▌Halides │*Reviews Showcase*│

Reactivity of Binary and Ternary Sulfur Halides towards Transition-Metal Compounds

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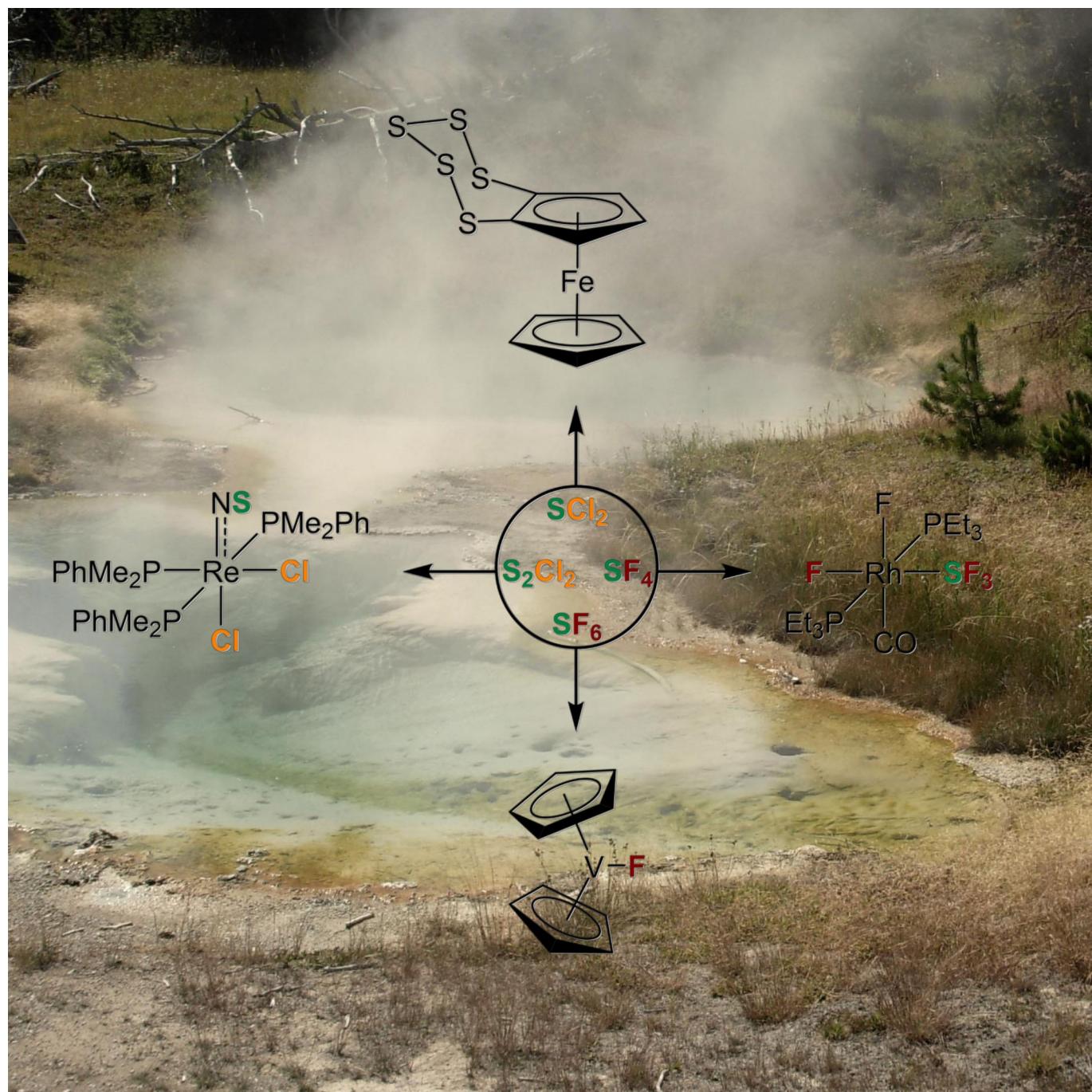
Abstract: Binary sulfur fluorides exhibit an interesting reactivity towards transition metal complexes. They open up routes for the generation of sulfur-containing building blocks. Often ligands with particular properties can be constructed. This includes their ability to transfer sulfur atoms or polysulfide units as well as fluorination reactions. This Minireview provides an insight into the reactivity of the binary and ternary sulfur halides S_2Cl_2, SCl_2, SF_4, SF_6 and SF_5Cl towards transition-metal compounds.

1. Introduction

Binary sulfur halides have been described in various oxidation states. The chloro derivatives SCl_2 and S_2Cl_2 are of importance in rubber as well as in lubricant industry because of their cross-linking and chlorination ability.[1] Both compounds are precursors for the synthesis of mustard gas and therefore are listed in the Chemical Weapons Convention.[2] Although S_2Cl_2 represents the most stable derivative of binary sulfur chlorides, it can easily be transformed into SCl_2 with chlorine gas.[3] The halides S_2Br_2 and S_2I_2 are both accessible from S_2Cl_2 but are significantly less stable than their chlorinated analogue.[4] SBr_2 and SI_2 have been observed in argon matrices and described theoretically, but attempts to isolate them in preparative amounts were not successful.[5] FSSF can be prepared by fluorination of elemental sulfur, whereas halide exchange at SCl_2 yields SF_2. Both compounds tend to convert into SSF_2 by isomerization or by disproportionation, respectively.[6] In addition, it has been reported that sulfur halides with higher sulfur contents S_yX_2 (X=Cl, y=1–30; X=Br, y=2–10) are accessible by treatment of thiols with sulfur halides, or for X=Cl by chlorination reactions of sulfur to produce for instance S_8Cl_2.[7]

SF_4 represents a very potent agent for a deoxyfluorination of organic precursors, but its gaseous character and high toxicity often hampers its use in synthetic chemistry.[8] However, SF_4 is a textbook example for a molecule that exhibits a see-saw shape geometry, which was elucidated by microwave, NMR, or Raman spectroscopy, electron diffraction and also by crystallography.[9] Among the heavier homologues of SF_4, SCl_4 is the most stable one, but it decomposes into SCl_2 and Cl_2 above $-31\,°C$, whereas SBr_4 and SI_4 have only been described theoretically, so far.[10] For SCl_4, IR and Raman spectroscopic data as well as powder XRD measurements suggest an ionic structure $[SCl_3]^+[Cl]^-$.[11]

In contrast to the other sulfur halides, SF_6 is a highly inert as well as a non-toxic and non-flammable compound.[12] Given its extraordinary properties, SF_6 is employed as a dielectric in high-voltage power applications.[13] Nevertheless, it is a potent greenhouse gas, and its use has been regulated by the Kyoto Protocol.[14] Reports on the heavier homologues of SF_6 are scarce and limited to DFT calculations on SCl_6, whereas SBr_6 and SI_6 have not been investigated yet.[15] Ternary sulfur halides are generally known, but only SF_5Cl and SF_5Br are used in synthetic chemistry for the introduction of SF_5 groups into organic compounds through radical pathways.[4d,e,16] SCl_nF_{4-n} (n=1–3),[17] SXF (X=Br, Cl),[18] SBrCl,[19] and S_2XY (X=F, Y=Br, Cl, I; X=Cl, Y=Br, I; X=Br, Y=I)[20] have only been observed under harsh conditions or described theoretically. Apparently, sulfur halides exhibit a decreasing tendency for the stabilization of higher oxidation states at sulfur with decreasing electronegativity of the halogen atom.[21]

In general, sulfur halides show a rich chemistry, but their reactivity at transition-metal centers is less explored, when, for instance, compared with studies of silicon or phosphorous halides. A derivatization of sulfur halides by transition-metal complexes might allow for the development of effective reaction routes to access novel sulfur containing reagents or building blocks. However, establishing metal-mediated conversions requires fundamental studies to investigate the behavior of sulfur halides at metal centers. An understanding of model reactions can subsequently be transferred into applications and might lead to new materials, reagents, or catalytic cycles.

This Minireview gives an overview on the reactivity of binary and ternary sulfur halides towards transition-metal compounds. The transformations involve reactions of S_2Cl_2, SCl_2, SF_4, SF_6, and SF_5Cl. Often sulfur atoms or sulfur-containing building blocks are accessible, which can be used for further synthesis. Chlorination, chlorofluorination, or fluorination at the metal centers can also occur.

Some aspects and reactivity patterns covered in section 2.4 and section 2.5 have been summarized and discussed in reviews focusing on the synthesis and chemistry of transition metal polysulfide complexes by Steudel, Schmidt, Laitinen, Rauchfuss, and Ogino.[22] A thorough guideline for the laboratory scale synthesis of sulfur halides is given by Brauer.[23] The structural as well as physical properties of chalcogen halides were covered extensively by Krebs and Ahlers in 1990.[5e]

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2. Sulfur(I)/(II) Compounds

2.1. Coordination of SCl₂

Particularly platinum-group metals have been studied by treatment of transition-metal chlorides or elemental transition metals with SCl₂, revealing that sulfur dichloride can either be a ligand, often at metal centers in a high oxidation state, or act as a chlorinating agent.[24] At $[Pt(Cl)_4(SCl_2)_2]$ (**1**) and $[Pd(Cl)_2(SCl_2)_2]$ (**2**) a pseudo-tetrahedral coordination sphere at the sulfur atom was found, when taking the additional electron pair at sulfur into account. This was confirmed by single-crystal X-ray diffraction analysis and the results are consistent with vibrational spectroscopic and powder X-ray diffraction data.[24g–j,m] Volkov and co-workers showed that SCl₂ ligands can also be generated from S₂Cl₂ or by decomposition of $[SCl_3]$ $[AuCl_4]$ (**3**) in the presence of elemental sulfur to give $[AuCl_3(SCl_2)]$ (**4**).[25]

2.2. Oxidation with sulfur halides

Reactions of transition metals and transition-metal chlorides with SCl₂ and S₂X₂ (X = Br, Cl) do not necessarily form SCl₂ ligands. Sulfur monohalides have been used for an oxidative generation of halido complexes to many different transition-metal compounds.[26] Typically, the reaction of sulfur mono- and dihalides with transition-metal compounds in lower oxidation states results also in the generation of metal halide sulfides and disulfides.[24f, 27] At transition-metal compounds in higher oxidation states, the formation of a variety of metal halide sulfide clusters was observed.[28] The composition of the furnished clusters strongly depends on the reaction conditions and the ratios of starting compounds, as for instance reported for the reaction of $[OsO_4]$ (**5**) towards S₂Cl₂.[28e,f,h–j] Additional sulfur or selenium in the reaction mixture seems to be a suitable tool to induce the formation of bridging polysulfide ligands[28h,i,29] or mixed polychalcogene entities in the clusters.[28e,f,j, 29]

It was also shown that SCl₂ can act as a chlorinating agent towards transition-metal complexes when reacted with $[Ind_2ZrMe_2]$ (Ind = indenyl, **6**) yielding $[Ind_2ZrCl_2]$ (**7**).[30] The reaction of SCl₂ at $(PPN)_2[Fe_8S_6(NO)_8]$ (**8**, PPN = bis(triphenylphosphine)iminium) resulted in the formal loss of two "{Fe(NO)}" fragments.[31] Thus, in the presence of DMF the structure $[Fe(DMF)_6][Fe_6S_6(NO)_6]$ (**9**) was afforded as the main product and $(PPN)[FeCl_3(NO)]$ (**10**) as a byproduct.

2.3. Reactivity of sulfur chlorides towards nitride complexes

It has been reported that S₂Cl₂ can act as reductive chlorinating agent to convert nitrido- into thionitrosyl complexes. Dilworth and co-workers reported on the formation of thionitrosyl phosphine complexes of rhenium and osmium by treatment of the nitrido compounds with S₂Cl₂ (Scheme 1).[32] Mixtures of $[Re(Cl)_2(NS)(PR_3)_3]$ (**11 a–11 d**) and $[Re(Cl)_3(NS)(PR_3)_2]$ (**12 a–12 d**) have been detected in reactions of $[Re(Cl)_2(N)(PR_3)_3]$ (**13 a–13 d**) [PR₃ = PMe₂Ph (**a**), PPh₂Me (**b**), PEt₂Ph (**c**), PPh₃ (**d**)]

with S₂Cl₂ but this could be avoided by introducing excess amounts of the sulfane to form exclusively **12 a–12 d**.[32c, 33] Treatment of the coordinatively unsaturated compounds $[Re(Cl)_2(N)(PPh_2R)_2]$ [R = Ph (**14 a**), nPr (**14 b**)] with S₂Cl₂ afforded the formation of the trichlorido rhenium thionitrosyl complexes **12 d** and $[Re(Cl)_3(NS)(PPh_2nPr)_2]$ (**12 e**).[32c]

The reaction of S₂Cl₂ with transition-metal nitrides **13 a–13 d** can further be extended to phosphine,[32c, 33, 34] arsine,[32c] dithiocarbamato,[35] thiocarbamoylbenzamidinato,[36] thiophosphorylamide,[37] (bi)pyridine,[32c] phenanthroline[38] nitride compounds of technetium(V), rhenium(V), and osmium(VI). In the reactions


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Thomas Braun (right) studied chemistry at the Julius-Maximilians-Universität Würzburg and received his Ph.D. under the supervision of Helmut Werner. After postdoctoral work with Pierre Dixneuf (Rennes, France) and Robin Perutz (York, UK), he obtained his habilitation with Peter Jutzi as mentor at the University of Bielefeld (Germany). In 2007, he was appointed Professor of Inorganic Chemistry at the Humboldt-Universität zu Berlin, where he is full professor since 2011. He received the Wöhler Award for Young Scientists in 2006, the RSC Fluorine Chemistry Prize in 2007, and the Fluorine Publication prize of the Fluorine Subject Group of the German Chemical Society in 2015. From 2010–2012 he served as the chair of the GDCh Fluorine Chemistry division and was from 2009–2018 vice-chair of the DFG (German Research Foundation) Research Training Group GRK 1582 "Fluorine as the Key Element". Currently he is vice-speaker of the DFG Collaborative Research Center "Fluorospecific Interactions: Fundamentals and Applications", and is also Executive Committee Member of the Fluorine Division of the ACS (American Chemical Society). From 2010–2012 he was head of Department of Chemistry at the Humboldt-Universität. His major interests are in fluorine chemistry as well as organometallic and coordination chemistry with an emphasis on the catalytic activation of small molecules. This involves C–F and C–H activation reactions, but also the chemistry of sulfur fluorides. He also has turned his attention to heterogeneous catalysis.

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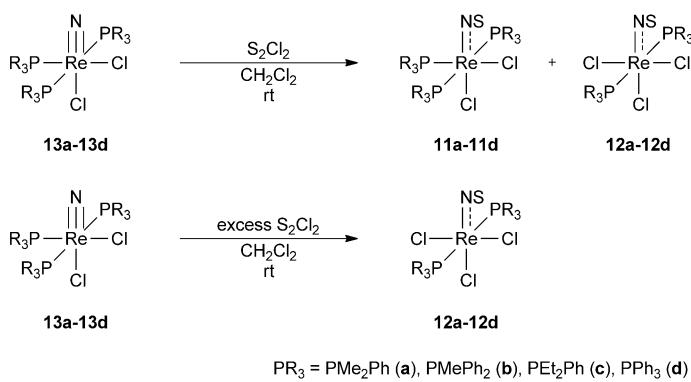
Scheme 1. Reactions of S_2Cl_2 towards [Re(Cl)$_2$(N)(PR$_3$)$_3$] [PR$_3$ = PMe$_2$Ph (**13a**), PPh$_2$Me (**13b**), PEt$_2$Ph (**13c**), PPh$_3$ (**13d**)].[32,33]

of [Re(A)(Cl)$_2$(N)(PMe$_2$Ph)$_2$] [A = N(SPPh$_2$)$_2$ (**15a**), N-(N,N-dialkylthiocarbamoylbenzamidinate) (**15b**), diethyldithiocarbamate (**15c**)] with S_2Cl_2, Abram and co-workers observed ligand dissociation yielding **11a** along with **12a** and [Re(N)(A)$_2$] (**16a–16c**) (Scheme 2).[37,39] Separation of the phosphine complexes was achieved by fractional crystallization.

Treatment of the technetium compounds [TcN(morphtcb)$_2$] [**17**, morphtcb = N-(N″-morpholinyl-thiocarbonyl)benzamidinato)] as well as [TcN{N(SPPh$_2$)$_2$}(PMe$_2$Ph)$_2$] (**18**) with S_2Cl_2 did not
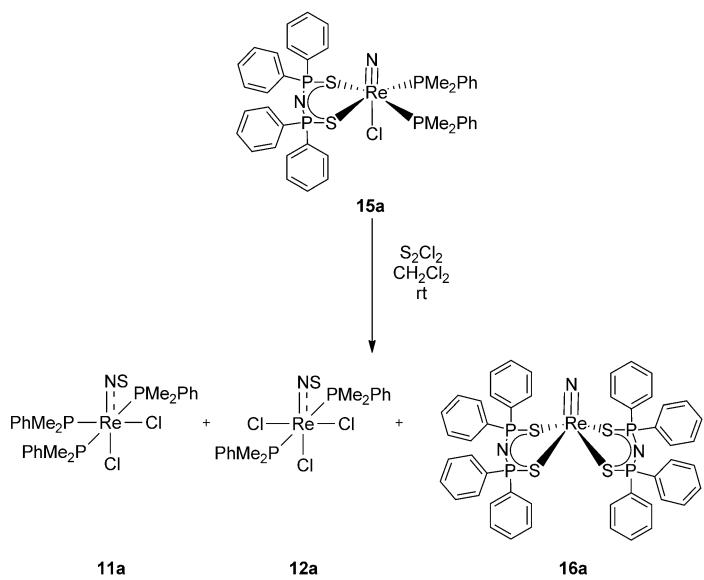
Scheme 2. Reactivity of S_2Cl_2 at [Re(N(SPPh$_2$)$_2$)(Cl)$_2$(N)(PMe$_2$Ph)$_2$] (**15a**).[37]
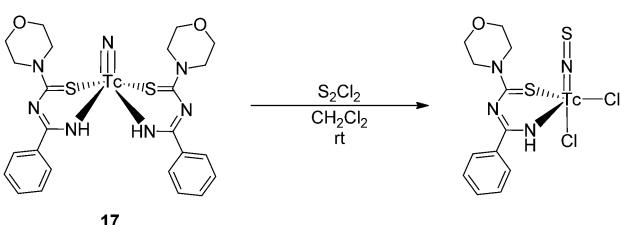
Scheme 3. Reduction of [TcN(morphtcb)$_2$] (**17**) with S_2Cl_2.[36]

furnish technetium(III) compounds, but formed complexes in the oxidation state +II (Scheme 3), as supported by EPR spectroscopy.[36–37]

The synthesis of the brominated thionitrosyl technetium complexes on using S_2Br_2 has not been reported so far. However, it is possible to synthesize [Tc(Br)$_3$(NS)(PMe$_2$Ph)$_2$] (**19**) through a bromine/chlorine exchange reaction by treating [Tc(Cl)$_3$(NS)(PMe$_2$Ph)$_2$] (**20**) with an excess of HBr.[40]

2.4. Formation of cyclic sulfur compounds by reaction of sulfido metal complexes with SCl_2 or S_2Cl_2

Treatment of [Cp$_2$Ti(SH)$_2$] (**21**) (Cp = η^5-C$_5$H$_5$) with S_xCl_2 (x = 1–3) gives [Cp$_2$Ti(S$_5$)] (**22**).[41] However, compounds of this type are more easily accessible by reactions of dichlorido complexes such as [Cp$_2$TiCl$_2$] (**23**) with sulfur-containing reagents.[41,42]

Titanocenium polysulfido complexes convert with S_xCl_2 (x = 1–2) to give cyclic polysulfanes as well as titanium dichlorido complexes (Scheme 4).[7f,43] For example, a reaction of [Cp$_2$Ti(S$_5$)] (**22**) with SCl_2 yields S_6 and S_{12}, whereas with S_2Cl_2 S_7 is formed.[43a] Mechanistically, Steudel and co-workers proposed the initial generation of intermediates like [Cp$_2$TiCl(S$_{5+x}$Cl)] (**24**), which either eliminate the cyclic sulfur molecules S_6 (x = 1) and S_7 (x = 2) or react for x = 1 with another equivalent of [Cp$_2$Ti(S$_5$)] (**22**) and subsequently SCl_2 generating S_{12} (Scheme 4).[44] In further studies mixtures or pure dichloropolysulfanes S_nCl_2 (n = 2–17) were treated with [Cp$_2$Ti(S$_5$)] (**22**) to result in sulfur cycles S_{5+n}, whereas S_y (y = 9, 11, 12, 13) was crystallized from product mixtures.[7f,43c–e] When SO_2Cl_2 reacts with the titanocenium polysulfide **22**, S_{10}, S_{20} and small amounts of S_{15} are formed with release of SO_2.[42k,43a,45]

Treatment of [Cp$^\#_2$Ti(S$_5$)] [Cp$^\#$ = Cp (**22**), Cp′ = η^5-MeC$_5$H$_4$ (**25a**), Cp^ = η^5-iPrC$_5$H$_4$ (**25b**)] with PnBu$_3$ or PCy$_3$ as desulfurizing agents led to the binuclear polysulfido complexes [{Cp$^\#_2$Ti(μ-S$_2$)}$_2$] [Cp$^\#$ = Cp (**26a**), Cp′ (**26b**), Cp^ (**26c**)] (Scheme 4), of which **26b** was also obtained by coupling of two molecules of [Cp′$_2$Ti(SH)$_2$] (**27**).[46a,b] The polysulfido complex [{Cp$_2$Ti}(μ-S$_2$)$_2${Cp^$_2$Ti}] (**26d**) was accessible by reaction of [Cp^$_2$Ti(S$_5$)] (**25b**) with [Cp$_2$Ti(CO)$_2$] (**28**). A reaction of [{Cp$_2$Ti(μ-S$_2$)}$_2$] (**26a**) with SCl_2 reproduced [Cp$_2$Ti(S$_5$)] (**22**) and [Cp$_2$TiCl$_2$] (**23**) and subsequently S_6, whereas treatment with two equivalents of S_2Cl_2 mainly led to the formation of S_8.[43b]

However, treatment of [Cp$^\#_2$Ti(S$_5$)] (**22**, **25a**, **25b**) with PPh$_3$ produced the dimeric metallosulfanes [{Cp$^\#_2$Ti(μ-S$_3$)}$_2$] (Cp$^\#$ = Cp (**29a**), Cp′ (**29b**), Cp^ (**29c**)), which implies a dependency of the desulfurizing extent on the nucleophilicity of the used phosphine (Scheme 4).[46a,c] Upon reaction of [{Cp$_2$Ti(μ-S$_3$)}$_2$] (**29a**) with S_2Cl_2 a product mixture was obtained consisting of S_7, S_8, and S_{10} as main products and S_{15} as well as S_{20} in traces.[43b] When the sterically more demanding Cp* (Cp* = η^5-

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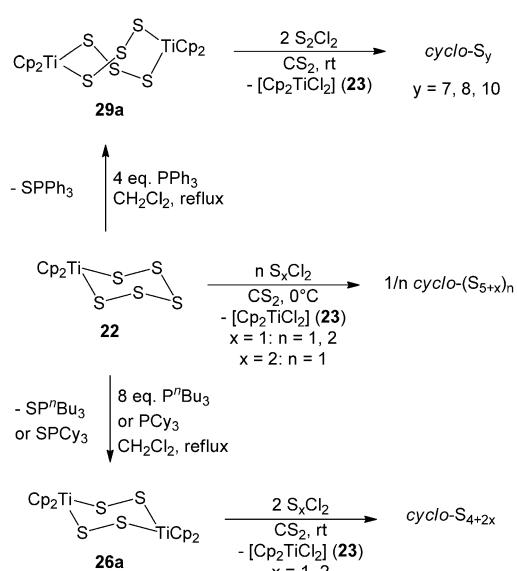
Scheme 4. Conversions of $[Cp_2Ti(S_5)]$ (**22**) into $[\{Cp_2Ti(\mu\text{-}S_3)\}_2]$ (**29a**) and $[\{Cp_2Ti(\mu\text{-}S_2)\}_2]$ (**26a**) by reactions with phosphines; reactivities towards S_xCl_2 ($x = 1, 2$).[43a,b, 46]

C_5Me_5) ligand was used, formation of binuclear complexes starting from complex $[Cp^*_2Ti(S_3)]$ (**30**) did not occur.[42d,46a,47]

A reaction of S_8Cl_2 with the zinc-based S_6 transfer agent $[(tmeda)Zn(S_6)]$ (**31**, tmeda = N,N,N',N'-tetramethylethylenediamine) led to the formation and isolation of the polysulfane S_{14} (Scheme 5).[48]

Another S_3 group-containing complex $[\{Cp'_2TiCl\}_2(\mu\text{-}S_3)]$ (**32**) was synthesized by treatment of $[\{Cp'_2Ti(\mu\text{-}S_2)\}_2]$ (**26b**) with $COCl_2$ under formation of COS.[49] For the reaction of $[\{Cp'_2TiCl\}_2(\mu\text{-}S_3)]$ (**32**) with S_2Cl_2, the generation of $[Cp'_2TiCl(S_5Cl)]$ (**33**) as intermediate followed by an intermolecular reaction with $[\{Cp'_2TiCl\}_2(\mu\text{-}S_3)]$ (**32**) to give $[\{Cp'_2TiCl\}_2(\mu\text{-}S_8)]$ (**34**) was proposed, finally yielding S_8 and S_{10} as main and S_7 as minor products (Scheme 6).

Titanocene complexes with larger polysulfide rings were accessible by the insertion of the $\{Cp_2Ti\}$ moiety of $[Cp_2Ti(CO)_2]$ (**28**) into S–S bonds of S_6 or S_7, resulting in the formation of product mixtures $[Cp_2Ti(S_x)]$ [$x = 5$ (**22**), 7 (**35**), 8 (**36**)].[43f,g]
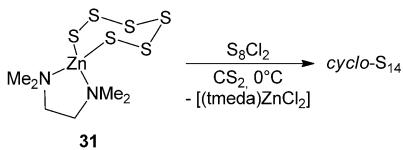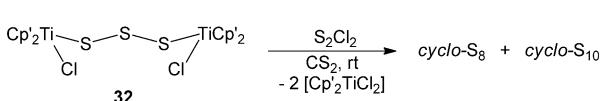
$[Cp_2Ti(S_8)]$ (**36**) was isolated and its reactivity was tested towards S_2Cl_2 producing S_{10}.

In a comparable way to the reactivity of titanium polysulfido complexes, polyselenido complexes open up synthetic pathways to access S–Se compounds when reacted with S_xCl_2 ($x = 1, 2$).[43b, 50] Accordingly, $[Cp_2Ti(Se_5)]$ (**37**) afforded the heterocyclic compounds Se_5S_x ($x = 1, 2$).[50a, c] Dimeric $[\{Cp'_2Ti(\mu\text{-}Se_2)\}_2]$ (**38**) gave access to the Se–S heterocycles $[Cp'_2Ti(Se_4S)]$ (**39**) by treatment with one equivalent of SCl_2.[43b,50d] When $[\{Cp'_2Ti(\mu\text{-}Se_2)\}_2]$ (**38**) was treated with one equivalent of S_2Cl_2, $[Cp_2Ti(Se_3S_2)]$ (**40**) resulted along with the loss of Se. $[Cp_2Ti(Se_3S_2)]$ (**40**) gave in further reactions with S_2Cl_2, 1,2,5-Se_3S_4, whereas usage of $[\{Cp^\#_2Ti(\mu\text{-}Se_2)\}_2]$ [$Cp^\# = Cp$ (**41**), Cp' (**38**)] with two equivalents of S_2Cl_2 produced 1,2,5,6-Se_4S_4.[50b] Other selenium and sulfur-containing heterocycles were synthesized by comparable strategies.[43b,50b,e, 51]

The syntheses of heterocycles bearing carbon and sulfur atoms involve the use of the respective titanocene derivatives in combination with S_xCl_2 ($x = 1$–34).[7f, 43f,g, 44, 52] Thus, treatment of $[Cp^\#_2Ti(CO)_2]$ [$Cp^\# = Cp$ (**28**), Cp' (**42**)] with CS_2 led to the formation of $[\{Cp^\#_2Ti\}_2(C_2S_4)]$ [$Cp^\# = Cp$ (**43a**), Cp' (**43b**)].[53] Reactions of the latter with one equivalent of S_nCl_2 ($n = 1, 2$) resulted in the generation of $[Cp^\#_2Ti(C_2S_5)]$ (**44a**, **44b**) or $[Cp^\#_2Ti(C_2S_6)]$ (**45a**, **45b**) [$Cp^\# = Cp$ (**a**), Cp' (**b**)], respectively (see Scheme 7 for the reactivity of $[\{Cp_2Ti\}_2(C_2S_4)]$ (**43a**).[52c] When $[Cp_2Ti(C_2S_6)]$ (**45a**) was allowed to react with S_2Cl_2 the heterocycle C_2S_8 was formed, which also was directly generated by treatment of $[\{Cp_2Ti\}_2(C_2S_4)]$ (**43a**) with two equivalents of S_2Cl_2.

$[Cp_2Ti(C_3S_5)]$ (**46**, Scheme 8) was prepared by ligand transfer from $(NEt_4)_2[Zn(C_3S_5)_2]$ (**47**) to $[Cp_2TiCl_2]$ (**23**).[52a] Both, the titanium and zinc complexes generated upon treatment with S_2Cl_2 and subsequent rearrangement reactions the polycycles C_3S_8 and C_6S_{12}.[54]

The compounds $[Cp_2Ti(S_4C_3H_6)]$ (**48**),[7f,55] $[Cp_2Ti(S_4C_6H_{10})]$ (**49**),[52b] and $[Cp_2Ti(S_2C_3H_6)]$ (**50**)[43f] were tested for their reactivities towards mixtures of sulfur chlorides S_xCl_2 ($x = 1$–30 for **48**; 1–8 for **49**; 2–8 for **50**) yielding the organic polysulfanes $C_3H_6S_n$ ($n = 5$–34 for **48**), $C_6H_{10}S_n$ ($n = 5$–12 for **49**), and $C_3H_6S_n$ ($n = 4$–10 for **50**) (Scheme 8). The complexes $[Cp_2Ti(S_2R)]$ **51**–**55** afforded in combination with SCl_2 or S_2Cl_2 the corresponding

Scheme 5. Reaction of $[(tmeda)Zn(S_6)]$ (**31**, tmeda = N,N,N',N'-tetramethylethylenediamine) with S_8Cl_2.[48]

**Scheme 6.** Reactivity of $[\{Cp'_2TiCl\}_2(\mu\text{-}S_3)]$ (**32**) towards S_2Cl_2.[49]
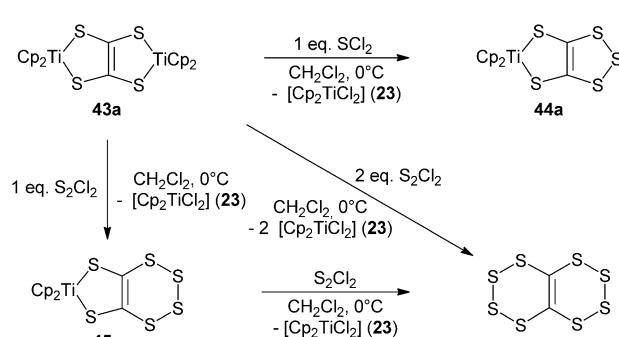
Scheme 7. Conversions of $[\{Cp_2Ti\}_2(C_2S_4)]$ (**43a**) into $[Cp_2Ti(C_2S_{4+n})]$ ($n = 1$, **44a**; $n = 2$, **45a**) and cyclo-C_2S_8 by reactions with S_nCl_2 ($n = 1, 2$).[52c]

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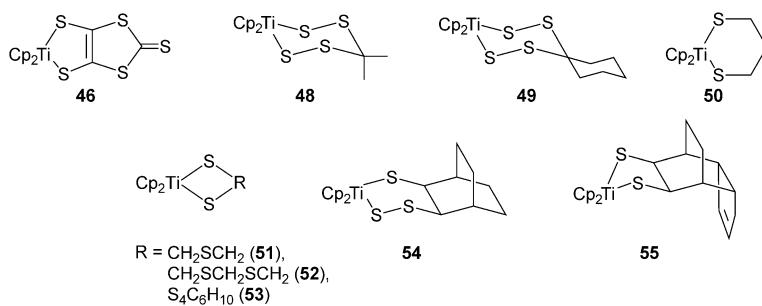
Scheme 8. Structures of carbon-containing polysulfido titanocene derivatives [Cp$_2$Ti(C$_3$S$_5$)] (**46**),[52a] [Cp$_2$Ti(S$_4$C$_3$H$_6$)] (**48**),[7f] [Cp$_2$Ti(S$_4$C$_6$H$_{10}$)] (**49**),[52b] [Cp$_2$Ti(S$_2$C$_3$H$_6$)] (**50**)[43f] and [Cp$_2$Ti(S$_2$R)] [R = CH$_2$SCH$_2$ (**51**), CH$_2$SCH$_2$SCH$_2$ (**52**), S$_4$C$_6$H$_{10}$ (**53**), SC$_8$H$_{12}$ (**54**), C$_{11}$H$_{14}$ (**55**)][43g] as substrates for the synthesis of organic polysulfanes.

cyclic products, in which the {Cp$_2$Ti} moiety is replaced by one or two S atoms (Scheme 8).[43g]

Reactions of **48** or **49** with stoichiometric amounts of bulky triphenylmethyl sulfenyl chloride (TrSCl) yielded [Cp$_2$TiCl(S$_2$RS$_3$Tr)] [R = C$_3$H$_6$ (**56a**), C$_6$H$_{10}$ (**56b**)].[44] Two equivalents of **56a** or **56b** produced after treatment with S$_x$Cl$_2$ (x = 1–2) the corresponding undeca- and dodecasulfane derivatives (TrS$_3$R)$_2$S$_{4+x}$ (R = C$_3$H$_6$, C$_6$H$_{10}$) (Scheme 9).

The four-membered heterocyclic Si and Ge titanocenium derivatives [Cp$^\#_2$Ti(S$_2$ER$_2$)] [Cp$^\#$ = Cp′, ER$_2$ = SiMe$_2$ (**57a**); Cp$^\#$ = Cp, ER$_2$ = SiPh$_2$ (**57b**), GePh$_2$ (**57c**), GeMes$_2$ (**57d**)] were transformed into the corresponding heterocycles when treated with S$_2$Cl$_2$ (Scheme 10).[56] Five or six-membered heterocycles were obtained, when the metallocene complexes [Cp$_2$M{S$_2${Si(Ph)(tBu)}$_2$}] [M = Ti (**58a**), Zr (**58b**)] were treated with S$_x$Cl$_2$ (x = 1, 2).[57]

The arsenic-containing titanocene complex [Cp$_2$Ti(S$_4$AsMe)] (**59**) serves as precursor for cyclic-arsenic sulfanes MeAsS$_{4+x}$ (x = 1, 2) (Scheme 11 a).[58] Treatment of the heterocyclic titanocene complexes [Cp$^\#_2$Ti(S$_4$NR)] (Cp$^\#$ = Cp, R = Me (**60a**), nOct (**60b**); Cp$^\#$ = Cp′, R = nOct (**60c**)) with S$_x$Cl$_2$ (x = 1, 2) yielded by ligand transfer the N-alkyl-substituted cyclic sulfurimines RNS$_{4+x}$ (Scheme 11 b).[59]

The employment of [Cp$_2$Ti(S$_7$NH)] (**61**) and [Cp$_2$Ti(S$_7$NMe)] (**62**) in reactions with S$_x$Cl$_2$ (x = 1, 2) led to the formation of HNS$_{7+x}$ and MeNS$_{7+x}$, respectively (Scheme 12).[60]

Steudel and Zanello developed reaction routes to ferrocene derivatized polysulfanes.[61] Thus, the bimetallic complexes [Cp$_2$Ti{(S$_2$)fc}] (**63a**) and [Cp$_2$Ti{(S$_3$)fc}] (**63b**, fc = 1,1′-ferrocenyl) were reacted with SCl$_2$ to afford the corresponding polythiaferrocenophanes [fc(S$_n$)] [n = 3 (**64a**), 4 (**64b**)] (Scheme 13). Muraoka et al. reported on the reaction of the five membered ring in [Cp*$_2$Ti{(S)$_2$fc′}] (**65**, fc′ = 1,2-ferrocenyl) with excess of SCl$_2$. This led to the formation of a ferrocene sulfane derivative [fc′(S$_5$)] (**66**).[62]

Cyclometalated zirconium complexes allow for the preparation of organic sulfur compounds by treatment with S$_x$Cl$_2$ (x = 1, 2) via zirconium mediated transfer of the organic entity.[63] With [Cp$_2$Zr(C$_{10}$H$_{14}$)] (**67**), one example is shown in Scheme 14.[63a] The described synthetic procedure allowed for the preparation of sulfur containing conjugated polymers[63g] and thiophene derived co-oligomers.[63h]

The nickel complex [Ni{SNS(NH)}$_2$] (**68**)[64] and the palladacycle [Pd(miqt)(iPr$_2$NCS$_2$)] (**69**, miqt = N-methylisoquinolinethione)[65] were also used for the synthesis of heterocyclic sulfane derivatives (Scheme 15). Treatment of [Ni{SNS(NH)}$_2$] (**68**) with S$_2$Cl$_2$ in the presence of NEt$_3$ gave upon ring closure

Scheme 9. Conversions of [Cp$_2$Ti(S$_4$R)] [R = C$_3$H$_6$ (**48**), C$_6$H$_{10}$ (**49**)] into [Cp$_2$TiCl(S$_2$RS$_3$Tr)] [R = C$_3$H$_6$ (**56a**), C$_6$H$_{10}$ (**56b**)] by reaction with TrSCl and reactivity towards S$_x$Cl$_2$ (x = 1, 2).[44]
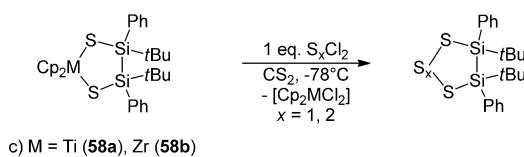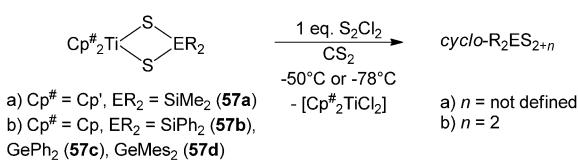
Scheme 10. Synthesis of Si or Ge containing heterocycles by reactions of [Cp$^\#_2$Ti(S$_2$ER$_2$)] [a) Cp$^\#$ = Cp″, ER$_2$ = SiMe$_2$ (**57a**); b) Cp$^\#$ = Cp, ER$_2$ = SiPh$_2$ (**57b**), GePh$_2$ (**57c**), GeMes$_2$ (**57d**)][56a,c] and c) [Cp$_2$M{S$_2${Si(Ph)(tBu)}$_2$}] [M = Ti (**58a**), Zr (**58b**)][57] with S$_x$Cl$_2$ (x = 1, 2).
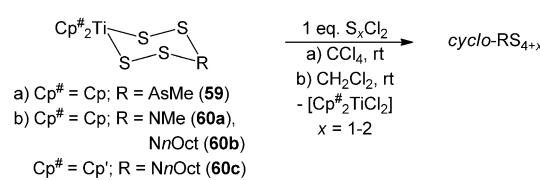
Scheme 11. Reactions of a) [Cp$_2$Ti(S$_4$AsMe)] (**59**)[58] and b) [Cp$^\#_2$Ti(S$_4$NR)] [Cp$^\#$ = Cp, R = Me (**60a**), nOct (**60b**); Cp$^\#$ = Cp″, R = nOct (**60c**)][59] with S$_x$Cl$_2$ (x = 1, 2).

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Scheme 12. Synthesis of HNS_{7+x} and $MeNS_{7+x}$ by reactions of $[Cp_2Ti(S_7NH)]$ (**61**) and $[Cp_2Ti(S_7NMe)]$ (**62**) with S_xCl_2 ($x = 1, 2$).[60]
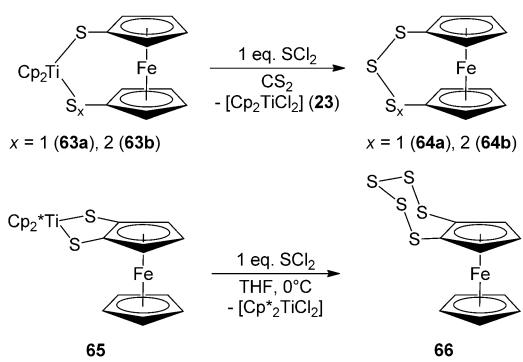
Scheme 13. Synthesis of $[fc(S_n)]$ [fc = 1,1'-ferrocenyl; $n = 3$, 4 (**64 a**, **64 b**)] and $[fc'(S_3)]$ (**66**, fc' = 1,2-ferrocenyl) by reactions of the bimetallic ferrocene titanocene complexes $[Cp_2Ti\{(S_2)fc\}]$ (**63 a**),[61] $[Cp_2Ti\{(S_3)fc\}]$ (**63 b**, fc = 1,1'-ferrocenyl) and $[Cp^*_2Ti\{(S)_2fc'\}]$ (**65**, fc' = 1,2-ferrocenyl)[62] with SCl_2.
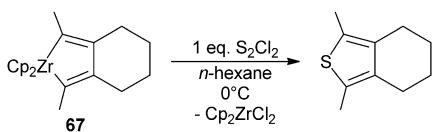
**Scheme 14.** Conversion of $[Cp_2Zr(C_{10}H_{14})]$ (**67**) into bicyclic $SC_{10}H_{14}$ by treatment with S_2Cl_2.[63a]

the cyclic sulfur nitride S_4N_2. By reaction of $[Pd(miqt)(iPr_2NCS_2)]$ (**69**) with SCl_2 the 1,2-dithiolylium salt $C_{10}H_8ClNS_2$ was generated along with the chloride bridged dimer $[Pd(\mu\text{-}Cl)(iPr_2NCS_2)]_2$ (**70**). Meuwsen reported on an alternative route to access S_4N_2 by reaction of $[Hg_5(NS)_8]$ (**71**) with S_2Cl_2 giving additionally $[Hg_2Cl_2]$ (**72**) and $[HgCl_2]$ (**73**) (Scheme 15).[66]

The reactions of $[HgPh(NS_7)]$ (**74**) with S_xCl_2 ($x = 1, 2$) to give $(NS_7)_2S_x$ and $[HgPhCl]$ (**75**) were also described.[68] The conversion of $[Hg(NSF_2)_2]$ (**76**) with S_2Cl_2 yielded $(SNSF_2)_2$ and $[HgCl_2]$ (**73**) (Scheme 15).[67] Furthermore, the reactivity of $[Hg(SCN)_2]$ (**77**) towards S_nCl_2 ($n = 1\text{--}7$) was studied to produce dicyanopolysulfanes $S_y(CN)_2$ ($y = 5\text{--}9$) and $[HgCl_2]$ (**73**).[69] Dicyanosulfanes were also accessible by treatment of the silver compounds $[AgX]$ [X = SCN (**78 a**), CN (**78 b**)] with SCl_2.[70]

2.5. Reactivity of sulfur chlorides towards carbonyl complexes

Several iron sulfur clusters were generated by reactions of various iron carbonyl complexes with S_xCl_2 ($x = 1, 2$).[71] After treatment of $[CpFe(CO)_2]_2$ (**79**) with SCl_2, the authors propose the formal insertion of SCl^+ into the Fe–Fe bond yielding $[\{CpFe(CO)_2\}_2(\mu\text{-}SCl)]Cl$ (**80**) as main product (Scheme 16).[71b]

The stabilization of S–Cl entities deriving from reactions with S_xCl_2 ($x = 1, 2$) at Fe complexes such as **80** is exceptional, and instead the formation of S_n bridges ($n = 1\text{--}4$) is usually found. The group of Schomaker et al. reported on the synthesis of $[\{CpFe(CO)_2\}_2(\mu\text{-}S_y)]$ [$y = 3$ (**81 a**), 4 (**81 b**)] by reaction of
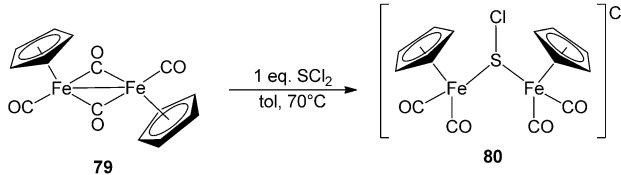
Scheme 16. Formation of $[\{CpFe(CO)_2\}_2(\mu\text{-}SCl)]Cl$ (**80**) by conversion of $[CpFe(CO)_2]_2$ (**79**) with SCl_2.[71b]
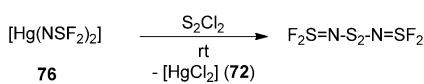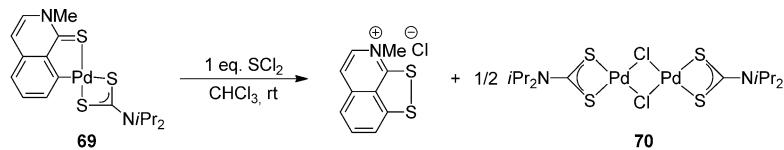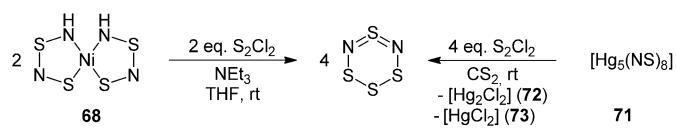
Scheme 15. Synthesis of S_4N_2 by treatment of $[Ni\{SNS(NH)\}_2]$ (**68**)[64] or $[Hg_5(NS)_8]$ (**71**)[66] with S_2Cl_2 (top). Reactivity of $[Pd(miqt)(iPr_2NCS_2)]$ (**69**)[65] towards SCl_2 (middle) and of $[Hg(NSF_2)_2]$ (**76**)[67] towards S_2Cl_2 (bottom).

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[CpFe(CO)$_2$]$^-$ (**82**) with S$_x$Cl$_2$ ($x = 1$, 2) (in Scheme 17 for $x =$ 1).[71f] Although the μ-S$_3$ complex **81a** was formed with SCl$_2$, a comparable reaction with S$_2$Cl$_2$, produced a mixture of **81a** and the μ-S$_4$ analogue **81b**. Additionally, in solution a slow conversion of **81b** into **81a** was observed. When a solution of **81a** was heated at 110 °C, the tetrameric cyclopentadienyl iron sulfide cluster [CpFe(μ$_3$-S)]$_4$ (**83**) was formed along with generation of CO and sulfur.

The Cr, Mo, and W complexes [CpM(CO)$_3$]$^-$ [M = Cr (**84a**), Mo (**84b**), W (**84c**)] show a slightly different reactivity towards S$_2$Cl$_2$ than the iron compounds (Scheme 18).[72] The low-temperature reaction of the Cr compound **84a** yielded selectively the binuclear μ-S bridged complex [{CpCr(CO)$_2$}$_2$(μ-S)] (**85**), whereas the same reaction at room temperature gave [{CpCr(CO)$_3$}$_2$] (**86**). The reactions of the related Mo and W complexes **84b** and **84c**, however, led to product mixtures consisting of the μ-S$_2$ bridged complexes [{CpM(CO)$_3$}$_2$(μ-S$_2$)] [M = Mo (**87a**), W (**87b**)], the chlorinated compounds [CpM(CO)$_3$Cl] [M = Mo (**88a**), W (**88b**)] and the dimers [{CpM(CO)$_3$}$_2$] [M = Mo (**89a**), W (**89b**)].

Treatment of [Fe$_2$(CO)$_8$]$^{2-}$ (**90**) with S$_2$Cl$_2$ led to the formation of the trimeric μ$_3$-S bridged complex [{Fe(CO)$_3$}$_3$(μ$_3$-S)$_2$] (**91**) (Scheme 19).[71e]

Other μ$_3$-S complexes were formed when the anionic iron carbonyl complexes [Fe$_3$(CO)$_{11}$]$^{2-}$ (**92**) and [Fe$_4$(CO)$_{13}$]$^{2-}$ (**93**) were treated with several equivalents of SCl$_2$.[71c] For the former the anionic complex [{Fe(CO)$_3$}$_3$(μ$_3$-S)]$^{2-}$ (**94**) along with [{Fe(CO)$_3$}$_4${Fe(CO)$_2$}(μ$_3$-S)$_2$]$^{2-}$ (**95**) and [Fe(CO)$_5$] (**96**) were generated; and for the latter **95**, **96** as well as [{Fe(CO)$_3$}$_3$(μ$_3$-S)$_2$] (**91**) were identified. Other complexes were obtained from reactions of [{Fe(CO)$_3$}$_3$(μ$_3$-StBu)]$^-$ (**97**) or [{Fe(CO)$_3$}$_3$(μ$_3$-PR)]$^{2-}$ [R = Ph (**98a**), Cy (**98b**)] with SCl$_2$ yielding [{Fe(CO)$_3$}$_3$(μ$_3$-S)$_2$] (**91**) or [{Fe(CO)$_3$}$_3$(μ$_3$-PR)(μ$_3$-S)] [R = Ph (**99a**), Cy (**99b**)], respectively.[71a]

The ionic butterfly complexes [{Fe(CO)$_3$}$_2$(μ-CO)(μ-ER)]$^-$ **100a–100l** were used to access the double butterfly compounds [{{Fe(CO)$_3$}$_2$(μ-ER)}$_2$(μ$_x$-S$_n$)]) **101a–101e** and **102a–102j** bearing μ$_x$-S$_n$ bridging units by treatment with S$_n$Cl$_2$ ($n = 1$, 2) (Scheme 20).[71d,g,h] The authors propose an initial nucleophilic attack of the formally negatively charged Fe center at the sulfur atom of SCl$_2$ followed by the loss of CO ligands.

The ionic double-butterfly Fe–S clusters [{Fe$_2$(CO)$_6$(μ-CO)}$_2$(μ-SRS)]$^{2-}$ [R = CH$_2$(CH$_2$OCH$_2$)$_x$CH$_2$, $x = 2$ (**103a**), 3 (**103b**)] were treated with S$_2$Cl$_2$ (Scheme 21). The macrocyclic clusters

Scheme 17. Formation of [{CpFe(CO)$_2$}$_2$(μ-S$_3$)] (**81a**) by treatment of [CpFe(CO)$_2$]$^-$ (**82**) with SCl$_2$ and conversion of **81a** into [CpFe(μ$_3$-S)]$_4$ (**83**).[71f]
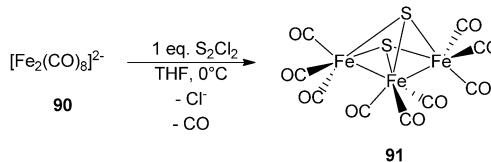
Scheme 19. Formation of [{Fe(CO)$_3$}$_3$(μ$_3$-S)$_2$] (**91**) by treatment of [Fe$_2$(CO)$_8$]$^{2-}$ (**90**) with S$_2$Cl$_2$.[71e]

Scheme 18. Reactions of [CpM(CO)$_3$]$^-$ (**84a–84c**) [M = Cr (**a**), Mo (**b**), W (**c**)] with S$_2$Cl$_2$ yielding [{CpCr(CO)$_2$}$_2$(μ-S)] (**85**) and [{CpM(CO)$_3$}$_2$(μ-S$_2$)] [M = Mo (**87a**), W (**87b**)].[72]
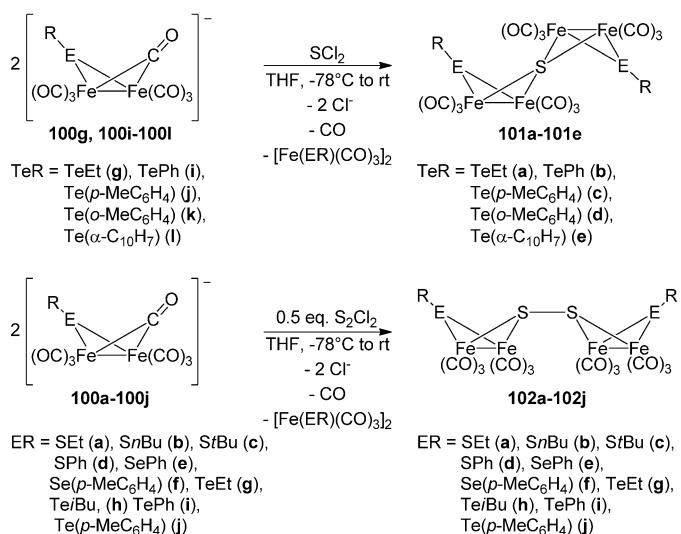
Scheme 20. Formation of double butterfly complexes [{{Fe(CO)$_3$}$_2$(μ-ER)}$_2$(μ$_x$-S$_n$)] ($x = 4$, $n = 1$, ER = TeEt (**a**), TePh (**b**), Te(p-MeC$_6$H$_4$) (**c**), Te(o-MeC$_6$H$_4$) (**d**), Te(α-C$_{10}$H$_7$) (**e**), **101a–101e**; $x = n = 2$, ER = SEt (**a**), SnBu (**b**), StBu (**c**), SPh (**d**), SePh (**e**), Se(p-MeC$_6$H$_4$) (**f**), TeEt (**g**), TeiBu (**h**), TePh (**i**), Te(p-MeC$_6$H$_4$) (**j**), **102a–102j**) by sulfurization with S$_n$Cl$_2$.[71d,g,h]

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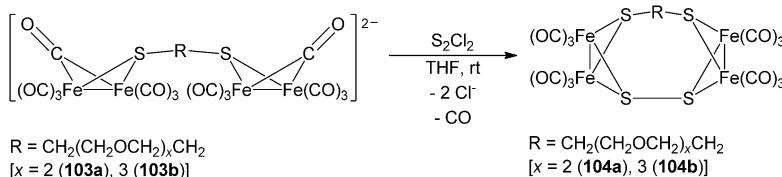
Scheme 21. Conversions of [{Fe₂(CO)₆(μ-CO)}₂(μ-SRS)]²⁻ [R=CH₂(CH₂OCH₂)ₓCH₂, x=2 (**103a**), 3 (**103b**)] into [{Fe₂(CO)₆}₂(μ-S₂)(μ-SRS)] [R=CH₂(CH₂OCH₂)ₓCH₂, x=2 (**104a**), 3 (**104b**)] by treatment with S₂Cl₂.[71i]

[{Fe₂(CO)₆}₂(μ-S₂)(μ-SRS)] [R=CH₂(CH₂OCH₂)ₓCH₂, x=2 (**104a**), 3 (**104b**)] were produced as the main products.[71i] Other reactions involve a sulfurization in the ligand sphere, only.[73]

3. Sulfur(IV) Compounds

Although structural motifs involving sulfur halides in the oxidation state +IV are commonly used in organic synthesis, the scope is mostly limited to either methylene transfer or deoxygenative fluorination reactions. The deprotonation of trimethylsulfonium halides (Me₃SX; X = Cl, Br, I) gives sulfonium ylides enabling, for instance, the synthesis of epoxides or aziridines from aldehydes, ketones and imines by the transfer of a methylene group.[74]

Deoxyfluorination can be applied to organic oxygen containing molecules, but can also be achieved at metal oxides to form metal fluorides.[8,75] Depending on the substrate, these fluorination reactions are either performed with sulfur tetrafluoride or with one of its derivatives like DAST (N,N-diethylaminosulfur trifluoride), MOST (morpholinosulfur trifluoride), Deoxo-fluor® (bis(2-methoxyethyl)aminosulfur trifluoride) or Fluolead™ (4-tert-butyl-2,6-dimethylphenylsulfur trifluoride).[76] Reactions towards transition-metal compounds are limited to SCl₄ and SF₄ and are described in the following paragraphs.

3.1. Formation of trihalosulfonium salts

Early reports on the stabilization of sulfur(IV) derivatives at transition-metal compounds were published by Ruff on the reaction of SCl₄ with titanium and tin tetrachlorides as well as iron and aluminum trichlorides.[10d,77] Originally, the products were described as simple adducts, but later it turned out that they are trichlorosulfonium salts.[78] An alternative route to access these trichlorosulfonium salts involves conversions of transition-metal halides or oxides with SCl₂ in an atmosphere of gaseous chlorine. This led to the isolation and characterization of [SCl₃][MClₙ] (M=Au (**3**), Fe (**105a**), MoO (**105b**), n=4; Ti (**105c**), Hf (**105d**), Zr (**105e**), n=5; Mo (**105f**), Nb (**105g**), Ta (**105h**), Os (**105i**), n=6) and [(SCl₃)₂][MCl₆] [M=Ti (**106a**), Zr (**106b**), Ir (**106c**), Os (**106d**)].[24b,g,27i,78c,d,79] Crystal structures of [(SCl₃)ₙ][A] (A=OsCl₆ (**106d**), n=2; FeCl₄ (**105a**), RuCl₃(SCl₂)₂ (**107**), IrCl₄(SCl₂)₂ (**108**), AuCl₄ (**3**), Ti₂Cl₉ (**109**), n=1) were determined by the research groups of Volkov and Fokina.[24d,h,28i,80]

Similar to interactions in [SCl₃]⁺ salts such as [SCl₃][ICl₄][81] and [(SCl₃)(SbCl₆)],[82] the sulfur atoms in [(SCl₃)(AuCl₄)]₂ (**3**), exhibit a distorted octahedral arrangement by six chlorine atoms as depicted in Figure 1.[80a] The structure reveals interactions of
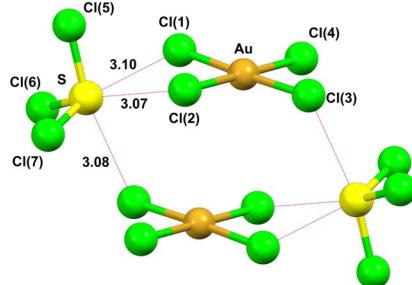
Figure 1. Structure of [SCl₃·AuCl₄] (**3**) in the solid state (distances in Å).[80a]

the sulfur atom and the chlorine atoms of the anion. Similar interactions were found in [(SCl₃)₂][OsCl₆] (**106d**),[24h,28i] [SCl₃][RuCl₃(SCl₂)₂] (**107**),[24d] and [SCl₃][IrCl₄(SCl₂)₂] (**108**)[80c] and the chlorine atoms of the two anions in [SCl₃][Ti₂Cl₉] (**109**).[80b] Thermal decomposition of [SCl₃][AuCl₄] (**3**) revealed a stepwise degradation which is initiated by the loss of a chlorine molecule at 133 °C to yield [AuCl₃(SCl₂)] (**4**) (see section **2.1**) followed by SCl₂ release at 151 °C and the precipitation of AuCl₃ which can be further decomposed to elemental gold by heating the sample up to 333 °C.[83] For [(SCl₃)₂][OsCl₆] (**106d**), the decomposition of the metal halide is presumably also preceded by the loss of SClₓ units.[84]

The formation of [SF₃]⁺ cations by treatment of platinum-group metal hexafluorides with SF₄ was reported by the groups of Westland and Bartlett.[85] When using the hexafluorides of the heavier platinum-group elements, [SF₃][MF₆] [M=Os (**110a**), Ir (**110b**)] were identified by magnetic susceptibility and powder XRD measurements (Scheme 22). Note that these compounds can also be generated by the reaction of MF₆ [M=Os (**111a**), Ir (**111b**)] with ZnS or B₂S₃ at temperatures above 210 °C.[86] For the reaction of PtF₆ (**112**) with SF₄ the generation of a mixture of SF₄·PtF₅ (**113**) and PtF₄ (**108**) was proposed.[85b] The low selectivity in this reaction was reasoned by the higher oxidation potential of PtF₆ (**114**).[12a]

At elevated temperatures, the trifluorosulfanyl cation can likewise be obtained by treatment of MF₅ [M=Ru (**115a**), Ir (**115b**)] with SF₄ (Scheme 22).[87] Further heating of [SF₃][MF₆] [M=Ru (**116**), Ir (**110b**)] leads to the generation of the corresponding metal trifluorides and SF₆. In contrast, the thermal

$$\text{IrF}_6 \xrightarrow[>-40°C]{\text{SF}_4} [\text{SF}_3][\text{IrF}_6] \xleftarrow[125°C]{\text{SF}_4} \text{IrF}_5$$

111b **110b** **115b**
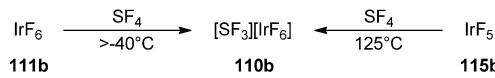
Scheme 22. Reactions of IrFₓ (x=5, 6) (**111b**, **115b**) with SF₄.[85,87]

decomposition of $[SF_3^+]_x[AF_n^{x-}]$ (A = As (**117a**), Sb (**117b**), $x = 1$, $n = 6$; Ge (**117c**), $x = 1$, $n = 5$; B (**117d**), $x = 1$, $n = 4$) usually led to a release of SF_4 and $[AF_{n-x}]$, but not to the reduction of the anion.[88]

3.2. Reactivity of SF₄ towards transition-metal phosphine complexes

In pioneering work by Ebsworth, Holloway et al. it was demonstrated that SF_4 reacts with transition-metal complexes of rhodium and iridium to furnish λ^4-trifluorosulfanyl ligands.[89] Thus, treatment of *trans*-[Ir(Cl)(CO)(PEt₃)₂] (**118**) with SF_4 resulted in an oxidative addition to give *trans*-[Ir(Cl)(F)(SF₃)(CO)(PEt₃)₂] (**119**) together with other isomers (Scheme 23). Due to the use of methylene chloride as solvent, fluorine/chlorine exchange reactions also occurred to form di- and trihalido complexes. The steric demand of the phosphines has a considerable impact on the outcome of the reactions. Thus, the addition of SF_4 to Vaska-type precursors of iridium did not lead to any reaction for phosphine ligands that possess a larger cone angle than that of PPh₃.[89c] Furthermore, neither the variation of the halido ligand by using *trans*-[Ir(X)(CO)(PEt₃)₂] [X = Br (**120a**), I (**120b**)] nor employment of *trans*-[Rh(X)(CO)(PEt₃)₂] [X = Br (**121a**), I (**121b**)] as starting materials led to a better selectivity, but instead to a lower stability of the SF₃-complexes in the product mixture.[89b,c] Nevertheless, *cis,trans*-[Rh(F)₂(SF₃)(CO)(PEt₃)₂] (**122**) was generated exclusively by a reaction of the fluorido complex *trans*-[Rh(F)(CO)(PEt₃)₂] (**123**) with SF_4 (Scheme 24).[90] This transformation further confirms the strong influence of the halido ligand on the selectivity of the reactions.

A S–F bond cleavage in SF_4 is not only limited to rhodium and iridium complexes, but was also achieved at *trans*-[Pt(PR₃)₂] [R = *i*Pr (**124a**), Cy (**124b**)] resulting in the formation of the SF₃ fluorido complexes *trans*-[Pt(F)(SF₃)(PR₃)₂] [R = *i*Pr (**125a**), Cy (**125b**)] (Scheme 25).[91]
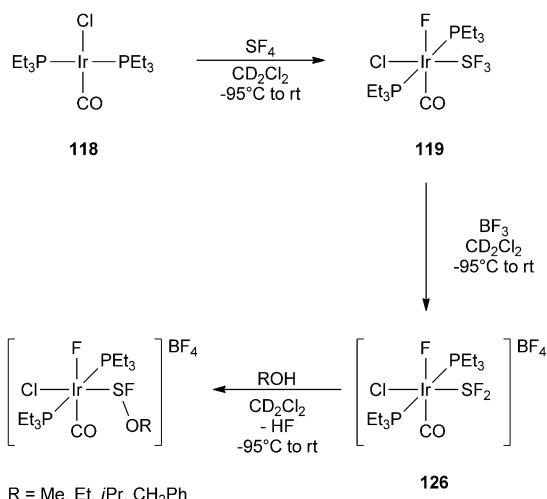
Scheme 23. Fluoride abstraction from *trans*-[Ir(Cl)(F)(SF₃)(CO)(PEt₃)₂] (**119**) and subsequent alcoholysis.[89a,c]
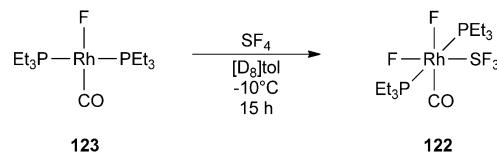
Scheme 24. Formation of *cis,trans*-[Rh(F)₂(SF₃)(CO)(PEt₃)₂] (**122**) by S–F bond cleavage of SF_4.[90]
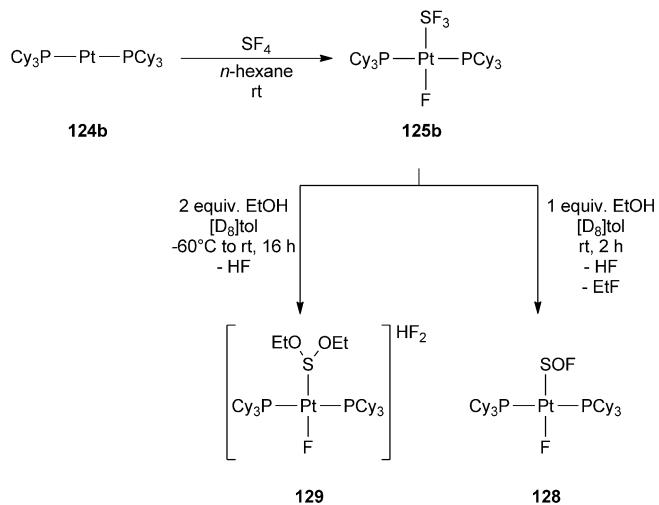
Scheme 25. Reactions of *trans*-[Pt(F)(SF₃)(PCy₃)₂] (**125b**) with ethanol.[93]

A characteristic property of all these transition-metal λ^4-trifluorosulfanyl complexes is their fluxionality on the NMR timescale at the pseudo trigonal-bipyramidal coordinated sulfur atom. Variable-temperature NMR spectroscopy indicates that two dynamic processes might proceed. A rotation about the metal–sulfur bond leads to the magnetic equivalence of both axial bound fluorine atoms at sulfur as well as to the equivalence of the phosphorus atoms of the phosphine ligands. In addition, exchange of axial and equatorial bound fluorine atoms, for instance by a Berry-pseudo or a turnstile type rotations, results in the equivalence of all sulfur-bound fluorine atoms.

Analogous to the reaction of SF_4 with Lewis acids,[88d, 92] a fluorine atom of the λ^4-trifluorosulfanyl moiety can be abstracted by treatment of *trans*-[Ir(Cl)(F)(SF₃)(CO)(PEt₃)₂] (**119**) or *trans*-[Pt(F)(SF₃)(PR₃)₂] [R = *i*Pr (**125a**), Cy (**125b**)] with boron trifluoride. The generated compounds $[A(SF_2)][BF_4]$ [A = Ir(Cl)(F)(CO)(PEt₃)₂ (**126**); Pt(F)(PR₃)₂ R = *i*Pr (**127a**), Cy (**127b**)] have been characterized by NMR spectroscopy and for [Pt(F)(SF₂)(PCy₃)₂][BF₄] (**127b**) a structure in the solid state was determined. The compounds **125** undergo full or partial alcoholysis of the sulfur-bound fluorine atoms when treated with alcohols (Scheme 25).[89c, 91b, 93] As it is well known for other sulfur trifluoride derivatives of SF_4, *trans*-[Pt(F)(SF₃)(PCy₃)₂] (**125b**) can be used for deoxyfluorination reactions of ethanol, but also of ketones (benzophenone and 3-(trifluoromethyl)benzophenone) to yield fluoroethane or *gem*-difluorobisaryl-methane compounds as well as *trans*-[Pt(F)(SOF)(PCy₃)₂]

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(128).[91] No deoxygenative fluorination occurs in the presence of an excess of ethanol, instead, at low temperatures *trans*-[Pt(F){S(OEt)$_2$}(PCy$_3$)$_2$][FHF] (129) was generated by alcoholysis (Scheme 25).[93] The reaction of *trans*-[Pt(F)(SF$_3$)(PCy$_3$)$_2$] (125 b) with trimethylethoxysilane exclusively furnished *trans*-[Pt(F)(SOF)(PCy$_3$)$_2$] (128) together with fluoroethane, which suggests that the deoxygenative fluorination of ethanol at *trans*-[Pt(F)(SF$_3$)(PCy$_3$)$_2$] (125 b) does not necessarily involve HF as intermediary fluorination agent.[91b, 93] Treatment of *trans*-[Pt(F)(SF$_2$)(PCy$_3$)$_2$][BF$_4$] (127 b) with trimethylethoxysilane or EtOH yielded *trans*-[Pt(F){SF(OEt)}(PCy$_3$)$_2$][BF$_4$] (130) (see also Scheme 23 for a reaction at 126).

3.3. Theoretical studies on fluorosulfanyl complexes

Characteristics of SF$_x$ complexes have been studied theoretically by King and co-workers.[94] They predict a dichotomy of the trifluorosulfanyl ligand analogous to the one that is well-known for nitrosyl ligands (Scheme 26). The experimentally observed pseudo-square-pyramidal (trigonal-bipyramidal) geometry at sulfur is consistent with a one-electron-donor ligand. In contrast, a tetrahedral arrangement at the sulfur atom is in accordance with a formal 3-electron donation to the metal center.[94f] Calculations on the experimentally known complexes *trans*-[Ir(Cl)(F)(SF$_3$)(CO)(PEt$_3$)$_2$] (119) *cis,trans*-[Rh(F)$_2$(SF$_3$)(CO)(PEt$_3$)$_2$] (122), and *trans*-[Pt(F)(SF$_3$)(PR$_3$)$_2$] [R = *i*Pr (125 a), Cy (125 b)] revealed a pseudo-square-pyramidal (trigonal-bipyramidal) coordination of the sulfur atom, which was also suggested based on variable temperature NMR spectroscopic data.[90, 91, 94f]

DFT studies on fluoride migration reactions in *trans*-[Ir(Cl)(F)(SF$_3$)(CO)(PEt$_3$)$_2$] (119), [M(SF$_3$)(CO)$_n$] (M = V (131 a), Ta (131 b), *n* = 5; M = Mn (131 c), Re (131 d), *n* = 4; M = Co (131 e), Ir (131 f), *n* = 3) and [CpM(SF$_3$)(CO)$_n$] (Cp = η^5-C$_5$H$_5$; M = Cr (132 a), W (132 b), *n* = 2; M = Fe (132 c), Os (132 d), *n* = 1; M = Ni (132 e), Pt (132 f), *n* = 0) to form the respective {[M](F)(SF$_2$)} complexes suggest an instability of SF$_3$ ligands at first- and third-row transition-metal derivatives.[94e,f] Exceptional cases are both iridium-based compounds, for which a fluoride shift in [Ir(SF$_3$)(CO)$_3$] (131 f) is almost thermoneutral and is clearly energetically not favored in *trans*-[Ir(Cl)(F)(SF$_3$)(CO)(PEt$_3$)$_2$] (119).[94e,f] Substitution of one of the sulfur bound fluorine atoms by NMe$_2$ again resulted in an energetically favored fluoride shift

for {M[SF$_2$(NMe$_2$)](CO)$_n$} [M = Ta, *n* = 5 (133 a); M = Re, *n* = 4 (133 b); M = Ir, *n* = 3 (133 c)] and {CpM[SF$_2$(NMe$_2$)](CO)$_n$} [Cp = η^5-C$_5$H$_5$; M = Cr (134 a), Mo (134 b), W (134 c), *n* = 2; M = Os, *n* = 1 (134 d); M = Pt, *n* = 0 (134 e)] to yield the respective {[M](F)[SF(NMe$_2$)]} complexes.[94a,b] Furthermore, calculations on the general feasibility of generating SF$_2$ ligands indicate a certain stability of [Fe$_2$(μ-SF$_2$)$_2$(CO)$_n$] [*n* = 8 (135 a), 7 (135 b)] and [Cp$_2$Fe$_2$(μ-SF$_2$)(CO)$_4$] (136), whereas in the mononuclear iron carbonyl complexes a fluoride migration is energetically favored.[94c,d] For the isomers [Cp$_2$Fe$_2$(SF$_2$)(μ-SF$_2$)(CO)$_3$] (137) and [Cp$_2$Fe$_2$(SF$_3$)(μ-SF)(CO)$_3$] (138) the latter was shown to be lower in energy.[94c]

4. Sulfur(VI) Compounds

4.1. Reactivity of SF$_5$Cl towards transition-metal complexes

The ternary sulfur(VI) halides SF$_5$Cl and SF$_5$Br are important tools to introduce SF$_5$ groups into organic molecules through radical reaction pathways resulting in an addition to unsaturated carbon–carbon bonds.[4d,e, 16]

Compounds bearing SF$_5$ moieties can show interesting bioactive properties, which are often compared to those of CF$_3$ groups. A comprehensive review on this topic was published by Welch and Savoie in 2015.[16b] Despite the extensive research studies on the development of reaction pathways to introduce SF$_5$ moieties into organic molecules using SF$_5$Cl or SF$_5$Br, it is somehow surprising that only a few examples exist on the activation of sulfur halide pentafluorides at transition metals. The examples are restricted to conversions with SF$_5$Cl as starting material.

Massey and Packer reported in 1961 on the reactions of SF$_5$Cl towards first-row transition-metal carbonyls.[96] Treatment of [Fe(CO)$_5$] (96) with an excess of SF$_5$Cl at room temperature led, based on IR spectroscopic data, to a mixture of iron fluorides and chlorides in addition to volatile compounds such as XYC=O (X = Y = Cl, F; X = F, Y = Cl) and O=C=S. Substoichiometric amounts of SF$_5$Cl gave a brown product, for the structure of which terminal carbonyl groups but no S–F bonds were identified. Stopping the reaction after five minutes resulted in all cases in the formation of a solid product bearing bridging carbonyl groups. The corresponding reactions with [Ni(CO)$_4$] (139) furnished neither bridging carbonyl ligands nor carbonyl halides, but a nickel chlorofluoride, CO and SF$_4$.

The reactions between SF$_5$Cl and the platinum(0) complexes [Pt(*E*-PhC=CPh)(PPh$_3$)$_2$] (140), [Pt(PhC≡CPh)(PPh$_3$)$_2$] (141) and [Pt(PPh$_3$)$_4$] (142) in benzene at 70 °C were investigated by Kemmit, Peacock, and Stocks.[97] In each case, the formation of the SF$_5$ complex *cis*-[Pt(Cl)(SF$_5$)(PPh$_3$)$_2$] (143), which is stable in dry air, has been proposed, but based only on IR spectroscopic data and elemental analysis of an orange precipitate. For the reaction of [Pt(PPh$_3$)$_4$] (142) F$_2$PPh$_3$ was identified as an additional product. However, on dissolving the solid in CH$_2$Cl$_2$ or acetone the generation of [Pt(Cl)$_2$(F)$_2$(PPh$_3$)$_2$] (144) was suggested. Reactions of SF$_5$Cl with complexes of platinum in oxidation state +2 gave only chlorinated complexes and no product containing SF bonds could be detected.[97] Reactions of

M—N≡O
linear
3-electron donor

M—N(•)=O
bent
1-electron donor

(tetrahedral S structure with M, F, F, F)
tetrahedral
3-electron donor

(pseudo-square pyramidal S structure with M, F, F, F)
pseudo-square pyramidal
(trigonal bipyramidal)
1-electron donor
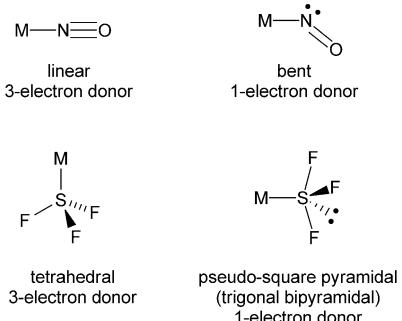
Scheme 26. Comparison of NO and SF$_3$ ligands.[94f, 95]

SF_5Cl with Vaska-type complexes and its rhodium analogues bearing various phosphine ligands give $[Ir(Cl)_2(F)(CO)(PEt_3)_2]$ (**145**), $[Rh(Cl)_2(F)(CO)(PPh_3)_2]$ (**146**) and $[Rh(Cl)_2(F)(CO)(PMe_2Ph)_2]$ (**147**) by chlorofluorination. Neither in these reactions nor after the treatment of the trisphosphine complex $[Rh(Cl)(PPh_3)_3]$ (**148**) with SF_5Cl could a sulfur-containing transition-metal complex be identified.

4.2. Reactivity of SF_6 towards transition-metal complexes

In contrast to SF_5Cl, SF_6 is a highly inert compound, which results, for instance, in its use as insulating gas in high-voltage power applications.[13] However, because of its inertness, the activation of SF_6 is considered as challenging in fluorine chemistry as well as in transition-metal chemistry.[12a, 98] The conversions include depletion, but also fluorination reactions as well as the generation of sulfur-containing building blocks.

Early results on the activation of SF_6 at various reducing metallocene-derivatives were reported by Ernst and co-workers in 2005.[99] At the Ti^{II} complex $[Ti\{1,3-C_5H_3(tBu)_2\}(6,6-dmch)(PMe_3)]$ (**149**, 6,6-dmch = 6,6-dimethylcyclohexadienyl) SF_6 activation leads to the tetranuclear fluorido-bridged Ti^{III} compound $[Ti(\mu-F)_2\{1,3-C_5H_3(tBu)_2\}]_4$ (**150**) and $SPMe_3$, which could not be quantified (Scheme 27).

The ability of SF_6 to act as fluorinating agent at early transition-metal complexes was additionally shown at $[Ni(PMe_3)_4]$ (**151**) and chromocene, vanadocene, and ferrocene-derivatives.[99b] Thus, $[Cp_2V]$ (**152**) is converted into its fluorinated derivative $[Cp_2VF]$ (**153**), which was characterized by elemental analysis, mass spectrometry, and X-ray diffraction studies (Scheme 28).

For $[Cp^*_2Cr]$ (**154**, $Cp^* = \eta^5-C_5Me_5$) the observed reaction pathways are highly dependent on the chosen solvent and reaction conditions.[99b] In contrast to the above mentioned complexes, all chromium(II) derivatives were oxidized to chromi-

um(III) under concomitant loss of one Cp* ligand (Scheme 29). In n-hexane, the fluorinated salt $[Cp^*_2Cr]^+[Cp^*_2Cr_2F_4(\mu-F)]^-$ (**155**) was isolated. However, in toluene in the presence of p-dimethylaminopyridine (dmap), the reaction between **154** and SF_6 delivers the neutral Cr^{III} fluorido complex $[Cp^*Cr(F)_2(dmap)]$ (**156**), with chromium being coordinated by the pyridine nitrogen of dmap (Scheme 29). In the absence of dmap, the authors presumed the formation of the salt $[\{Cp^*Cr(\mu-F)\}_3(\mu_3-S)]^+[Cp^*CrF_3]^-$ (**157**) (based on microanalysis), providing a rare example for a sulfur-containing complex after SF_6 activation. After a reaction time of 5 days, a minor product was formed that was characterized by X-ray diffraction analysis to be $[Cp^*_6Cr_8(\mu-F)_{12}(F)_6]$ (**158**).
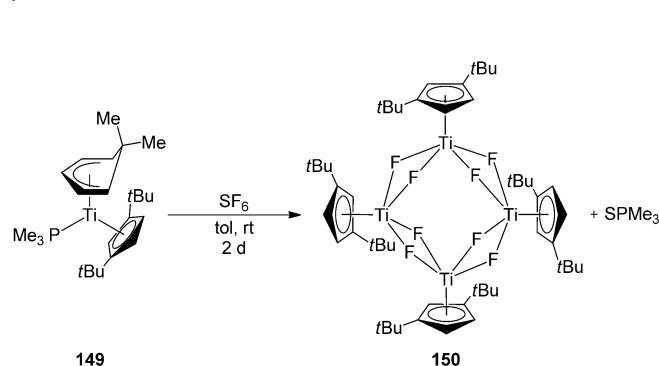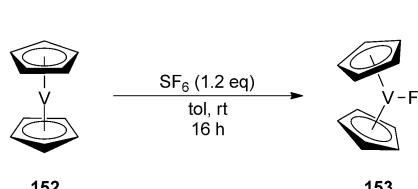
In 2014, Limberg et al. reported on the generation of $[L^{tBu}Ni(F)]$ (**159**, $L^{tBu} = [HC(CtBuNC_6H_3(iPr)_2)_2]^-$) and the sulfido-bridged binuclear nickel(II) complex $[(L^{tBu}Ni)_2(\mu-S)]$ (**160**) in a 2:1 ratio after treatment of the reducing diketiminate nickel complex $K_2[(L^{tBu}Ni)_2(\mu-\eta^1:\eta^1-N_2)]$ (**161**) with SF_6 at room temperature (Scheme 30).[100]

A rhodium-mediated activation of SF_6 was reported in 2014.[101] In the presence of $HSiEt_3$, the hydrido-bridged binuclear Rh^I complex $[\{Rh(\mu-H)(dippp)\}_2]$ (**162**, dippp = 1,3-bis(di-iso-propylphosphanyl)propane) was converted selectively with SF_6 into the silylthiolato-bridged complex $[Rh_2(\mu-H)(\mu-SSiEt_3)(dippp)_2]$ (**163**), $FSiEt_3$, and H_2 (Scheme 31). Note that SF_5CF_3 and SF_5Ph react in a comparable way with **162** to yield **163** as well as $[Rh_2(\mu-H)(\mu-SCF_3)(dippp)_2]$ (**164**) or $[Rh_2(\mu-H)(\mu-SPh)(dippp)_2]$ (**165**), respectively.[101]

The nonclassical silane complex $[Rh(H)(\eta^2-HSiEt_3)(dippp)]$ (**166**) was detected as an intermediate and was generated independently by treatment of the fluorido complex $[\{Rh(\mu-F)(dippp)\}_2]$ (**167**) with an excess of $HSiEt_3$ (Scheme 32).[102] A subsequent addition of SF_6 gives $[Rh_2(\mu-H)(\mu-SSiEt_3)(dippp)_2]$ (**163**). $[\{Rh(\mu-H)(dippp)\}_2]$ (**162**) is not in equilibrium with $HSiEt_3$ to give $[Rh(H)(\eta^2-HSiEt_3)(dippp)]$ (**166**).[102] In the absence of $HSiEt_3$, $[\{Rh(\mu-H)(dippp)\}_2]$ (**162**) is being fully converted upon treatment with SF_6 (1 atm) at room temperature within one day. According to the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture, the fluorido complex $[\{Rh(\mu-F)(dippp)\}_2]$ (**167**) was

Scheme 27. Activation of SF_6 at the titanium complex **149**.[99a]

Scheme 28. Fluorination of vanadocene **152** with SF_6.[99b]
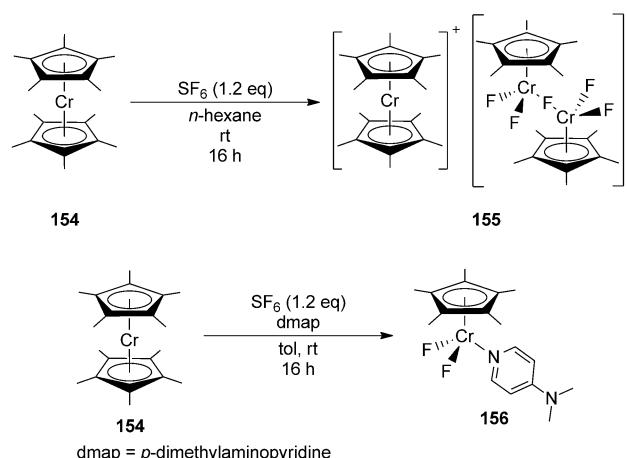
Scheme 29. Reactivity of $[Cp^*_2Cr]$ (**154**) towards SF_6.[99b]

dmap = p-dimethylaminopyridine

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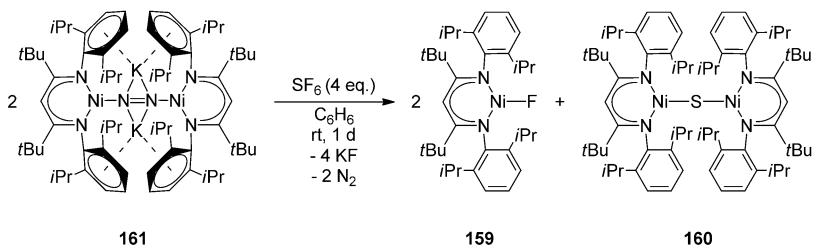
Scheme 30. Reactivity of SF_6 at the β-diketiminate nickel complex **161**.[100]
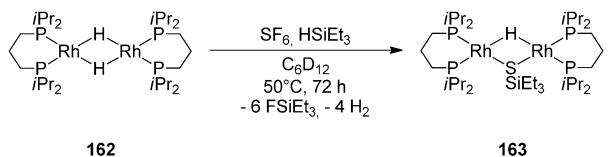
Scheme 31. Formation of $[Rh_2(\mu\text{-}H)(\mu\text{-}SSiEt_3)(dippp)_2]$ (**163**).[101]
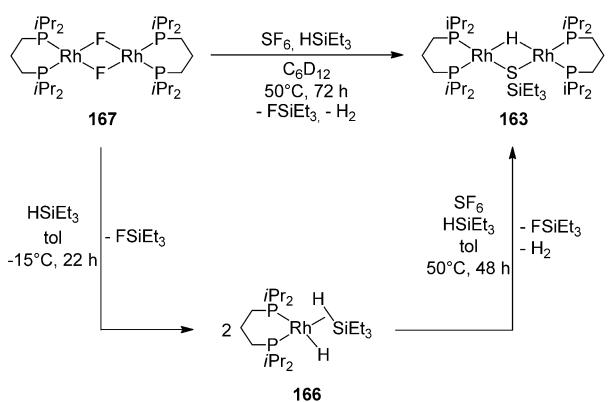
Scheme 32. S–F bond activation reactions of SF_6 at **167** and **166**.[101]

formed in approximately 70 % yield. LIFDI MS studies led to the assumption that rhodium–sulfido clusters as sulfur-containing products were generated, most of which appeared to be trinuclear.

Sulfur hexafluoride also reacts with the xantphos-type rhodium complex $[Rh(H)\{^{tBu}xanPOP\}]$ (**168**, ^{tBu}xanPOP = 9,9-dimethyl-4,5-bis(di-tert-butylphosphino)xanthene) to form $[Rh(FHF)\{^{tBu}xanPOP\}]$ (**169**) as the only transition-metal complex.[103] Furthermore, in the presence of the hydrogen source $HSiEt_3$ the activation of SF_6 at **168** led to the formation of $[Rh(F)_2(H)\{^{tBu}xanPOP\}]$ (**170**) as well as $[Rh(SH)\{^{tBu}xanPOP\}]$ (**171**) and $S(SiEt_3)_2$ as sulfur-containing products (Scheme 33).
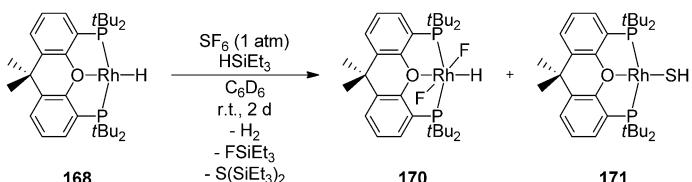
Scheme 33. Reduction of SF_6 at $[Rh(H)\{^{tBu}xanPOP\}]$ (**168**) in the presence of $HSiEt_3$.[103]

A catalytic degradation of SF_6 was reported at $[Rh(H)(PEt_3)_3]$ (**172**) as catalyst.[104] Silanes and phosphines were employed as scavengers for the sulfur and fluorine atoms. In the presence of PEt_3, **172** is in equilibrium with $[Rh(H)(PEt_3)_4]$ (**173**).[105] The conversions without the presence of silane at room temperature led to the formation of several Rh complexes out of which $[Rh(PEt_3)_4][HF_2]$ (**174**), $[Rh(F)(PEt_3)_3]$ (**175**),[106] and $[\{Rh(\mu\text{-}F)(PEt_3)_2\}_2]$ (**176**) were identified. However, at 80 °C, the ionic complex $[Rh(PEt_3)_4][HF_2]$ (**174**) as sole transition-metal complex in addition to $SPEt_3$ as the only sulfur-containing product and F_2PEt_3 were furnished with a TON of 4.8 [TON = mol of $SPEt_3$ per mol^{-1} of $[Rh(H)(PEt_3)_3]$ (**172**)] after two days. In the presence of $HSiEt_3$ (ratio $HSiEt_3:PEt_3 = 1:1$), the catalytic degradation of SF_6 at $[Rh(H)(PEt_3)_3]$ (**172**, 2.5 mol %) gave the ionic dihydrido complex $[Rh(H)_2(PEt_3)_4][HF_2]$ (**177**) as the only rhodium species along with H_2, F_2PEt_3, $FSiEt_3$, and $SPEt_3$ (Scheme 34). With a catalyst loading of 0.2 mol %, a TON of 76 was achieved after five days based on the formation of $SPEt_3$. A dependency of the catalytic activity on the steric demand of the alkyl phosphine exists with increasing TON in the order $PtBu_3 < PiPr_3 < PEt_3 < PMe_3$. A maximum TON of 86 was found for the reaction of SF_6 in the presence PMe_3 and $HSiEt_3$ (0.2 mol % $[Rh(H)(PEt_3)_3]$ (**172**)).

Mechanistically, it has been suggested that the conversions at rhodium are initiated by an electron transfer to SF_6 yielding SF_6^-, which is not stable and degrades further to fluoride complexes and lower sulfur fluoride moieties.[99]

McTeague and Jamison successfully applied SF_6 as a fluorinating agent in 2016.[107] They developed catalytic deoxyfluorination reactions of allylic alcohols based on a photoredox catalytic process on using ruthenium or iridium complexes as photocatalysts (with loadings up to 3 mol %). The conversions were run in the presence of diisopropylethyl amine (DIPEA) as reductant under blue LED (470 nm) irradiation. Moreover, a continuous-flow deoxyfluorination with commercially available $[Ir(dtbbpy)(ppy)_2][PF_6]$ (**178**, dtbbpy = 4,4′-di-tert-butyl-2,2′-bipyridine, ppy = 2-phenylpyridine) was realized (Scheme 35). The authors suggest a mechanism that involves an activation of the alcohol by O–S bond formation leading to R–O–SF_x as intermediate. Subsequent C–O bond cleavage and fluorination gives the products.

Note that several activation reactions of SF_6 were reported that are based on an initial electron transfer from electron-rich organic molecules to sulfur hexafluoride.[98a,d,e, 108] Again SF_6^- is presumably formed initially and then two possible decomposition pathways

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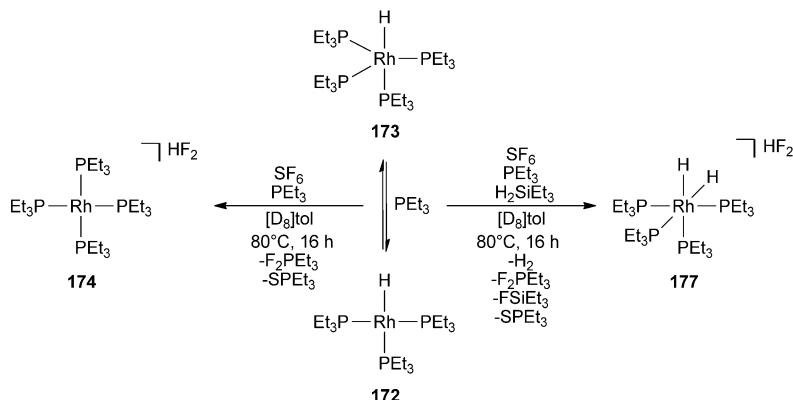
Scheme 34. Catalytic degradation of SF_6 at $[Rh(H)(PEt_3)_3]$ (**170**) in the presence of free PEt_3 (left) and in the presence of PEt_3 and $HSiEt_3$ (right).[104]
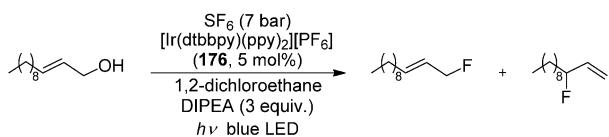
Scheme 35. Deoxyfluorination of (E)-dodec-2-en-1-ol at $[Ir(dtbbpy)(ppy)_2]$ $[PF_6]$ (**178**, dtbbpy = 4,4′-di-tert-butyl-2,2′-bipyridine, ppy = 2-phenylpyridine) in a continuous-flow photoredox catalysis.[107]

are conceivable. Either a SF_5 radical and a fluoride ion are formed or SF_5^- and a fluorine radical are generated. In general, the decomposition pathway of the SF_6^- in the gas phase depends on the kinetic energy of the electron and thermal energy of the SF_6 molecule.[109]

Wagenknecht and co-workers utilized the strongly reducing photocatalyst N-phenylphenothiazine to photolytically activate both SF_6 and a styrene derivative as substrate.[98d, 110] The generated SF_5 radical and radical cation of the styrene substrate combine to yield a cationic SF_5 intermediate. A subsequent fluorination with a fluoride anion gives $Ph_2CFCH_2SF_5$ as the final product (Scheme 36).[98d] The authors speculated that addition of $[Cu(acac)_2]$ (**179**) stabilizes the SF_5 radical.

Dielmann et al. reported in 2018 on the activation of SF_6 by using highly basic imidazolin-2-imine type phosphines.[98c] Based on DFT calculations, it has been proposed that in an initial step the phosphines react via a S_N2 type mechanism. The

final products are difluorophosphoranes and phosphine sulfides. In one case a SF_5^- salt was isolated.

As indicated above, it has been shown by groups of Beier, Dielmann, Kirsch, Roeschenthaler, Rueping, and Wagenknecht that SF_6 can be converted into SF_5^- or organo SF_5 compounds originating from styrene derivatives.[98a–d, 108] In another approach at transition-metal complexes, it was demonstrated at platinum that SF_6 can also be transformed into a SF_3 building block. Activation of SF_6 at trans-$[Pt(PR_3)_2]$ [R = iPr (**124a**), Cy (**124b**)] in the presence of the respective phosphines yielded fluorophosphoranes and trans-$[Pt(F)(SF_3)(PR_3)_2]$ [R = iPr (**125a**), Cy (**125b**)]. As mentioned above, the latter can also be synthesized by an oxidative addition of SF_4 at trans-$[Pt(PR_3)_2]$ (**124a,b**) (Scheme 37). Complex trans-$[Pt(F)(SF_3)(PCy_3)_2]$ (**125b**) can be applied for the deoxyfluorination of EtOH or benzophenone derivatives (see section 3.2).[91a, 93]
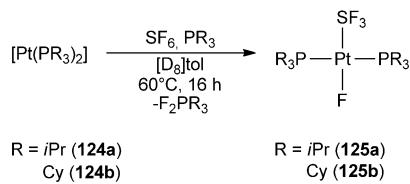
Scheme 37. Formation of trans-$[Pt(F)(SF_3)(PR_3)_2]$ [R = iPr (**125a**), Cy (**125b**)] by SF_6 activation.[91a]

5. Conclusion and Outlook

Transition-metal complexes open many inspiring reaction pathways when reacted with sulfur halides. Often chlorination, chlorofluorination, or fluorination reactions of metal centers can occur. The development of carbofluorinations on using transition-metal-mediated processes can be envisioned.

In addition, unusual ligands and moieties can also be constructed, which show interesting binding properties. SF_2 or SF_3 ligands were furnished and used for fluorination reactions. An SF_3 ligand can exhibit a certain electronic flexibility, but reactivity studies are so far hampered by the instability of the complexes. Future studies might lead to the discovery of interest-

Scheme 36. Photocatalytic SF_5 group transfer on using SF_6.[98d]

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ing coordination modes of ligand systems containing sulfur halide moieties.

Transition-metal mediated conversions of sulfur halides can also open up reaction pathways for the generation of sulfide and polysulfide ligands, which can be employed for the generation of organic molecules. Studies on the generation, and reactivity or ligand transfer of SF_5 complexes are an exciting challenge. It should be noted that SF_5-containing building blocks are considered as promising groups for materials, agrochemicals and pharmaceutical agents.[16b, 111]

In many recent studies the activation, depletion or derivatization of SF_6 has been in focus. Depletion processes are of certain importance, because of the use of SF_6 as dielectric in high-voltage power applications, but at the same time, its negative environmental impact has to be taken into account. Using SF_6 as fluorinating agent can be considered of interest, and the studies might reveal fundamental insights, although many other superior sulfur fluoride-based fluorinating agents are commercially available. The generation of sulfur fluoride-containing building blocks from SF_6, in contrast, can again open up opportunities for the formation of sulfur containing molecules and materials.

Acknowledgements

Conflict of interest

The authors declare no conflict of interest.

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