

The Chemistry of Gold-fluoro compounds: A continuing challenge for Gold Chemists

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Abstract

This article gives a brief overview of the chemistry of gold-fluoro compounds known to date. The synthesis, structures, reactivity and computational results of gold fluorides are reviewed, discussed according to the gold oxidation state. The literature up to (and including) 2003 has been covered.

Introduction

Although the existence of a gold fluoride species was noted by Moissan as early as 1889 (1), the number of gold-fluoro compounds known today is still very small compared to the vast number of gold compounds containing chlorine, bromine and iodine. Partly, this may be due to the fact that many gold fluorides are highly reactive, moisture-sensitive materials which require specialized equipment for their synthesis, manipulation and characterization. A further reason may be the lack of readily available reagents to cleanly introduce fluoride ions: Silver(I) fluoride, for example, contains traces of water which can lead to formation of hydroxy compounds rather than fluoride species. Such problems might be overcome by using commercially available XeF_2 under strictly anhydrous conditions. On purely qualitative grounds a soft acid such as gold(I) tends to form stable complexes with soft bases such as I^- , Br^- and Cl^- . Furthermore, metal atoms in high oxidation states behave as hard acids and thus could be expected to form stable complexes with the hard base F. For gold, these predictions are indeed confirmed as will be shown in the subsequent sections of this article. This however, has not precluded isolation and characterization of fluoride compounds of other elements above and next to gold in the Periodic Table including Cu(I), Ag(I), Pt(II), Pd(II), Rh(I) and Ir(I) (2-5) and both AgF and AgF_2 are commercially available. This article will give a brief overview of the synthesis, structures and reactivity of gold-fluoro compounds known to date. Previous reviews on this subject matter were published in 1992 (6) and 1999 (7).

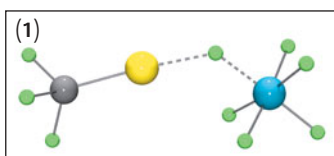
Gold +1

Early theoretical work based on the calculation of lattice energies and enthalpies of formation of AuF and CuF concluded that AuF is unstable even to decomposition to gold and fluorine atoms and the compound could not exist at any accessible temperature (8). More recently, Schwerdtfeger and his group have studied in some detail the properties of AuF and related species using high-level computational methods and have predicted its existence in the gas phase (9-15). In 1994 Schwarz and co-workers unambiguously identified AuF in the gas phase using neutralization-reionization mass spectrometry (16). Both computational results and experimental data showed that AuF is thermodynamically unstable and easily disproportionates to Au and AuF_3 .

Simple gold(I) complexes of the type LAuX , where L is any donor ligand (e.g. tertiary phosphine, tertiary arsine or organic sulfide) and X is any anionic ligand (e.g. halide, acetate, nitrate, triflate) have long been used as precursors in

gold chemistry and a vast number of such complexes have been described (17,18). Curiously, analogous fluoride complexes LAuF have not been observed to date. Pyykkö and co-workers have studied geometries and energies of $[\text{AuX}(\text{PH}_3)]$ compounds and found that $[\text{AuF}(\text{PH}_3)]$ was energetically similar to $[\text{AuMe}(\text{PH}_3)]$ at the MP_2 level of theory (19). In light of these encouraging computational results, attempts have been made to prepare $[\text{AuF}(\text{PPh}_3)]$ by treatment of $[\text{AuCl}(\text{PPh}_3)]$ with AgF in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (20). However, instead of isolating the gold(I) fluoro complex, the gold(I) oxonium cation $[\text{O}(\text{AuPPh}_3)_3]^+$ containing an $[\text{H}_2\text{F}_3]^-$ anion was obtained in high yield. The anion presumably derives from hydrolysis, generating HF which in the presence of fluoride ions forms the $[\text{H}_2\text{F}_3]^-$ species. It is interesting to note that no reaction is observed when $[\text{AuCl}(\text{PPh}_3)]$ is treated with AgF in the complete absence of water. Surprisingly, the copper(I) fluoride complex $[\text{CuF}(\text{PPh}_3)_3]$ can easily be prepared by reduction of CuF_2 with PPh_3 in MeOH (2,21) and the analogous silver(I) complex $[\text{AgF}(\text{PR}_3)_2]$ ($\text{R} = 4\text{-CH}_3\text{C}_6\text{H}_4$) is formed by reaction of the phosphine with AgF (3).

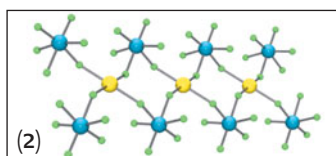
Seppelt and Küster obtained $[\text{F}_3\text{AsAu}]^+[\text{SbF}_6]^-$ (**1**) by reduction of AuF_3 in anhydrous HF using SbF_5 and AsF_3 (22). The Au-F distance in (**1**) is 2.118(6) Å, similar to the Au-F distances in $[\text{Au}(\text{SbF}_6)_2]$ (2.09(2) and 2.15(2) Å) (23). In addition, the Sb-F distance of the fluorine atom closest to Au is 1.934(6) Å, longer than the other five Sb-F distances (1.85-



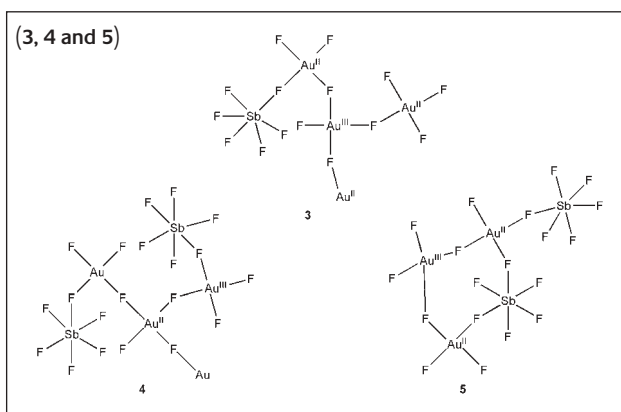
1.89 Å). On the basis of these data complex (**1**) can be formulated as either an ion pair of $[\text{F}_3\text{AsAu}]^+$ and $[\text{SbF}_6]^-$ or an SbF_5 adduct of $[\text{AuF}(\text{AsF}_3)]$. No matter which structural formulation is chosen, this complex represents the closest analogue of an LAuF complex known to date.

Gold +2

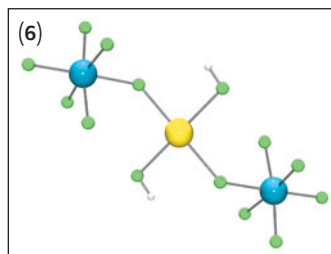
The +2 oxidation state is rarely observed in mononuclear gold compounds but quite a significant number of metal-metal bonded gold(II) complexes is known (17). Recently, some mononuclear gold(II) fluoride compounds have been reported and structurally characterized. Gold metal reacts with F_2 in anhydrous HF containing SbF_5 to give orange crystals of $[\text{Au}^{\text{II}}(\text{SbF}_6)_2]$ (**2**) (23). In this compound each Au(II) atom lies at the centre of an elongated octahedron of six fluoride ligands, each of which originates from a different SbF_6 moiety. The four equatorial Au-F distances are 2.09(2) and 2.15(2) Å, while the two axial ones



are 2.64(2) Å. The SbF_6 units are considerably distorted because of two Sb-F-Au interactions, resulting in elongated Sb-F distances of 1.99(2) and 1.94(2) Å. Further fluorination of $[\text{Au}^{\text{II}}(\text{SbF}_6)_2]$ yields the red mixed-valence compound $[\text{Au}^{\text{II}}(\text{SbF}_6)_2\text{Au}^{\text{III}}(\text{AuF}_4)_2]$ (**3**) (23). The structure consists of a polymeric sheet of Au(III) centers and two different Au(II) centers each coordinated to four fluoride ligands in a square planar arrangement. If this compound is treated with $\text{K}[\text{AuF}_4]$ a paramagnetic material formulated as $[\text{Au}^{\text{II}}(\text{Au}^{\text{III}}\text{F}_4)_2]$ is produced (23). Other workers have obtained similar polymeric gold(II) and mixed-valence gold(II)/gold(III) compounds, such as $[\text{Au}_3\text{F}_8](\text{SbF}_5)_2$ and $[\text{Au}_3\text{F}_7](\text{SbF}_5)_3$, by reduction of AuF_3 in anhydrous HF/SbF_5 in the presence of oxygen, hydrazinium difluoride or xenon (24). These complexes (**4-6**) are also built up from square planar $\text{Au}^{\text{II}}\text{F}_4$ and $\text{Au}^{\text{III}}\text{F}_4$ building blocks, the two being distinguishable by their different Au-F bond lengths: those for Au(II) range from 2.076(9) Å to 2.190(9) Å, whilst those for Au(III) range from 1.862(6) to 1.987(6) Å (24). The +2 oxidation state for gold in all these compounds was confirmed by magnetic measurements. Complex (**6**) also represents a rare example of a metal complex containing HF as ligand.

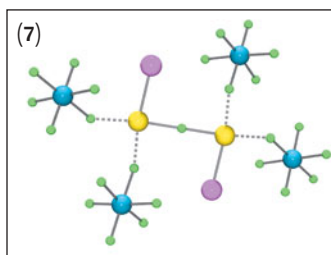


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The reaction of Au powder in anhydrous HF/SbF_5 with Xe gives the green binuclear gold-xenon complex $[\text{Au}_2\text{Xe}_2\text{F}](\text{SbF}_6)_3$ (**7**) (25). The complex consists of a Z-shaped $[\text{Au}_2\text{Xe}_2\text{F}]^{3+}$ cation containing a bridging fluorine atom with a short Au-F distance of 2.045(2) Å. The ionic complex $\text{Au}^{\text{II}}[\text{Au}^{\text{III}}\text{F}_4]_2$ consists of severely distorted octahedral Au^{2+} cations surrounded by six fluoride ligands, each one of which originates from a



different square planar $[\text{AuF}_4]^-$ anion (26). The equatorial Au-F distances in this compound are 2.141(8) Å and 2.100(8) Å, whilst the axial ones are 2.651(8) Å.

Attempts to prepare gold-gold bonded Au(II) fluoride complexes have been made but conclusive proof for their existence remains to be found. Bennett and Welling treated $[\text{Au}_2\text{Cl}_2(\mu\text{-C}_6\text{H}_4\text{PPh}_2)_2]$ with AgF and isolated a material that showed singlet ^{31}P and ^{19}F resonances. This may have been the hoped for $[\text{Au}_2\text{F}_2(\mu\text{-C}_6\text{H}_4\text{PPh}_2)_2]$ though the absence of P-F coupling requires explanation and single crystals suitable for an X-ray diffraction study could not be obtained (27). The attempted reaction of XeF_2 with $[\text{Au}_2(\mu\text{-2-MeC}_6\text{H}_3\text{PPh}_2)_2]$ with XeF_2 gave a material with a complex NMR spectrum, inconsistent with the hoped for F_2 oxidative addition product $[\text{Au}_2\text{F}_2(\mu\text{-2-MeC}_6\text{H}_3\text{PPh}_2)_2]$ (28). High-level DFT calculations using the model complex $[\text{Au}_2\text{F}_2(\mu\text{-C}_6\text{H}_4\text{PH}_2)_2]$ give Au-Au and Au-F bond lengths of 2.626 Å and 2.083 Å, respectively, consistent with observed Au-Au distances in other binuclear gold(II) complexes of this type (29). Attempts to prepare fluoride derivatives of binuclear bis(ylide) complexes such as $[\text{Au}_2\text{F}_2(\mu\text{-}\{\text{CH}_2\}_2\text{PPh}_2)_2]$ have not been reported.

Gold +3

Gold trifluoride has been known for more than 50 years and has been used as starting material for most of the known gold fluoride compounds. AuF_3 was first prepared by pyrolysis of the $\text{AuF}_3\cdot\text{BrF}_3$ adduct formed upon treatment of gold powder with BrF_3 (30). Recently a simpler and safer method for the preparation of pure AuF_3 directly from the elements was

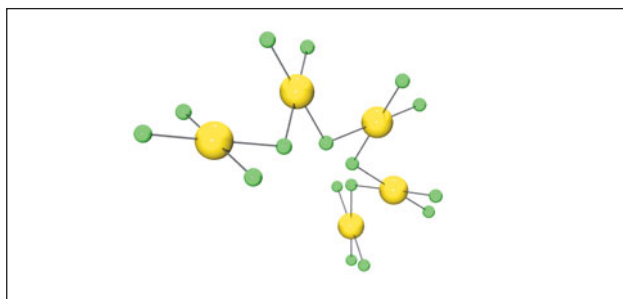


Figure 1A
Solid-state structure of AuF_3 .

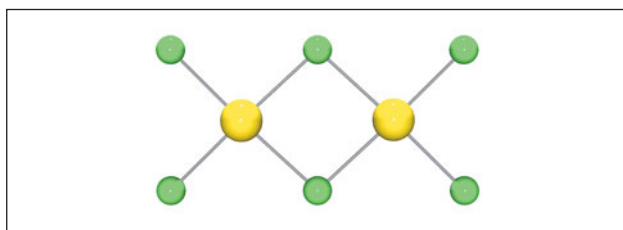
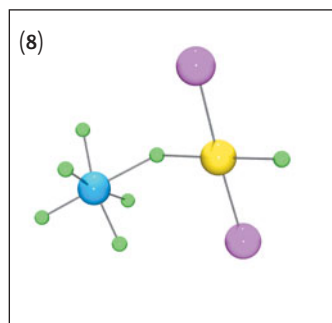


Figure 1B
Solid-state structure of AuCl_3 .

published (31). Gold trifluoride is a highly reactive material, decomposing in water with evolution of heat forming $\text{Au}(\text{OH})_3$ and HF (32) and also reacting violently with organic compounds, often causing ignition of the material! The solid-state structure of AuF_3 was first studied by X-ray powder diffraction, where it became apparent that the material was structurally very different from AuCl_3 (33). This was later confirmed by a single crystal X-ray diffraction experiment (34,35). The structure consists of a fluorine bridged helical chain polymer (Figure 1A), in which the chains are further cross-linked by weak fluorine-gold contacts (2.69 Å). The Au-F bridging distances (2.04 Å) are slightly longer than the non-bridging ones (1.91 Å). In comparison, AuCl_3 exists as a chloro-bridged dimer in the solid state (Figure 1B) (14,36). The gas-phase structures of AuX_3 (X = F, Cl, Br and I) have recently been investigated using computational methods (14,37,38). These results show that AuX_3 compounds are T-shaped (C_{2v}) structures due to first-order Jahn-Teller distortion. These T-shaped molecules are able to dimerize (AuCl_3) or polymerize (AuF_3), depending on the strength of electrostatic interactions between Au and Cl or F, respectively (14).

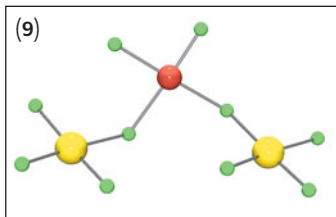
Gold trifluoride reacts with a wide range of metal fluorides to give cationic complexes containing the square planar tetrafluoroaurate $[\text{AuF}_4]^-$ anion. $\text{K}[\text{AuF}_4]$ (prepared from gold metal, KCl and BrF_3) was first reported in 1959 and unit cell dimensions were found to be very similar to those of $\text{K}[\text{AuBr}_4]$ (39). Neutron powder diffraction data obtained some years later confirmed that the anion consists of a square planar gold(III) atom with Au-F distances of 1.95 Å. In addition, the anions are packed such that weak secondary Au-F contacts of 3.12 Å result (40). Since then a large number of compounds containing this anion have been prepared and characterized using powder diffraction and/or single-crystal X-ray diffraction techniques. These include $\text{M}^+[\text{AuF}_4]^-$ M = Li, Na, Rb and Cs (41-43), $\text{M}^{II}[\text{AuF}_4]_2$ M = Mg, Ni, Zn, Ba, Cd, Ag, Au, Hg and Pd (26,44-47), $\text{CuF}[\text{AuF}_4]$ (48), $\text{O}_2[\text{AuF}_4]$ (49), $\text{Th}_2\text{F}_7[\text{AuF}_4]$ (50), as well as the lanthanide compounds $\text{M}_2\text{F}[\text{AuF}_4]_5$ M = Tb, Dy, Ho, Er (51) and $\text{MF}[\text{AuF}_4]_2$ M = Tm, Yb and Lu (52). The noble-gas compound $[\text{XeF}_5][\text{AuF}_4]$ has been obtained from $\text{BrF}_3\cdot\text{AuF}_3$ and XeF_6 and was characterized by X-ray powder diffraction and Raman spectroscopy (53). The anion in this



(8)
($[\text{Sb}_2\text{F}_{11}]^-$ anion not shown)

compound can be further oxidized by fluorination with KrF_2 to give $[\text{XeF}_5][\text{AuF}_6]$. The noble-gas gold(III) compound *trans*- $[\text{AuXe}_2\text{F}_2]^{2+}[\text{Sb}_2\text{F}_{11}]^-$ (8) was obtained from the reaction of gold metal with XeF_2 in

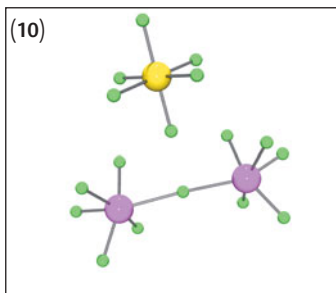
HF/SbF₅ (5:1) and characterized by single crystal X-ray diffraction (25). The Au-F distances were measured to be 1.878(3) Å and 1.981(3) Å for Au-F and Au-F-Sb, respectively.



Recently, a low-precision single crystal X-ray structure of the AuF₃·BrF₃ adduct was obtained (54). The structure (9) consists of planar BrF₄ groups bridging two planar AuF₄ units through *cis*-fluoride ligands to give a polymeric ribbon structure. The Au-F distances were measured to be 2.03(4) Å and 2.10(5) Å for the bridging fluorides and 1.77(5) Å and 1.84(5) Å for the non-bridging ones. The Raman spectrum of this compound indicate that this adduct has some [BrF₂]⁺[AuF₄]⁻ character (54).

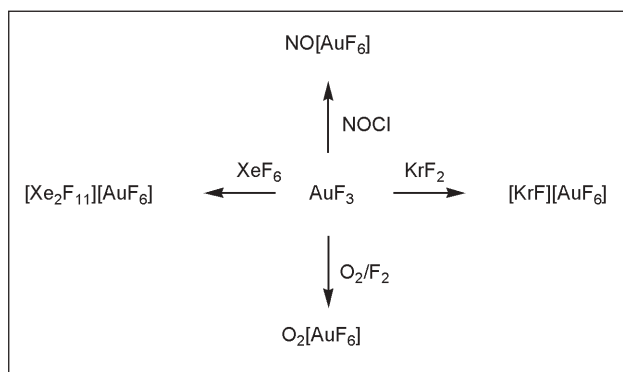
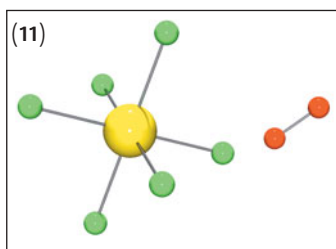
Gold +5

The +5 oxidation state of gold has only ever been observed in AuF₅ and various species containing the hexafluoroaurate anion [AuF₆].



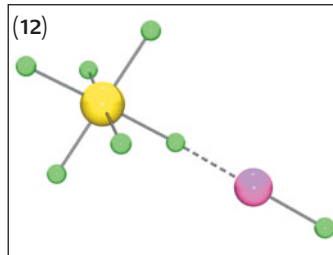
The reaction of AuF₃ with XeF₆ produces [Xe₂F₁₁][AuF₆] (Scheme 1) (55). The X-ray crystal structure of [Xe₂F₁₁][AuF₆] (10) has been determined and showed that the compound consists of an

octahedral [AuF₆]⁻ anion with two equatorial fluorides in close contact with the [Xe₂F₁₁]⁺ cation (56,57). The pentavalent state of gold was also confirmed by ¹⁹⁷Au Mössbauer spectroscopy



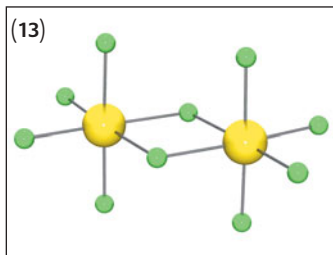
Scheme 1

(58). Since this first discovery a variety of other compounds containing [AuF₆]⁻ anions have been prepared by oxidation of gold trifluoride with NOCl, XeF₆, O₂/F₂ and KrF₂ as illustrated in Scheme 1 (56,59,60). The crystal structure of O₂[AuF₆] (11) has been determined and the Au-F bond lengths were measured to be 1.875(9), 1.895(9) and 1.889(10) Å for the



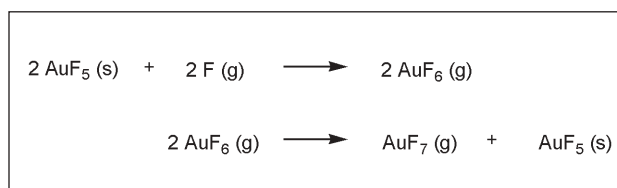
equatorial and axial fluorides, respectively (49,61,62). The X-ray crystal structure of [KrF][AuF₆] (12) has also been determined (62). The structure consists of an AuF₆⁻ anion that

strongly interacts with a KrF⁺ cation through a fluoride bridge. The equatorial and non-bridging Au-F distances range from 1.89(1) to 1.90(1) Å, while that of the axial Au-F-Kr bridge is 1.96(1) Å. Gold pentafluoride is formed by vacuum pyrolysis of [KrF][AuF₆] at 60-65° C or [O₂][AuF₆] at 150-180° C (60,63,64). In the gas-phase AuF₅ consists of a ca. 82:18 mixture of dimeric (D_{2h}) and trimeric (D_{3h}) molecules as determined by a vapor-phase electron diffraction (65). In both structures the gold atom is octahedrally coordinated with Au-F distances of 1.889(9) Å, 1.822(8) Å and 2.030(7) Å for the axial, terminal and bridging fluorides, respectively. A



recent single crystal X-ray diffraction study has shown that AuF₅ exists as the dimer (13) in the solid-state (61). The Au-F distances measured from the X-ray diffraction data are in excellent

agreement with the values obtained by electron diffraction. Gold pentafluoride is a very reactive compound and a strong fluorinating agent. AuF₅ reacts with xenon to produce XeF₄, and with bromine to form [BrF₂][AuF₄]; it also undergoes oxidative addition with fluorine to produce AuF₇ (63,66). In water AuF₅ explosively decomposes to produce gold metal, HF, O₂ and Au(OH)₃ but in anhydrous HF or BrF₅ hexafluoroaurates are formed (63,67).



Scheme 2

Gold +7

In 1986 a group of Russian workers claimed to have isolated AuF₇ by fluorinating AuF₅ with atomic fluorine in an oxygen free vacuum system and subsequently condensing the gaseous product into a liquid nitrogen cooled trap (Scheme 2) (66). The yellow crystalline solid has a high vapour pressure and is stable at room temperature. The compound was characterized in the gas phase by IR spectroscopy (band at 734 ± 3 cm⁻¹) and molecular weight determination. Elemental analysis data consistent with formulating the material as AuF₇ was also obtained. The gaseous material decomposes rapidly above 100° C into AuF₅ and F₂. However, to date these results have never been reproduced or confirmed.

Conclusions

The exploration of gold fluoride compounds by both theoretical and synthetic chemists began more than 50 years ago. Early endeavors in this field suffered from the high reactivity and difficulties in handling and characterizing gold fluorine compounds. As technology advanced and new materials became available, the field experienced rapid growth. Gold fluorides were the first compounds that exhibited the +5 and possibly +7 oxidation state of gold and also provided new examples of the rare +2 oxidation state. Furthermore, gold-fluoro compounds were instrumental in opening the field of gold-noble gas chemistry exemplified by the isolation and characterization of the tetraaxenonogold(II) cation in 2000 (68). Despite all these developments it is surprising that seemingly simple gold fluoride complexes such as [AuF(PPh₃)] have never been reported. The successful isolation and characterization of such complexes remains one of the biggest challenges in inorganic gold chemistry today.

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About the Author

Fabian Mohr is a graduate from RMIT University in Melbourne, Australia where he also completed his PhD working on cyclometallated gold complexes. Currently, Fabian is working with Professor Mariano Laguna at the University of Zaragoza, Spain where his research is focused on the development of water

soluble gold complexes as homogeneous catalysts as well as the characterisation and isolation of catalytically active intermediates. Outside the laboratory, Fabian is an accomplished harpsichordist and organist performing regularly as soloist and with baroque ensembles.

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Colours used in figures and structures: Au = yellow, F = green, As = grey, Sb = blue, H = pale blue, Br = brown Xe = magenta, O = red and Kr =pink.