte Chemie International Edition **2018**, *57*, 7210 – 7214.

<https://doi.org/10.1002/anie.201802952>

German Edition (see Appendix for full version):

Stabilisierung von Lewis-azidem AuF₃ mithilfe eines N-heterocyclischen Carbens: Herstellung und Charakterisierung von [AuF₃(SIMes)]

Angewandte Chemie **2018**, *130*, 7328 – 7332.

<https://doi.org/10.1002/ange.201802952>

Author Contribution

M. A. E. carried out most of the experiments and characterization, all of the computational studies and wrote the manuscript. S. S. conducted the crystallographic studies and revised the manuscript. P. G. (Bachelor thesis) carried out some of the experiments under M. A. E.'s supervision. T. B. and S. R. managed the project and revised the manuscript.

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C.3 Tuning the Lewis Acidity of Difluorido Gold(III) Complexes: the Synthesis of $[\text{AuClF}_2(\text{SIMes})]$ and $[\text{AuF}_2(\text{OTeF}_5)(\text{SIMes})]$

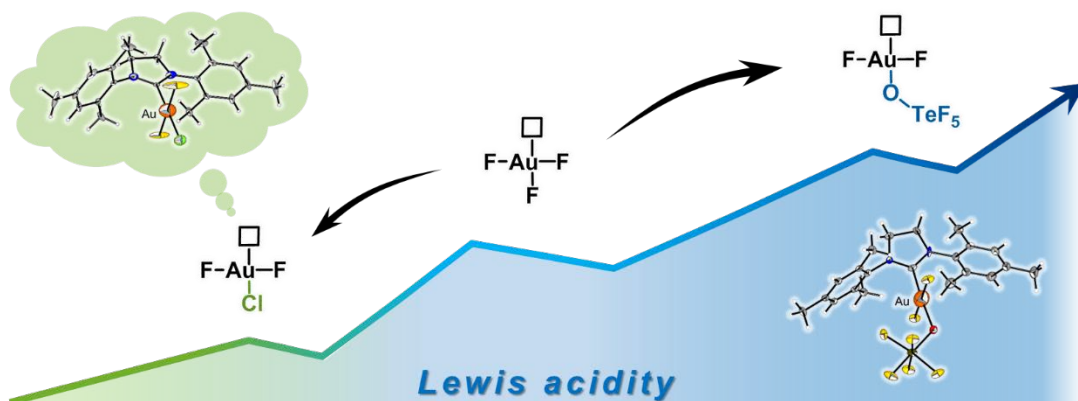


Figure 5. Graphical abstract. This figure and the following pages contain a modified reprint of the reference cited below by permission of The Royal Society of Chemistry. Copyright 2018 The Royal Society of Chemistry.

Mathias A. Ellwanger, Clara von Randow, Simon Steinhauer, Yunfei Zhou, Anja Wiesner, Helmut Beckers, Thomas Braun, and Sebastian Riedel*

Chemical Communications **2018**, 54, 9301 – 9304.

<https://doi.org/10.1039/c8cc05233f>

Author Contribution

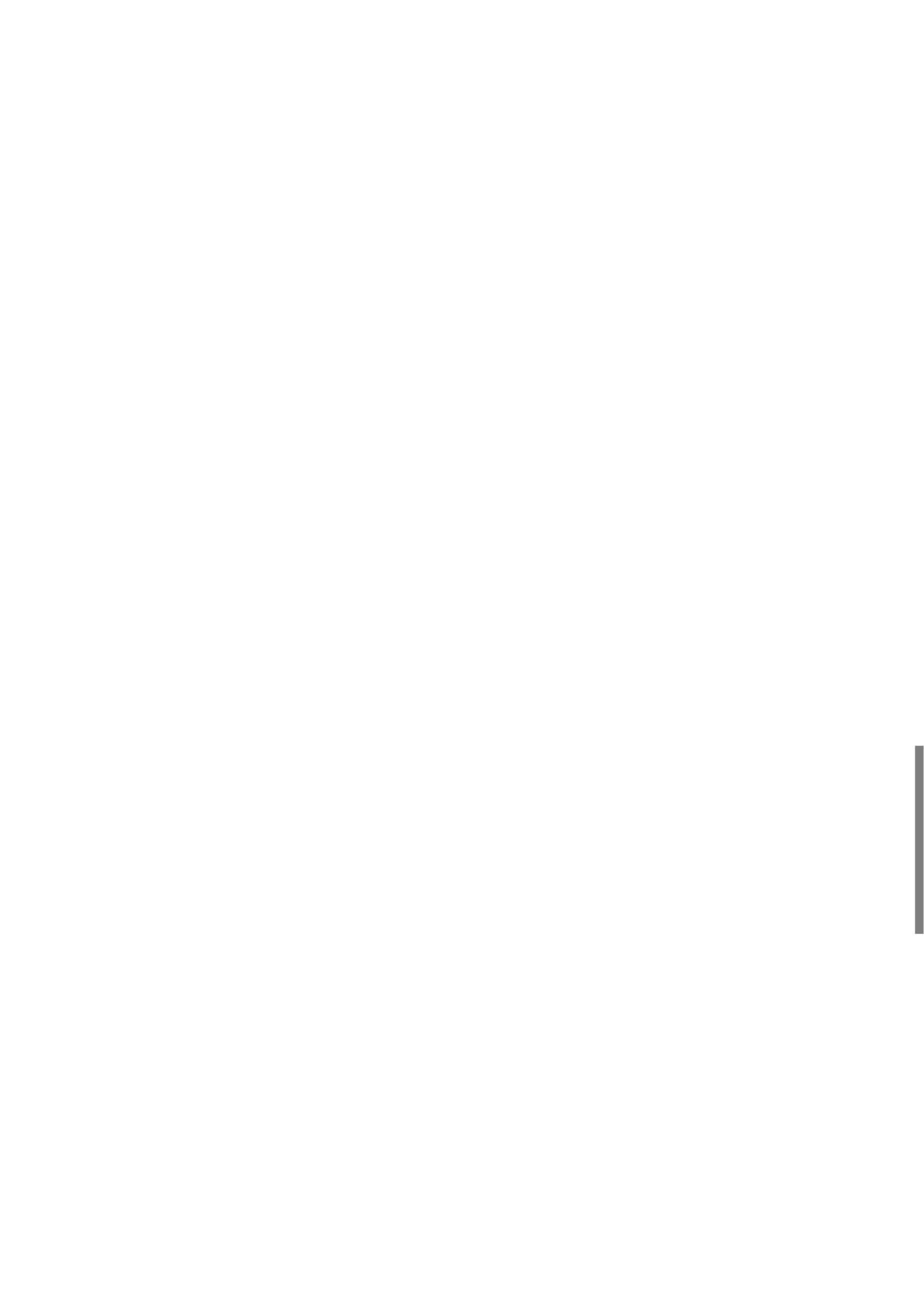
M. A. E. carried out most of the experiments and characterization, all of the computational studies and wrote the manuscript. C. v. R. (research internship) carried out some of the experiments under M. A. E.'s supervision. S. S. conducted the crystallographic studies on $[\text{AuClF}_2(\text{SIMes})]$ and $[\text{AuF}_2(\text{OTeF}_5)(\text{SIMes})]$ and revised the manuscript. Y. Z. (research internship) carried out some of the experiments (synthesis of $\text{Me}_3\text{SiOTeF}_5$) under M. A. E.'s supervision. A. W. conducted the crystallographic studies on $\text{Me}_3\text{SiOTeF}_5$. T. B. and S. R. managed the project and revised the manuscript.

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D The Behavior of Trifluorido Gold(III) Complexes

The introduction of gold fluorides into a wider range of synthetic chemistry is considered a central aspect of this thesis. Withal, a convenient access as well as stable and good to handle gold fluorides as precursor materials are necessary and will be discussed in the following chapter.

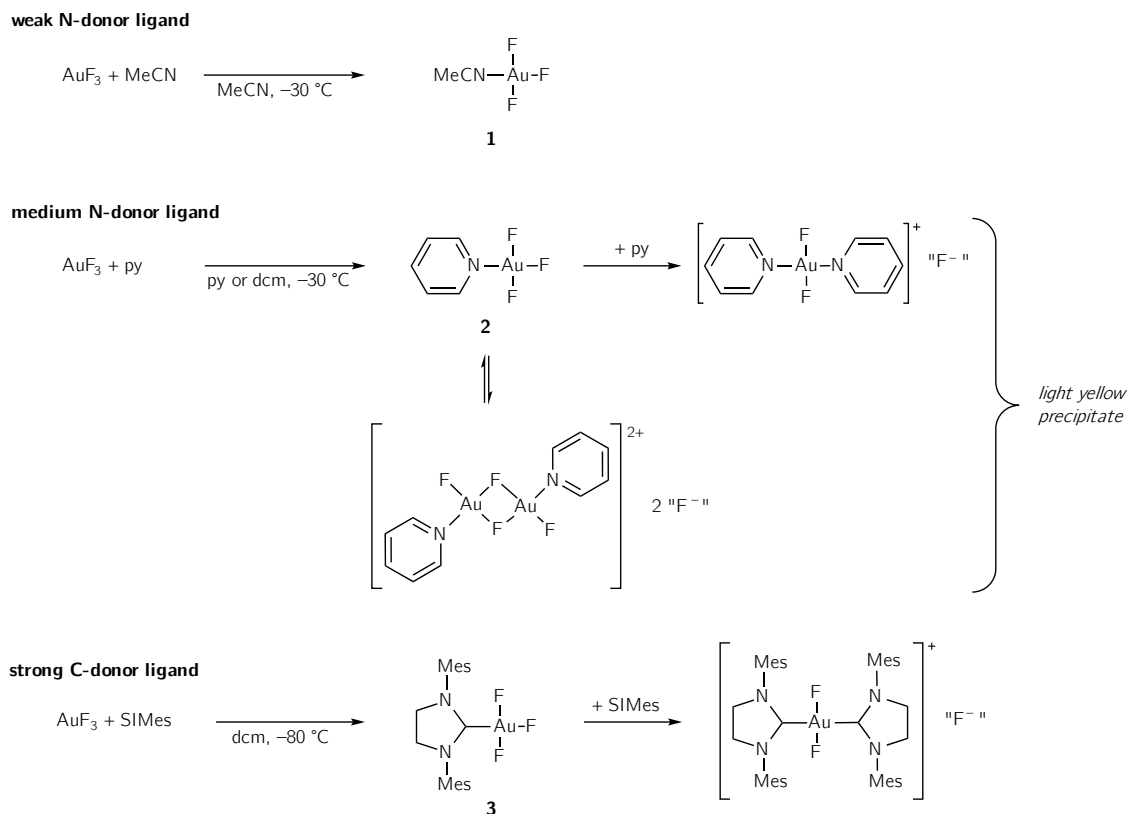
D.1 Synthesis of Gold(III) Fluorides

The most convenient synthesis of AuF_3 has been reported by Sharpe in the reaction of Au with BrF_3 , which is readily available by synthesis from Br_2 and 20% F_2 in N_2 .^[1,2] For the $\text{M}[\text{AuF}_4]$ derivatives usually solid state reactions between AuF_3 and MF or direct fluorination of $\text{M}[\text{AuCl}_4]$ (M: alkaline metals, earth alkaline metals, more), both at high temperatures have been state of the art.^[3] The introduction of the method from Sharpe for the synthesis of $\text{M}[\text{AuF}_4]$ (M: K, Cs) which will similarly work for the majority of cations was shown. Further development resulted in a convenient one-pot synthesis starting either from Au or AuF_3 in a PFA reactor which could be heated in order to remove residual BrF_3 . It has been shown that the cations $[\text{NAlk}_4]^+$ are also stable in a BrF_3 solution that is diluted with Br_2 . The stability decreases in the expected order where $\text{Alk} = \text{Me} > \text{Et} > \text{Pr}$ and it was possible to synthesize the $[\text{NMe}_4][\text{AuF}_4]$, $[\text{NEt}_4][\text{AuF}_4]$ and $[\text{NPr}_4][\text{AuF}_4]$ salts. During the BrF_3 removal step by cautious heating of the samples the $[\text{NMe}_4][\text{AuF}_4]$ salt is the only one where the cation is not attacked. In case of $[\text{NEt}_4][\text{AuF}_4]$ 5 % of the ethyl groups were mono-fluorinated and in case of $[\text{NPr}_4][\text{AuF}_4]$ a significant amount of the propyl groups were fluorinated. Only $[\text{NMe}_4][\text{AuF}_4]$ is stable at room temperature under inert conditions for long-term storage (more than 1 year) which is the reason why we limited reactivity studies on the $[\text{NMe}_4][\text{AuF}_4]$ salt.

D.2 Solvents for Gold(III) Fluorides and their Complexes

In order to use gold(III) fluorides as precursor compounds for the synthesis of soluble trifluorido organo gold(III) compounds the probably highest initial barrier is to find a suitable solvent which is compatible with the high fluorination potential of neat gold(III) fluorides. Furthermore, the ligand precursor molecules as well as the product must be stable in the solvent. All of which have been a significant challenge in the progress of this work.

The Lewis acid AuF_3 reacts violently with benzene and alcohol as has been reported by Sharpe.^[2] The reactivity of AuF_3 towards aromatic solvents decreases with its grade of fluorination ($\text{C}_6\text{H}_6 > \text{C}_6\text{FH}_5 > \text{C}_6\text{F}_2\text{H}_4 > \text{C}_6\text{F}_6$). Benzene reacts under ignition whereas for *ortho*-difluorobenzene the reaction is already significant less violent and hexafluorobenzene does not react at all. In general, perfluorinated solvents such as perfluoro-hexane, FC-770 (perfluorinated *N*-butylmorpholine), perfluoro-tributylamine do not react with gold fluorides. However, they are not suitable because neither AuF_3 or any tested $[\text{AuF}_4]^-$ salt nor the potential ligands such as NHC or pyridine dissolve. Alkanes are also unreactive but even a solution of SIMes (1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene) in *n*-pentane does not react with AuF_3 , probably because the product $[\text{AuF}_3(\text{SIMes})]$ is not soluble as well. All tested sulfur-containing solvents, SO_2 , SO_2ClF , and $\text{C}_4\text{F}_9\text{SO}_3\text{F}$ showed decomposition with AuF_3 , as well as with the $[\text{AuF}_4]^-$ salts. Chlorine containing solvents undergo a chlorine-fluorine exchange reaction with AuF_3 and $[\text{NMe}_4][\text{AuF}_4]$ due to the high stability of the fluorinated carbon derivatives (see chapter A.1), but the speed of this reaction is strongly temperature and substrate dependent. Suitable combinations were found with dichloromethane and $[\text{NMe}_4][\text{AuF}_4]$ at $-30\text{ }^\circ\text{C}$ as well as AuF_3 at $-80\text{ }^\circ\text{C}$. The solubility of these gold fluorides at these temperatures is extreme low and no corresponding signals were seen in the ^{19}F NMR spectra. In this case the products of the reaction with SIMes are better soluble and can well be seen in a ^{19}F NMR spectrum. The reaction is also possible in *ortho*-difluorobenzene at $-30\text{ }^\circ\text{C}$ but the yields are worse. Solvents with a donor functionality such as acetonitrile (MeCN), pyridine, or THF are generally compatible but often react themselves with the gold(III) fluorides. MeCN reacts with AuF_3 and forms the $[\text{AuF}_3(\text{MeCN})]$ complex (**1**) which decomposes above $-20\text{ }^\circ\text{C}$. The more stable $[\text{NMe}_4][\text{AuF}_4]$ does not react with acetonitrile and reactions can conveniently be done at room temperature if the product is stable. Acetonitrile also dissolves small amounts of $\text{Cs}[\text{AuF}_4]$. The stronger donor solvent pyridine reacts with both, AuF_3 and $[\text{NMe}_4][\text{AuF}_4]$ under formation of $[\text{AuF}_3(\text{py})]$ (**2**). Ligand precursors with a strong donor functionality can be reacted with AuF_3 or $[\text{NMe}_4][\text{AuF}_4]$ in donor solvents with a weaker donor functionality. Therefore, the reaction of AuF_3 or $[\text{NMe}_4][\text{AuF}_4]$ with pyridine is possible in acetonitrile which is a weaker donor. Further, the reaction with SIMes is possible in MeCN, pyridine, THF and probably many more solvents.



Scheme 11. Scheme for the formation of $[\text{AuF}_3(\text{L})]$ complexes with $\text{L} = \text{MeCN}$ (**1**, top), pyridine (**2**, middle), and SIMes (**3**, bottom). Observed secondary reactions are also shown. The compounds $[\text{AuF}_3(\text{SIMes})]$ and $[\text{AuF}_2(\text{SIMes})]^+$ are stable for several days in a dichloromethane solution as neat solutions.

During the synthesis of $[\text{AuF}_3(\text{MeCN})]$ (**1**) no other fluorido gold species were seen in the ^{19}F NMR spectrum and at -30°C the trifluorido acetonitrile gold(III) complex is stable for several days up to weeks. The substitution of a fluorido ligand by a acetonitrile ligand is most probably thermodynamically not favored and, hence, also no substitution reaction is observed for $[\text{AuF}_4]^-$ salts.

The pyridine complex **2** reacts differently, and here the formation of $[\text{AuF}_2(\text{py})_2]^+$ indeed has been observed. However, compound **2** still is the main component, which slowly, during a few hours to some days, reacts further to the bimetallic dication $[\text{Au}_2\text{F}_4(\text{py})_2]^{2+}$ which has been characterized spectroscopically by its unique spin system (Scheme 11). In acetonitrile a quicker decomposition under formation of mainly $[\text{HF}_2]^-$ and a yellow precipitate was found. Any attempt to crystallize the fluorido pyridine gold(III) compounds resulted in either crystals of $[\text{NMe}_4][\text{HF}_2]$ or in a probably amorphous phase.

The best results for the synthesis of $[\text{AuF}_3(\text{SImes})]$ (**3**) were achieved in a dichloromethane solution at $-80\text{ }^\circ\text{C}$ starting from AuF_3 and SImes . In case of **3** AuF_3 outperformed $[\text{NMe}_4][\text{AuF}_4]$ always as starting material due to a decomposition reaction of $[\text{NMe}_4]\text{F}$ and **3**. Surprisingly, the synthesis in *ortho*-difluorobenzene seems to facilitate the formation of the double substituted gold complexes $[\text{Au}^{\text{III}}\text{F}_2(\text{SImes})_2]^+$ or the reduced $[\text{Au}^{\text{I}}(\text{SImes})_2]^+$ with $[\text{AuF}_4]^-$ as anion. Complex **3** is stable in diluted dichloromethane solutions but in highly concentrated solutions it decomposes under formation of a deep red solution containing elemental gold. Dichloromethane dissolves $[\text{AuF}_3(\text{SImes})]$ (**3**) very well until close to its freezing point and also in the crystal structure one CH_2Cl_2 molecule co-crystallized. In contrast, **3** precipitates in *ortho*-difluorobenzene around $-30\text{ }^\circ\text{C}$ nearly quantitatively.

Note, donor solvents seem to interact with the fluoro gold(III) complexes and showed in all cases a significant faster decomposition. The reaction of $[\text{NMe}_4][\text{AuF}_4]$ with SImes in MeCN at $-30\text{ }^\circ\text{C}$ gave an almost quantitative decomposition resulting first in a red-purple solution and followed by gilding of the reaction flask. A similar bad stability was observed when using pyridine or THF as solvent in the $[\text{AuF}_3(\text{SImes})]$ synthesis and the main products usually were elemental gold, HF, and $[\text{HF}_2]^-$.

In acetonitrile a potential decomposition mechanism is the autoionization of the neutral complex $[\text{AuF}_3(\text{L})]$ (L: SImes , py) to $[\text{AuF}_2(\text{L})_2]^+[\text{AuF}_4]^-$ as reported in the literature for other systems where the adduct $\text{SbF}_3(\text{IPr})$ isomerizes to $[\text{SbF}_2(\text{IPr})_2]^+[\text{SbF}_4]^-$ with one mesoionic IPr ligand.^[4] Autoionization reactions are facilitated due to the high dielectric constant of acetonitrile ($\epsilon = 36.6$).^[5] Furthermore, a ligand substitution reaction is similarly conceivable where one fluoro ligand is substituted temporarily by a solvent molecule. A cationic gold(III) intermediate, a potential $[\text{AuF}_2(\text{SImes})(\text{solvent})]^+$, is expected to have a high reactivity and the decomposition of such species is conceivable. Similarly, the formation of the side product $[\text{Au}^{\text{I}}(\text{SImes})_2][\text{AuF}_4]^-$ would be comprehensible through formation of a cationic gold(III) intermediate, that is easily trapped after a reductive elimination reaction by a second SImes ligand. Generally, $[\text{Au}(\text{MeCN})(\text{L})]^+$ (L: PPh_3 , NHC , other strong donor ligands) species have been reported and show a certain stability.^[6]

D.3 Stability and Reactivity the Trifluorido Gold(III) Complexes

The stability and reactivity of trifluorido gold(III) complexes is mainly influenced by the ligand which stabilizes the AuF₃ unit beside the solvent effects as discussed above. The σ -donor strength of the ligands increases in the row acetonitrile, pyridine, and SIMes and all of the ligands have rather weak π -acceptor capabilities. This is well seen in the calculated Gibb's energies for the Au–ligand dissociation reaction that follows the order **1** (202 kJ·mol⁻¹) < **2** (289 kJ·mol⁻¹) < **3** (463 kJ·mol⁻¹). Secondly, acetonitrile and pyridine are N-bonded ligands and SIMes binds through the carbene carbon atom. Due to the high electronegativity of the nitrogen atom Au–N bonds have a high ionic part.^[7] This results in a weak *trans* influence and *trans* effect for the complexes [AuF₃(MeCN)] (**1**) and [AuF₃(py)] (**2**). Therefore, the synthesis of **1** is only possible from AuF₃ but not from [NMe₄][AuF₄] because the similarly weak fluorido ligand is still a stronger ligand which also explains the fact that no substitution to the cationic [AuF₂(MeCN)₂]⁺ is found even though [Au(MeCN)₂]⁺ is known.^[6] Additionally, the fluorido ligand in *trans* position to the acetonitrile ligand (*trans*-F) is not significantly more reactive than in [AuF₄]⁻ and no further reaction has been observed such as a dimerization reaction as in case of **2**.

In contrast, pyridine is a stronger σ -donor and thus has a stronger *trans* influence which promotes the formation of the bimetallic dication [Au₂F₄(py)₂]²⁺ from complex **2** because of the increased reactivity of the *trans*-F ligands. Complex **2** is predicted by calculation to be planar and has been experimentally supported by a ¹H, ¹⁹F HOESY NMR experiment which showed a close proximity between the *cis*-F ligands and the *ortho*-H atoms of the pyridine ligand. Quantum-chemical calculations predict an H...F distance of 207 pm which would imply a significant interaction. Such an interaction would activate the Au–F_{*cis*} bond and further simplify the dimerization process of **2** under formation of [Au₂F₄(py)₂]²⁺ because both, *cis* and *trans* bonded fluorido ligands are involved (Scheme 11).

The tendency of fluorido gold(III) complexes to form fluorido-bridged bimetallic species has been observed before by Toste et al. who identified the dication [Au₂F₂(Me)₂(SIPr)₂]²⁺ (SIPr: 1,3-Bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene) by X-ray crystallography instead of the expected *cis*-[AuF₂(Me)(SIPr)].^[8] Herein, both fluorido ligands experience the *trans* influence/effect of a carbon donor ligand, either SIPr or methyl that both increase the reactivity of the fluorido ligands. As a conclusion it should be possible to omit the formation of a bimetallic species by omitting an activation of the *cis*-F ligands.

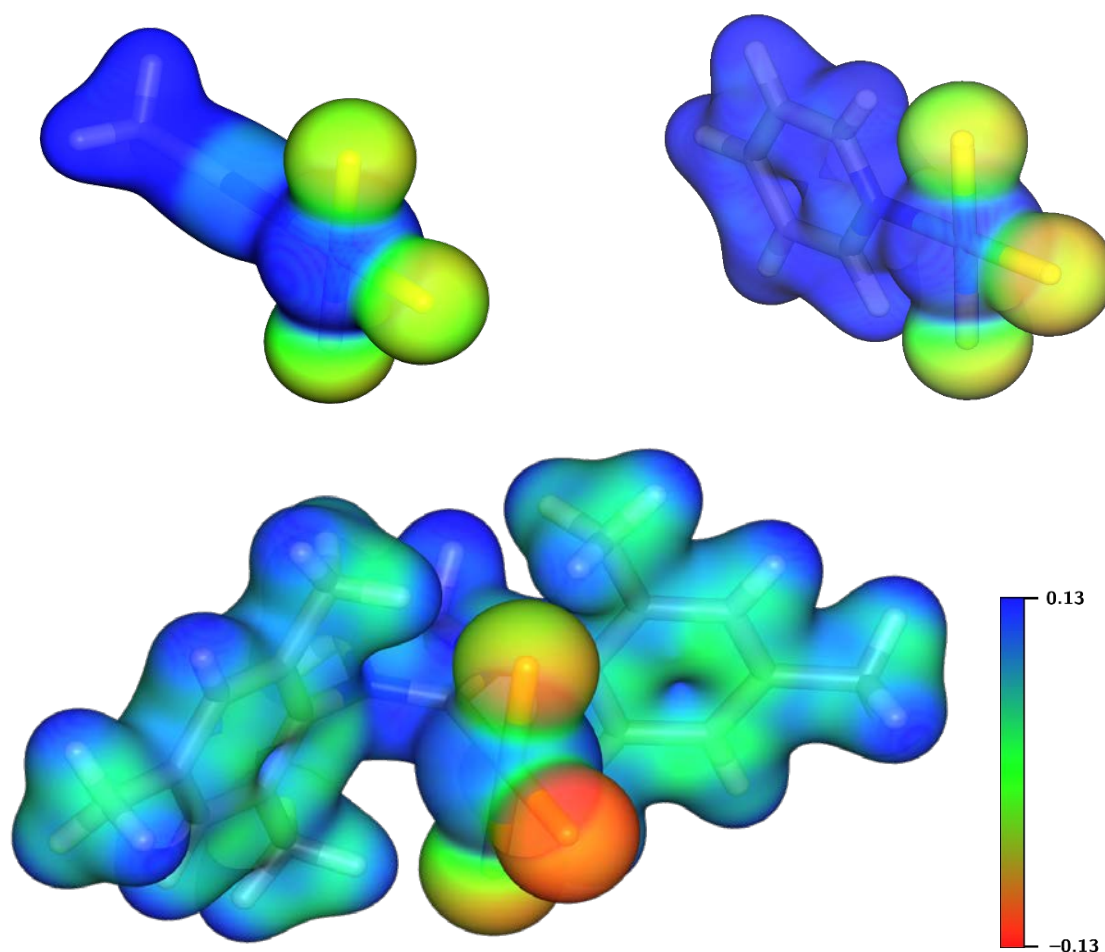
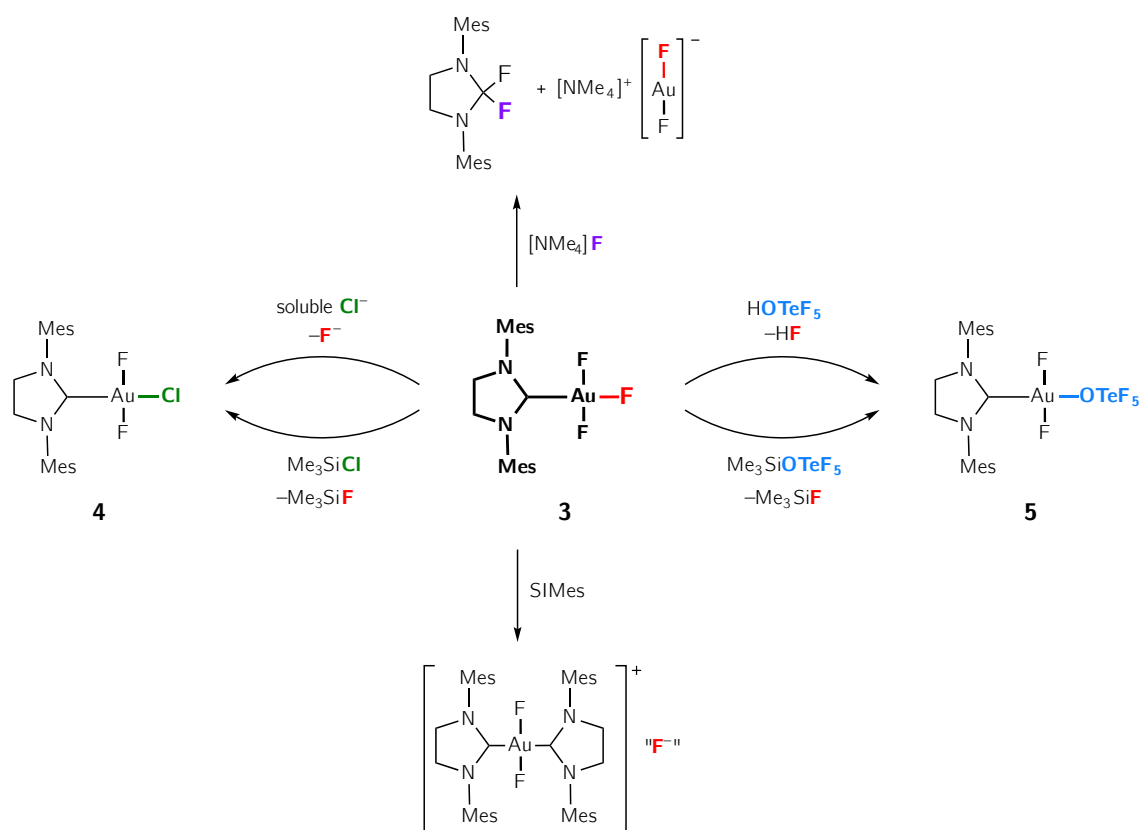


Figure 6. Electrostatic potential (0.13 to -0.13 a.u.) plotted on the electron density isosurface (0.025 e-bohr $^{-3}$) of $[\text{AuF}_3(\text{MeCN})]$ (**1**), $[\text{AuF}_3(\text{py})]$ (**2**), and $[\text{AuF}_3(\text{SIMes})]$ (**3**). Structures from ref.^[14]

Indeed, we did not observe any of such tendency for the complex $[\text{AuF}_3(\text{SIMes})]$ (**3**) where the F_{cis} ligands are not activated and the closest $F_{cis}\cdots(\text{H})\text{-C}$ distance is $328.4(4)$ pm, which is above the range of a significant interaction. The strong *trans* influence of the SIMes ligand is seen in an elongation of the Au-F_{trans} bond ($197.2(3)$ pm) compared to the Au-F_{cis} bonds ($191.6(1)$ pm and $192.1(1)$ pm).

These findings strongly influence the ^{19}F NMR chemical shifts of the fluoro ligands. A study of Gabuda et al. correlated the solid state ^{19}F NMR chemical shifts with the Au-F bond lengths for AuF_3 and $\text{Cs}[\text{AuF}_4]$ and found a good agreement.^[9] Elongation of the Au-F bond would result in a down-field shift of the ^{19}F NMR resonance. An according influence is found for **3**, where the ^{19}F NMR resonance of the *trans*-F nucleus (-217 ppm) is found about 100 ppm shifted down-field in comparison to the resonance for the *cis*-F nuclei (-316 ppm). In case of gold complexes, such an empirical correlation can be very



Scheme 12. Reactivity of $[\text{AuF}_3(\text{SIMes})]$ (**3**) towards nucleophiles (Cl^-), strong acids (HOTeF_5), and ligand transfer reagents (Me_3SiCl , $\text{Me}_3\text{SiOTeF}_5$). In these cases a selective substitution reaction of the *trans*-fluorido ligand was observed under the applied conditions. The reaction with a source of highly nucleophilic F^- leads to the fluorinated carbene ligand (top). $[\text{NMe}_4][\text{AuF}_2]$ expectedly is unstable and decomposes further. The reaction with one equivalent of SIMes leads to the cation $[\text{AuF}_2(\text{SIMes})_2]^+$ with a “free” fluoride anion which readily reacts with the solvent dichloromethane to Cl^- .

supportive for species that are stable only in solution and withdraw themselves from a structural characterization by single crystal X-ray diffraction such as $[\text{AuF}_2(\text{Me})(\text{SIPr})]$.^[8] The accurate quantum-chemical calculation of the NMR parameters for such compounds still is complicated, despite the development of the recent past.^[10]

The *trans* influence of the SIMes ligand increases the basicity of the *trans*-fluorido ligand in $[\text{AuF}_3(\text{SIMes})]$ significantly. A plot of the electrostatic potential on the isosurface of the electron density (Figure 6) shows a more negative potential on the F_{trans} ligand compared to the F_{cis} ligands. This illustrates the increased reactivity of the F_{trans} ligand which makes selective substitution reactions for this ligand feasible. A nucleophile like Cl^- reacts in a substitution reaction under formation of $[\text{AuClF}_2(\text{SIMes})]$ (**4**). However, a nucleophilic source of F^- (such as $[\text{NMe}_4]\text{F}$) instead attacks at the electrophilic carbene carbon atom and initiates a reductive elimination to form 2,2-difluoro-1,3-(dimesityl)imidazolidine

(Scheme 12). Most likely F^- simultaneously undergoes a substitution reaction with **3** but product and starting material are similar in this case and were not distinguished. Strong acids similarly activate the Au–F bond and react under liberation of HF as shown for the pentafluoro-orthotelluric (tefluc) acid ($HOTeF_5$) by formation of $[AuF_2(OTeF_5)(SIMEs)]$ (**5**). It was shown that the substitution reactions are much cleaner when trimethylsilane derivatives are used. The reaction of **3** with Me_3SiR (R: Cl, $OTeF_5$) is much faster and the product Me_3SiF can easily be removed under reduced pressure. Secondly, no acids, salts or reactive fluoride sources (such as $[NMe_4]F$) are formed and **4** and **5** only react very slowly with excess of Me_3SiR (R: Cl, $OTeF_5$).

One of the most useful tools to characterize carbene gold complexes in solution is the ^{13}C NMR chemical shift of the carbene carbon atom. It is very sensitive towards the electronic environment at the bonded atom, in case of a gold center its resonance in the ^{13}C NMR spectrum spreads over a wide range from the free carbene (240 ppm) to complex **3** (152 ppm) and even further for other atom centers.^[11] It was shown that the ^{13}C NMR chemical shift correlates with the Au–C bond strength and, thus, can be seen as probe for the Lewis acidity of the metal center. The *trans* influence is a main factor affecting the Lewis acidity and reactivity of metal centers and for the new complexes it follows the order **4** < **3** < **5**. The teflato ligand in complex **5** seemingly causes an increase in Lewis acidity of the Au^{III} center strengthening the Au–C bond similarly found by quantum-chemical calculations. Compound **5** is the only one of the SIMEs complexes in this thesis which is not stable in glassware and decomposes during a few days in solution – emphasizing its different reactivity compared to **3**. A probe to measure the Lewis acidities of metal centers and similarly the influence of different ligands is a helpful tool to understand stability and reactivity of transition metal complexes. Such characterization is still pending for the intermediate species in the frequently investigated reactions using Selectfluor with gold complexes and urgently required to acquire an understanding on these systems.

Comparison of the complexes **1** to **3** with their corresponding trichlorido gold(III) complexes shows many similarities. The acetonitrile trichlorido gold(III) complex is longly known and can be used as precursor for trichlorido gold complexes.^[12] The trichlorido pyridine complex is even one of the oldest gold complexes and also the cation $[AuCl_2(py)_2]^+$ is known. The molecular structure in the solid state of **3** is almost identical to $[AuCl_3(SIMEs)]$. However, significant differences between the fluoro and the chlorido gold complexes are obvious.

Alkyne bond insertion into Au^I-F bonds and catalytic cycles with external oxidants like Selectfluor are already known.^[13] The tendency to form bimetallic species such as [Au₂F₄(py)₂]²⁺ and also the C-F reductive elimination from a fluoro pyridine gold(III) species are similarly unique and might be facilitated by an intramolecular C-H activation due to the short calculated F...H-C distance. Complex **3** has a very Lewis acidic gold center which contrasts the otherwise as rather soft considered gold complexes by means of the HSAB concept. Therefore, it most certainly opens new pathways for reactivity and already showed in the synthesis of **5** that oxygen moieties might be reacted more easily at such gold centers. The instability of **5** further shows that it can be considered as precursor for a [AuF₂(SIMes)]⁺ reaction center because the decomposition most likely passes through formation of [AuF₂(SIMes)]⁺ or [AuF₂(solvent)(SIMes)]⁺.

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E Conclusion

A convenient one-pot synthesis of the gold(III) fluorides AuF_3 , $\text{Cs}[\text{AuF}_4]$, and $[\text{NAlk}_4][\text{AuF}_4]$ (Alk: Me, Et) with readily available reactants has been reported. For the first time, the stability of $[\text{NAlk}_4]^+$ (Alk: Me, Et, Pr) salts in liquid BrF_3 has been shown and can readily be applied for other projects including reactive ionic liquids. The $[\text{NAlk}_4][\text{AuF}_4]$ salts are the first good soluble gold fluorides and can easily be used in metalorganic chemistry. They are equally promising for synthesis of other inorganic gold(III) compounds via simple and thermodynamically most commonly favored substitution reactions, as shown for other fluoro gold(III) in this thesis. Further, the Lewis acid AuF_3 has been introduced as precursor for trifluoro gold(III) complexes with σ -donor ligands.

The first neutral trifluoro gold(III) complexes $[\text{AuF}_3(\text{MeCN})]$, $[\text{AuF}_3(\text{py})]$, and $[\text{AuF}_3(\text{SIMes})]$ have been synthesized and all three show a unique behavior. The acetonitrile complex $[\text{AuF}_3(\text{MeCN})]$ is a ready precursor in solution and the MeCN moiety is easily replaceable by stronger donor ligands. In case of $[\text{AuF}_3(\text{py})]$ a complex equilibrium between cationic and bimetallic species has been investigated. A C–F reductive elimination from one of these species was observed, and is expectedly facilitated by an intra- or intermolecular C–H bond activation. The carbene complex $[\text{AuF}_3(\text{SIMes})]$ has an unprecedented stability, can conveniently be handled, and does not show the formation of any bimetallic species. The *trans*-F ligand of $[\text{AuF}_3(\text{SIMes})]$ can selectively be substituted and the compounds *trans*- $[\text{AuF}_2(\text{L})(\text{SIMes})]$ (L: Cl, OTeF_5) have been synthesized and characterized.

Introduction of a SIMes affinity scale allowed an easy evaluation of the Lewis acidity of the gold center towards carbene ligands and showed differences to the fluoride ion affinity. We found indications for a stronger electron withdrawing power of the teflate group compared to fluorine. Isolation of $[\text{AuClF}_2(\text{SIMes})]$ as first structurally characterized chlorido fluoro organo gold(III) species is an important step towards the understanding of the proposed intermediates in $\text{Au}^{\text{I}}/\text{Au}^{\text{III}}$ catalytic cycles. The complex $[\text{AuF}_2(\text{OTeF}_5)(\text{SIMes})]$ can be seen as potent precursor for a *trans*- $[\text{AuF}_2(\text{SIMes})]^+$ cation with a highly active reaction center. This work showed a new route to fluoro gold compounds and is an important step towards catalytic redox chemistry of gold.

Appendix

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Article C.2 (German Version)

The following pages contain the German version of the main article from chapter C.2 as a modified reprint of the reference cited below by permission of Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

German Title:

Stabilisierung von Lewis-azidem AuF_3 mithilfe eines N-heterocyclischen Carbens: Herstellung und Charakterisierung von $[\text{AuF}_3(\text{SIMes})]$

Mathias A. Ellwanger, Simon Steinhauer, Paul Golz, Thomas Braun,* and Sebastian Riedel*

Angewandte Chemie **2018**, *130*, 7328 – 7332.

<https://doi.org/10.1002/ange.201802952>

The pages 118 – 122 contain the printed article and were removed due to the Copyright.

The article is available at

<https://doi.org/10.1002/ange.201802952>

Supplementary Info (Introduction)

Table 3. Experimental bond energies of the diatomic molecules taken from reference.^a

		...-F	...-Cl	...-Br	...-I
bond energies kJ·mol ⁻¹	Au-...	294	280±21	213±21	276
	C-...	514±10	395±13	318±8	253±36
	Si-...	576±17	417±6	358±8	243±8
	B-...	732	427	391±1	361

a: Y.-R. Luo, *Comprehensive Handbook of Chemical Bond Energies*, CRC Press, Boca Raton, **2007**.

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- [1] **M. A. Ellwanger**, S. Steinhauer, P. Golz, H. Beckers, A. Wiesner, B. Braun-Cula, T. Braun, S. Riedel, *Chem. Eur. J.* **2017**, *23*, 13501–13509.
- [2] **M. A. Ellwanger**, S. Steinhauer, P. Golz, T. Braun, S. Riedel, *Angew. Chem. Int. Ed.* **2018**, *57*, 7210–7214; *Angew. Chem.* **2018**, *130*, 7328–7332.
- [3] **M. A. Ellwanger**, C. von Randow, S. Steinhauer, Y. Zhou, A. Wiesner, H. Beckers, T. Braun, S. Riedel, *Chem. Commun.* **2018**, *54*, 9301–9304.

Conference Contributions - Oral Presentations

- [1] **M. A. Ellwanger**, B. Schröder, T. Braun, S. Riedel: Gold trifluoride – Routes to Fluoroorganogold(III) Compounds
GRK 1582 “Fluorine as a Key Element” Workshop **2015**, Caputh, Germany
- [2] **M. A. Ellwanger**, N. Subat, B. Schröder, T. Braun, S. Riedel: F_x -Au-L? – AuF_3 Route(s) to Fluoroorganogold(III) Compounds
GRK 1582 “Fluorine as a Key Element” Workshop **2016**, Strausberg, Germany
- [3] **M. A. Ellwanger**, P. Golz, N. Subat, B. Schröder, T. Braun, S. Riedel: F_x -Au-L? – AuF_3 Route(s) to Fluoroorganogold(III) Compounds
GRK 1582 “Fluorine as a Key Element” Meeting **2016**, Berlin, Germany
- [4] **M. A. Ellwanger**, P. Golz, N. Subat, B. Schröder, L. Hettmanczyk, B. Sarkar, S. Riedel: Routes to Fluorine-rich Fluoroorganogold(III) Compounds
17. Deutscher Fluortag **2016**, Schmitten, Germany
- [5] **M. A. Ellwanger**, P. Golz, S. Steinhauer, T. Braun, S. Riedel: Gold Fluorides as Precursors – Towards Fluoroorgano Gold(III) Compounds
GRK 1582 “Fluorine as a Key Element” Workshop **2017**, Zeuthen, Germany
- [6] **M. A. Ellwanger**, P. Golz, S. Steinhauer, T. Braun, S. Riedel: Gold Fluorides as Precursors – Taming the High Reactivity of Gold(III) Fluoride
GRK 1582 “Fluorine as a Key Element” Meeting **2017**, Berlin, Germany

- [7] **M. A. Ellwanger**, C. von Randow, S. Steinhauer, T. Braun, S. Riedel: Gold(III) Fluoride – Metalorganic [AuF₃R] Complexes
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- [8] **M. A. Ellwanger**, S. Steinhauer, C. von Randow, T. Braun, S. Riedel: Synthesis and Reactivity of Trifluorido Organo Gold(III) Complexes, [F₃AuR]
22nd International Symposium on Fluorine Chemistry **2018**, Oxford, United Kingdom
- [9] **M. A. Ellwanger**, C. von Randow, S. Steinhauer, H. Beckers, T. Braun, S. Riedel: Trifluorido Organ Gold(III) Complexes – Synthesis and Reactivity of [AuF₃R]
18. Deutscher Fluortag **2018**, Schmitten, Germany

Conference Contributions - Poster Presentations

- [1] **M. A. Ellwanger**, F. Brosi, F. A. Redeker, S. Kieninger, C. Müller, H. Beckers, S. Riedel: Polyfluoride Anions – New Insights
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- [2] **M. A. Ellwanger**, P. Golz, N. Subat, B. Schröder, S. Riedel: Gold(III) fluorides – Routes to Fluorine-rich Fluoroorganogold Compounds
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- [3] **M. A. Ellwanger**, P. Golz, N. Subat, B. Schröder, S. Riedel: Gold(III) fluorides – Routes to Fluorine-rich Fluoroorganogold Compounds
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- [4] **M. A. Ellwanger**, S. Steinhauer, P. Golz, T. Braun, S. Riedel: Taming Gold(III) Fluoride – A convenient Route to Complexes of AuF₃
GDCh Wissenschaftsforum Chemie **2017**, Berlin, Germany