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Gold trifluoromethyl complexes

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This article reviews the synthesis, reactivity and applications of gold trifluoromethyl complexes, which are the only isolated perfluoroalkyl complexes of gold. The most reported examples are neutral Au(I) complexes of the type $[\text{Au}(\text{CF}_3)_n\text{L}]$, whereas only two Au(II) trifluoromethyl complexes have been reported, both being diamagnetic and containing a strong Au–Au bond. A number of Au(III) trifluoromethyl complexes have been prepared by oxidative addition of halogens or iodotrifluoromethane to Au(I) complexes or, in a few cases, by transmetallation reactions. Owing to the limitations of the available synthetic methods, a lower number of examples is known, particularly for the oxidation states (II) and (III). Gold trifluoromethyl complexes present singular characteristics, such as thermal stability, strong Au–C bonds and, in some cases, reactive $\alpha\text{-C-F}$ bonds. Some of the Au(III) complexes reported, show unusually easy reductive elimination reactions of trifluoromethylated products which could be applied in the development of gold-catalyzed processes for the trifluoromethylation of organic compounds.

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Introduction

Perfluoroalkyl complexes form a special class among transition metal organometallic compounds. After the first examples were synthesized in the middle of the past century, it has been realized that their properties are remarkably different

from those of their non-fluorinated analogues.^{1,2} Thus, it is commonly accepted that they are generally more stable than their alkyl counterparts and that, owing to this stability, the metal–perfluoroalkyl bond presents low reactivity, particularly in reductive elimination or migratory insertion reactions,^{3–5} which are the key steps in metal-promoted coupling reactions.

Efficient synthetic methods for the introduction of fluorinated substituents into organic molecules are currently demanded because fluoroorganic compounds are scarce in nature,^{6–8} and they offer industrial applications as advanced

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José Vicente

José Vicente received his Ph.D. in Chemistry from the University of Zaragoza in 1973 under the supervision of Profs Rafael Usón and Victor Riera. He was a postdoctoral fellow at Bristol University (1976–7) with Prof. F. Gordon A. Stone. He was appointed as a Lecturer in Zaragoza (1978), a Reader (1980) in the University of Murcia, later (1981) a Full Professor, and currently he is an Emeritus Professor. He was awarded in 2001

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materials,^{9–12} in fluorine chemistry^{13–17} and, most importantly, in medicine.^{18,19} Owing to their pharmaceutical applications, trifluoromethylated organic compounds have received special attention. This demand has stimulated the search for reactive perfluoroalkyl metal complexes, giving rise to the recent development of a plethora of new metal mediated or catalyzed trifluoromethylation reactions.^{20–27}

Most metal-promoted synthetic routes for trifluoromethylated organic compounds make use of copper trifluoromethyl complexes,^{22,24,26,28–31} some of which were used as trifluoromethylating agents in organic synthesis for a long time.^{32,33} Methods based on other metals, such as silver^{34–39} or palladium,^{40–47} have also been developed, although they are less used. Overall, these advances have revealed an unforeseen synthetic potential for perfluoroorganotransition metal compounds, which should be further developed by the investigation of new types of transition metal perfluoroalkyl complexes.

There is still a limited knowledge of the chemistry of gold perfluoroalkyl complexes, which contrasts with the remarkable progress made in the organometallic and catalytic chemistry of gold over the last 25 years.^{48–55} The first gold perfluoroalkyls were prepared rather late (1973) by Puddephatt and co-workers.^{56,57} Since then, a relatively low number of trifluoromethyl complexes has been reported. For instance, no higher perfluoroalkyls of gold have been described, with the exception of $[\text{Au}(\text{C}_2\text{F}_5)(\text{PEt}_3)]$, which was spectroscopically observed but not isolated.⁵⁸ It is also noteworthy that the synthetic routes to simple complexes such as $[\text{Au}(\text{CF}_3)_x]^-$ ($x = 2, 4$) have been only recently reported.^{59–61} Interestingly, Au(III) complexes present a low activation barrier for the reductive elimination of R–R' products,^{62–66} including those with R = CF₃.⁶⁷ This is of considerable interest, because reductive elimination is one of the key steps in metal mediated- or catalyzed coupling reactions and its activation barrier is usually very high for perfluoroalkyl complexes, limiting their applicability in this field.^{40–42,68}

The pioneering work on the synthesis of fluorocarbon metal complexes was compiled in three reviews by Stone *et al.*^{1,2,69} The field of transition metal trifluoromethyl complexes has been reviewed by Morrison (1993),⁵ and Menjón *et al.* (2012).⁷⁰ In this Perspective, we have reviewed the synthesis, properties and reactivity of gold trifluoromethyl compounds, putting emphasis on recently reported reactions with potential synthetic interest.

Structure, bonding and spectroscopic properties of gold trifluoromethyl complexes

The available experimental evidence suggests that, as observed for other metal perfluoroalkyls, gold trifluoromethyl complexes are more stable than their methyl analogues. For instance, the compounds $[\text{Au}(\text{CF}_3)(\text{CNR})]$ (R = Me,⁷¹ ^tBu⁶¹) melt without decomposition at 110 and 119 °C, respectively, whereas their

methyl analogues decompose at 95 and 62 °C, respectively.⁷² The salts $[\text{PPh}_4][\text{Au}(\text{CF}_3)_x]$ ($x = 2, 4$) start to decompose at 275 °C ($x = 2$) and 370 °C ($x = 4$),⁶¹ whereas di- and tetramethylaurates $[\text{Q}[\text{AuMe}_n]]$ ($n = 2, \text{Q} = \text{Li}(\text{MeN}(\text{CH}_2\text{CH}_2\text{NMe}_2)_2)$; $n = 4, \text{Q} = \text{N}^t\text{Bu}_4$) readily decompose at 140 °C.^{73,74} This stability can be attributed to a stronger Au–CF₃ bond, as evidenced by the generally shorter Au–CF₃ distances compared to those for the Au–CH₃ bonds in analogous compounds (Table 1).

In addition, gold trifluoromethyl complexes show two characteristic structural features usually found in other trifluoromethyl complexes: (i) the elongation of the MC–F bonds with respect to the C–F distances observed in non-metallic trifluoromethyl derivatives,⁷⁵ and (ii) the decrease of the F–C–F bond angle and the increase of the M–C–F bond angle⁷⁶ with respect to the ideal tetrahedral angle. Interestingly, whereas the feature (ii) is always found in all reported structures, the feature (i) is not observed in some Au(II) and Au(III) trifluoromethyl complexes.

The stability and special structural features of Mn, Rh, Ni and Pt perfluoroalkyl complexes have been addressed by theoretical studies. Thus, in 1972 Hall and Fenske reported the molecular orbital calculations of complexes $[\text{Mn}(\text{CX}_3)(\text{CO})_5]$ (X = H, F),⁸³ and in 2012 Macgregor and Grushin reported Natural Bonding Orbital (NBO) analyses of Mn, Rh, Pt and Ni trifluoromethyl and methyl complexes.³ These studies show that: (i) the C 2s character of the M–C bonding orbitals and the strength of the $\sigma(\text{M}-\text{C})$ interaction are higher for the CF₃ complexes than for the analogous methyl complexes, which accounts for the observed M–C bond shortening; (ii) the contribution of the metal-to-CF₃ π -backbonding to the overall M–CF₃ bonding is small, as also noted by Graham⁸⁴ and Harvey,⁸⁵ and it alone cannot account for the observed bond strengthening; (iii) the lone pair of the CF₃[–] anion^{86,87} has antibonding character with respect to the C–F bond, and therefore the degree of donation of this lone pair to a metal or non-metal acceptor significantly influences the strength of the C–F bonds; (iv) the high positive charge on the CF₃ carbon stabilizes the metal-based orbitals, conferring stability to the whole molecule.

Although NBO analyses have not been reported for Au trifluoromethyl complexes, similar effects could account for their

Table 1 Au–C bond distances in analogous Au(I) methyl and trifluoromethyl complexes

Compounds	$d(\text{Au}-\text{C})/\text{\AA}$	
	X = H	X = F
$\text{Ph}_3\text{P}-\text{Au}-\text{CX}_3$	2.124(28) ⁷⁷ 2.065(10) ⁷⁸	2.045(10) ⁷⁹
$\text{IPr}-\text{Au}-\text{CX}_3^a$	2.042(10) ⁸⁰	2.042(10), 2.030(14) ⁸¹
$[\text{Q}[\text{Au}(\text{CX}_3)_2]]$	2.075 (average, $\text{Q} = \text{N}^t\text{Bu}_4$) ⁸²	2.033(2) ($\text{Q} = \text{PPh}_4$) ⁶¹
$[\text{Q}[\text{Au}(\text{CX}_3)_4]]$	2.100 (average, $\text{Q} = \text{NMe}_2\text{Br}_2$) ⁸²	2.059(6), 2.072(6) ($\text{Q} = \text{PPN}$) ⁶⁰ 2.075(6), 2.085(7) ($\text{Q} = \text{N}^t\text{Bu}_4$) ⁶¹

^a IPr = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene.



amounts and the syntheses require special equipment which is not available in common synthetic laboratories.¹⁰⁴

Au(I) trifluoromethyl complexes

Puddephatt and coworkers isolated the first gold trifluoromethyl complexes by reacting [Au(Me)L] (L = phosphine) with ICF₃ (Scheme 1).^{56,57} Thus, when L = PPh₃ the complex [Au(CF₃)(PPh₃)] was formed, likely by the reductive elimination of MeI from the expected oxidative addition product, [Au(Me)(CF₃)(I)L], which was not detected. When L is PMe₃ or PMe₂Ph, the reactions gave Au(III) trifluoromethyl complexes, and for L = PPh₃ both Au(I) and Au(III) derivatives were obtained (see below). Evidence to show that these reactions occur at least in part through radical intermediates was obtained. Glocking and coworkers reported the formation of [Au(CF₃)(PPh₃)] in the reaction of [Au{CH(SiMe₃)₂}(PPh₃)] with ICF₃ (Scheme 1).¹⁰⁵

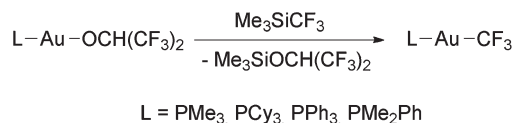
Toste and coworkers have reported that [Au(Me)(PCy₃)] does not react with ICF₃ in the dark. However, the complex [Au(CF₃)(PCy₃)] was quantitatively formed upon irradiating the mixture with ambient light (Scheme 1).⁶⁷ The reaction was fast and no Au(III) intermediates were detected by NMR spectroscopy. Interestingly, HCF₃ was formed when the same reaction was run in THF, which may be attributed to H[•] abstraction from the solvent, suggesting that the [•]CF₃ radicals are formed by photoactivation of ICF₃ in the presence of the Au(I) complex.

A series of [Au(CF₃)L] complexes (L = phosphine or phosphine) was obtained by the reactions of [Au(Cl)L] with Cd(CF₃)₂·DME as reported by the groups of Morrison,⁵⁸ Sanner⁸⁸ and Kruck¹⁰⁶ (Scheme 2). The volatile complex [Au(CF₃)(CNMe)] was similarly prepared by Puddephatt and coworkers and then used for the preparation of gold films by chemical vapour deposition (Scheme 2).⁷¹ Decomposition of this

complex takes place by CNMe dissociation, followed by Au and C₂F₆ formation. The only higher gold perfluoroalkyl reported, [Au(C₂F₅)(PEt₃)], was detected by NMR spectroscopy in the mixture of compounds resulting from the reaction between [Au(CF₃)(PEt₃)] and IC₂F₅, although it was not isolated.⁵⁸

The reactions of Me₃SiCF₃ with [Au(OR)L] (R = CH(CF₃)₂, L = PMe₃, PCy₃, PPh₃, PMe₂Ph; R = Ph, L = PCy₃, PPh₃) were used by Komiya and coworkers to prepare a series of trifluoromethyl complexes of the type [Au(CF₃)(phosphine)] (Scheme 3).⁹⁸ In contrast, the complex [Au(OH)(IPr)] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)¹⁰⁷ did not react with Me₃SiCF₃ at room temperature or at 80 °C.¹⁰⁸

Recently, we reported the synthesis of a family of Au(I) trifluoromethyl complexes by the reaction of Au(I) chloro complexes with AgF and Me₃SiCF₃ (Scheme 4).⁸¹ This method allows the synthesis of new examples of [Au(CF₃)L] complexes, where L is phosphine, phosphite, or isonitrile, and the first Au(I) trifluoromethyl complexes containing NHC ligands. The analogous reaction with PPN[AuCl(C₆F₅)] (PPN⁺ = Ph₃PNPPh₃⁺) gave the anionic complexes [Au(CF₃)(C₆F₅)]⁻, [Au(CF₃)₂]⁻ and [Au(C₆F₅)₂]⁻. Single crystals of PPN[Au(CF₃)(C₆F₅)]⁻ were iso-




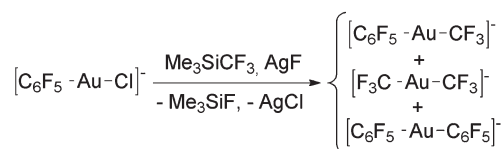
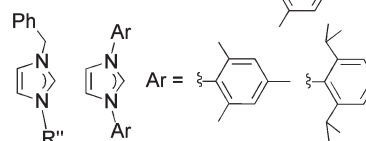
Scheme 3 Synthesis of [Au(CF₃)L] complexes by the reaction of Au(I) alkoxy complexes with Me₃SiCF₃.⁹⁸



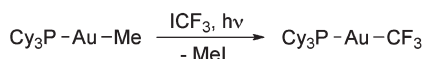
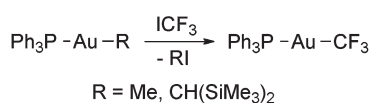
PR₃ R = Me, Ph, *p*-Tol, OMe

1/2 (Ph₂PCH₂)₂

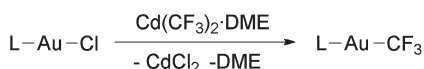
C≡N-R' R' = ^tBu, 



Scheme 4 Synthesis of Au(I) trifluoromethyl complexes by the reaction of Au(I) chloro complexes with *in situ* generated AgCF₃.⁸¹



Scheme 1 Synthesis of [Au(CF₃)L] complexes (L = PPh₃,^{56,57,105} PCy₃⁶⁷) by the reaction of Au(I) alkyls with ICF₃.



L

CNMe

PMe₃, PEt₃, PPh₃

PF₂X (X = NMe₂, NEt₂, ^tBu, Ph, C₅H₄, F)

Scheme 2 Synthesis of [Au(CF₃)L] complexes (L = PR₃,^{58,88} PF₂X,¹⁰⁶ CNMe⁷¹) by transmetalation using Cd(CF₃)₂·DME.



lated and used for a crystal structure determination (Fig. 2). Notably, this is the only transition metal complex reported that contains a CF_3 and a C_6F_5 ligand attached to the same metal. The isonitrile complexes reacted with NHEt_2 to give Au(I) trifluoromethyl complexes containing nitrogen acyclic carbene (NAC) ligands (Scheme 5).

The groups of Tyrra,⁶⁰ Forniés⁵⁹ and Menjón^{59,61} independently reported the synthesis of the complex $[\text{Au}(\text{CF}_3)_2]^-$ by using the reactions of AuCl or $[\text{AuCl}(\text{tht})]$ with Me_3SiCF_3 and F^- (Scheme 6). This is the only anionic Au(I) trifluoromethyl complex prepared in practical amounts, and it was obtained as PPh_4^+ , NMe_4^+ , PNP^+ , $\text{K}(18\text{-crown-6})^+$ or $[\text{Ag}(\text{py})_2]^+$ salts. Remarkably, this complex is sensitive to hydrolysis, decomposing to form Au nanoparticles. Tyrra and coworkers reported that the treatment of $[\text{Au}(\text{CF}_3)_2]^-$ with $(\text{CF}_3\text{CO})_2\text{O}$ led to a mixture of CF_3COF , $[\text{Au}(\text{CF}_3)(\text{CF}_2\text{OC}(\text{O})\text{CF}_3)]^-$ and $[\text{Au}(\text{CF}_2\text{OC}(\text{O})\text{CF}_3)_2]^-$, which were detected by NMR spectroscopy (Scheme 6).⁶⁰ On the other hand, Forniés, Menjón and coworkers reported that BF_3 -assisted fluoride abstraction of $[\text{Au}(\text{CF}_3)_2]^-$ led to nearly quantitative formation of $[\text{Au}(\text{CF}_3)(\text{CO})]$ (Scheme 6).^{59,61} These reactions probably proceed through the extremely electrophilic Au(I) difluorocarbene¹⁰⁹ $\text{CF}_3\text{-Au}=\text{CF}_2$, which was not detected.

Despite its thermal instability and extreme moisture-sensitivity, the carbonyl $[\text{Au}(\text{CF}_3)(\text{CO})]$ was isolated and structurally characterized.⁵⁹ The crystal structure shows a rare trigonal arrangement of molecules connected by aurophilic interactions (Fig. 3). The weak nature of these interactions, the bond distances and angles, and the position of the $\nu(\text{CO})$ band in the IR spectrum suggest that the CO ligand acts as a weak σ -donor coordinated to a highly electrophilic AuCF_3 fragment. Thus, the CO ligand is very labile, being immediately substi-

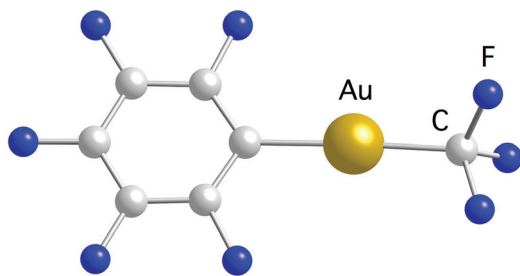
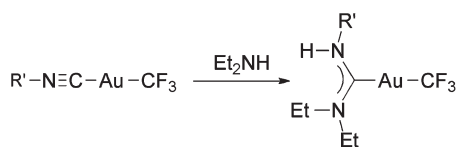
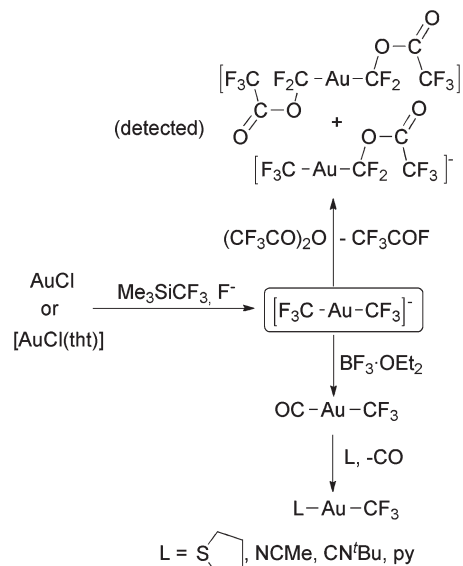


Fig. 2 Molecular structure of the anion in the crystal structure of the $\text{PPN}[\text{Au}(\text{CF}_3)(\text{C}_6\text{F}_5)]$ salt.⁸¹



Scheme 5 Synthesis of Au(I) trifluoromethyl complexes containing NAC ligands by the reaction of (trifluoromethyl)isocyanide complexes with Et_2NH .⁸¹



Scheme 6 Synthesis and fluoride abstraction reactions of $[\text{Au}(\text{CF}_3)_2]^-$.^{59–61} Substitution reactions of $[\text{Au}(\text{CF}_3)(\text{CO})]$.⁶¹

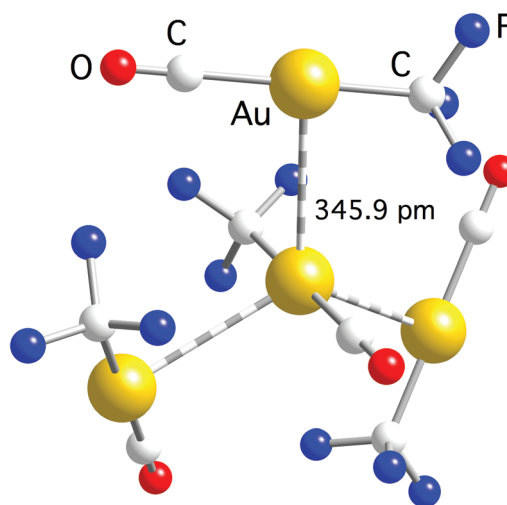


Fig. 3 Trigonal arrangement of molecules connected by aurophilic interactions in the crystal structure of $[\text{Au}(\text{CF}_3)(\text{CO})]$. Owing to the C_3 symmetry axis, the three Au–Au bond distances are equal to the indicated one.⁵⁹

tuted at 0 °C by tetrahydrothiophene (tht), MeCN, pyridine or $t\text{-BuNC}$ (Scheme 6). The more thermally robust and air-stable complex $[\text{Au}(\text{CF}_3)(\text{tht})]$ has been proposed as a convenient source for the “ $\text{Au}(\text{CF}_3)$ ” synthon,⁶¹ in analogy to $[\text{AuR}(\text{tht})]$ being a source for complexes containing the “ AuR ” fragment.^{110–114}

The anions $[\text{Au}(\text{CF}_3)\text{X}]^-$ ($\text{X} = \text{F}, \text{OC}(\text{O})\text{CF}_3$) have been detected by mass spectrometry in the collision-induced dissociation of the $[\text{Au}(\text{OC}(\text{O})\text{CF}_3)_2]^-$ ion.¹¹⁵ $[\text{Au}(\text{CF}_3)\text{Cl}]^-$ was detected by IR spectroscopy in the reaction of laser-ablated Au atoms with ClCF_3 .¹¹⁶



Au(II) trifluoromethyl complexes

Only two Au(II) trifluoromethyl complexes have been reported to date (Scheme 7), both being diamagnetic and displaying strong Au–Au bonds.

The first example is $[\text{Au}_2(\text{CF}_3)_2\{\mu\text{-Ph}_2\text{P}(\text{CH}_2)_2\}_2]$, prepared by using the reaction of $[\text{Au}_2\text{Cl}_2\{\mu\text{-Ph}_2\text{P}(\text{CH}_2)_2\}_2]$ with $\text{Cd}(\text{CF}_3)_2\cdot\text{DME}$, which contains two bridging bis(ylide) ligands.¹¹⁷ The other compound is $[\text{Au}_2(\text{CF}_3)_4(\text{py})_2]$, obtained after irradiating a solution of $[\text{Ag}(\text{py})_2][\text{Au}(\text{CF}_3)_2]$ with UV light. In this remarkable reaction, the $[\text{Ag}(\text{py})_2]^+$ cation is reduced to metallic Ag and oxidizes $[\text{Au}(\text{CF}_3)_2]^-$ to Au(II).¹¹⁸ This compound is a rare example of a dinuclear Au(II) complex where the Au–Au bond is not supported by the bridging ligands, and it has been the object of a theoretical study.¹¹⁹ The computational results showed that the bond between both the Au(II) centers is of covalent nature. Moreover, the analysis of the bonding orbitals suggested that they can be described by an uncommon $6s6p_z5d_{xy}$ hybridization type. $[\text{Au}_2(\text{CF}_3)_4(\text{py})_2]$ was characterized in the solid state by single crystal X-ray diffraction (Fig. 4), but no data could be obtained in solution because it spontaneously disproportionates into a 1:1 mixture of $[\text{Au}(\text{CF}_3)$

$(\text{py})]$ and $[\text{Au}(\text{CF}_3)_3(\text{py})]$, both being detected by NMR spectroscopy.

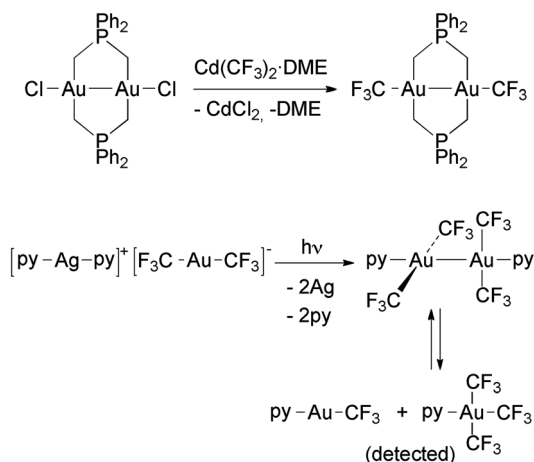
Au(III) trifluoromethyl complexes

Au(III) trifluoromethyl complexes have been prepared either (i) by oxidative addition of ICF_3 to Au(I) complexes, (ii) by halogenation of Au(I) trifluoromethyl complexes, or (iii) by trifluoromethylation of Au(III) complexes.

The first reported Au(III) perfluoroalkyls were obtained by Puddephatt and coworkers in the reaction of $[\text{Au}(\text{Me})\text{L}]$ with ICF_3 (Scheme 8), which gave mixtures of *cis*- and *trans*- $[\text{Au}(\text{CF}_3)_2\text{Me}_2\text{L}]$ ($\text{L} = \text{PMe}_3, \text{PMe}_2\text{Ph}$) in variable ratios depending on the solvent and the nature of the ligand L.^{56,57} From these mixtures, only the *trans* isomers were isolated. These reactions seem to proceed by the oxidative addition of ICF_3 to the Au(I) complexes to give a $[\text{Au}(\text{CF}_3)(\text{Me})\text{IL}]$ intermediate, which undergoes Me for I ligand exchange with the unreacted $[\text{Au}(\text{Me})\text{L}]$. The intermediate complex was detected in certain experiments and independently prepared by the reaction of *trans*- $[\text{Au}(\text{CF}_3)\text{Me}_2(\text{PMe}_3)]$ with HCl and NaI. Evidence of a radical chain mechanism for these oxidative addition reactions was obtained (Scheme 9).

The photooxidative addition of ICF_3 to $[\text{Au}(\text{Ar})\text{L}]$ ($\text{L} = \text{PPh}_3, \text{Ar} = 4\text{-X-C}_6\text{H}_4$ ($\text{X} = \text{Me}, \text{F}$); $\text{L} = \text{PCy}_3, \text{Ar} = 4\text{-X-C}_6\text{H}_4$ ($\text{X} = \text{H}, \text{Me}, \text{F}, \text{MeO}$), $3,5\text{-F}_2\text{C}_6\text{H}_4$) has been reported by Toste's group (Scheme 10).⁶⁷ The complexes $[\text{Au}(\text{CF}_3)(\text{Ar})\text{I}(\text{PR}_3)]$ were isolated in high yields as single isomers. Detailed mechanistic studies support a radical chain mechanism as depicted in Scheme 9. The radical chain is initiated by electron transfer from the Au(I) complex or PCy_3 to a photoexcited molecule of ICF_3 , giving rise to I^- and a $\cdot\text{CF}_3$ radical. However, in contrast to the analogous Au(III) complexes containing a methyl ligand (see above), the complexes $[\text{Au}(\text{CF}_3)(\text{Ar})\text{I}(\text{PR}_3)]$ are stable against reductive elimination and do not undergo R for I ligand exchange with the starting $[\text{Au}(\text{R})\text{L}]$ complexes.

Interestingly, the complexes $[\text{Au}(\text{CF}_3)(\text{Ar})\text{I}(\text{PR}_3)]$ underwent thermal reductive elimination to afford ArI and $[\text{Au}(\text{CF}_3)(\text{PPh}_3)]$ (Scheme 10, reaction (a)). The complete inhibition of this reaction in the presence of added PPh_3 suggests that it proceeds through PPh_3 dissociation to give a neutral tricoordinate intermediate which eliminates ArI . In contrast, a very fast



Scheme 7 Formation of Au(II) trifluoromethyl complexes by (i) transmetalation in an Au(II) chloro complex,¹¹⁷ and (ii) photo-disproportionation of $[\text{Ag}(\text{py})_2][\text{Au}(\text{CF}_3)_2]$.¹¹⁸ The unstable Au(II) complex $[\text{Au}_2(\text{CF}_3)_4(\text{py})_2]$ disproportionates in solution to an Au(I) and an Au(III) complex.

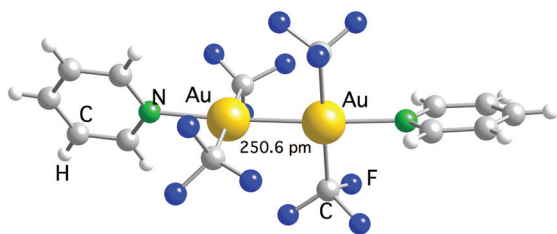
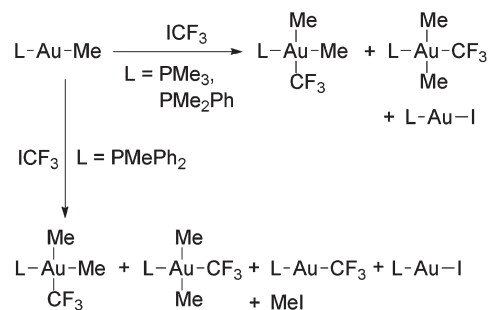
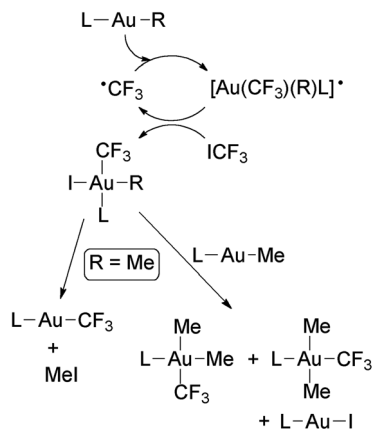


Fig. 4 Molecular structure of $[\text{Au}(\text{CF}_3)_4(\text{py})_2]$. The Au–Au bond distance is indicated.¹¹⁸

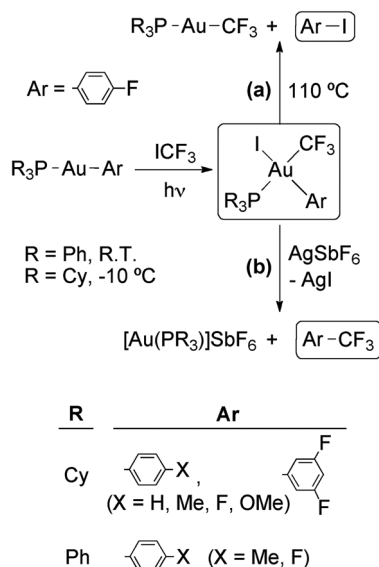


Scheme 8 Reactions of Au(I) methyl complexes with ICF_3 which lead to mixtures of Au(I) and Au(III) complexes.^{56,57}





Scheme 9 Proposed radical chain mechanism for the oxidative addition of ICF_3 to Au(I) complexes. Subsequent evolution of the formed Au(III) trifluoromethyl complexes with $\text{R} = \text{Me}$ to give mixtures of Au(I) and Au(III) complexes.⁶⁷



Scheme 10 Photooxidative addition of ICF_3 to Au(I) aryl complexes. The resulting Au(III) complexes may undergo (a) thermal reductive elimination of ArI or (b) fast reductive elimination of ArCF_3 after removal of an I^- ligand.⁶⁷

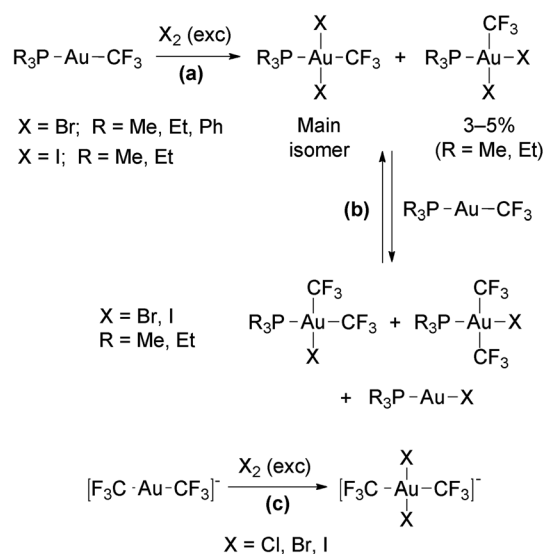
reductive elimination of ArCF_3 was observed when the complexes $[\text{Au}(\text{CF}_3)(\text{Ar})(\text{PR}_3)]$ were treated with AgSbF_6 to abstract an I^- anion and generate a cationic tricoordinate intermediate (Scheme 10, reaction (b)). The last process is remarkable taking into account (i) the known reluctance of transition-metal trifluoromethyl complexes to undergo reductive elimination of trifluoromethylated products, and (ii) the potential synthetic utility for a gold-catalyzed aromatic trifluoromethylation reaction. In this respect, the authors of this study have demonstrated the feasibility of each individual step in a

hypothetical catalytic cycle for the gold-catalyzed photoactivated trifluoromethylation of an arylstannane.

The reactions of the Au(I) trifluoromethyl complexes $[\text{Au}(\text{CF}_3)\text{L}]$ ($\text{L} = \text{phosphine}$) or $[\text{Au}(\text{CF}_3)_2]^-$ with an excess of Cl_2 , Br_2 or I_2 afforded Au(III) complexes resulting from the oxidative addition of the halogens (Scheme 11, reactions (a) and (c)).^{61,88} In these complexes, the halo ligands are disposed mutually in *trans* (only small amounts of the *cis* isomers were observed for $\text{L} = \text{PMe}_3$ and PEt_3). When equimolar amounts of $[\text{Au}(\text{CF}_3)\text{L}]$ and halogen were used, the additional products resulting from CF_3/X exchange with the remaining starting complex were also observed (Scheme 11, reaction (b)). The Au(III) complexes obtained in these reactions are stable against thermal reductive elimination.

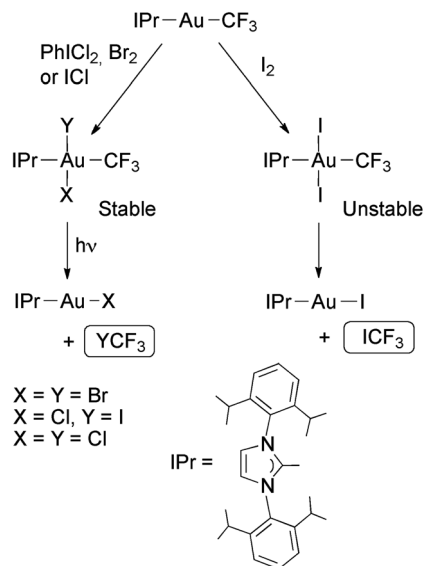
The complexes $[\text{Au}(\text{CF}_3)(\text{IPr})]$ react similarly with PhICl_2 , Br_2 , I_2 or ICl , affording exclusively the isomers with the halogens disposed mutually in *trans* (Scheme 12). These complexes are thermally stable except in the case of *trans*- $[\text{Au}(\text{CF}_3)_2\text{I}(\text{IPr})]$, which reductively eliminates ICF_3 even at low temperature. However, on irradiating with UV light the compounds $[\text{Au}(\text{CF}_3)\text{XY}(\text{IPr})]$ ($\text{X} = \text{Y} = \text{Cl}$ or Br ; $\text{X} = \text{Cl}$, $\text{Y} = \text{I}$) underwent reductive elimination of halotrifluoromethane (Scheme 12). Remarkably, the chloro(iodo) complex selectively eliminated ICF_3 instead of ClCF_3 .⁸¹

The oxidative addition of ICF_3 to $[\text{Au}(\text{CF}_3)(\text{PR}_3)]$ ($\text{R} = \text{Me}$,^{58,88} Et ⁸⁸) gave mixtures of *cis*- and *trans*- $[\text{Au}(\text{CF}_3)_2\text{I}(\text{PR}_3)]$, where the *cis* isomer is the predominant product (Scheme 13).⁸⁸ Inhibition of the reactions by a radical scavenger (galvinoxyl) suggests that they also proceed through a radical mechanism. The partial reactions between $[\text{Au}(\text{CF}_3)_2\text{I}(\text{PEt}_3)]$ and $[\text{Au}(\text{CF}_3)(\text{PR}_3)]$ to give mixtures of $[\text{Au}(\text{CF}_3)_3(\text{PR}_3)]$ and $[\text{AuI}(\text{PR}_3)]$ have been also reported (Scheme 13).⁵⁸ No reductive elimination of ICF_3 or $\text{CF}_3\text{-CF}_3$ from these Au(III) complexes was described.

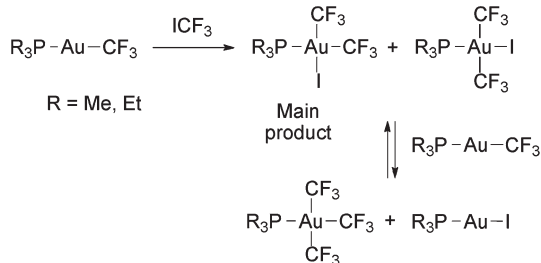


Scheme 11 Oxidative addition of halogens to neutral¹²² and anionic⁹⁸ Au(I) trifluoromethyl complexes.



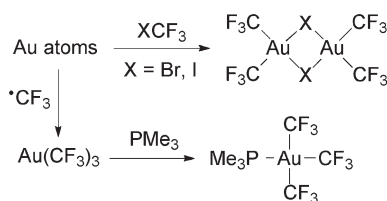


Scheme 12 Oxidative addition of halogens to Au(I) trifluoromethyl complexes containing a bulky NHC ligand. Photochemical or thermal reductive eliminations of halotrifluoromethanes.⁸¹



Scheme 13 Oxidative addition of ICF_3 to Au(I) trifluoromethyl complexes. A further ligand exchange with the remaining starting material leads to tris(trifluoromethyl) complexes.^{58,88}

The dinuclear complexes $[\text{Au}_2(\text{CF}_3)_4(\mu\text{-X})_2]$ ($\text{X} = \text{Br}, \text{I}$) were prepared by condensation of Au atoms with XCF_3 (Scheme 14). The isolated compounds are moderately stable and have been characterized by single crystal X-ray diffraction and NMR spectroscopy.¹²⁰

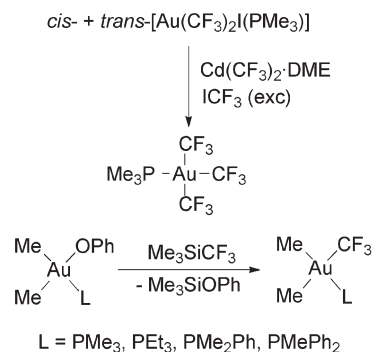


Scheme 14 Synthesis of Au(III) trifluoromethyl complexes by the reaction of Au atoms with halotrifluoromethanes or trifluoromethyl radicals.^{120,121}

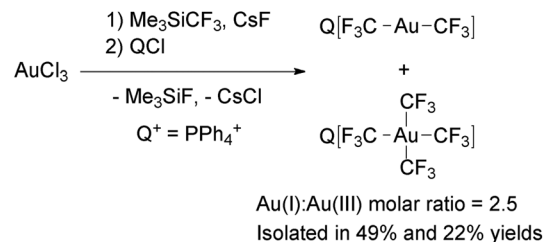
An unstable compound formulated as $\text{Au}(\text{CF}_3)_3$ was isolated from the reaction of trifluoromethyl radicals and Au atoms (Scheme 14).¹²¹ The NMR data of its PMe_3 adduct are in agreement with those reported for $[\text{Au}(\text{CF}_3)_3(\text{PMe}_3)]$ ⁸⁸ (see below).

Most attempts to obtain Au(III) trifluoromethyls by transmetalation reactions of Au(III) complexes and $\text{Cd}(\text{CF}_3)_2 \cdot \text{DME}$ resulted in the formation of Au(I) complexes as the side or main products, although the desired Au(III) trifluoromethyls are stable once isolated.⁸⁸ For instance, the reaction of $[\text{Au}(\text{CF}_3)_2\text{I}(\text{PMe}_3)]$ with $\text{Cd}(\text{CF}_3)_2 \cdot \text{DME}$ gave $[\text{Au}(\text{CF}_3)(\text{PMe}_3)]$, ICF_3 and CdI_2 instead of the expected $[\text{Au}(\text{CF}_3)_2\text{I}(\text{PMe}_3)]$. The reaction of $[\text{Au}(\text{CF}_3)_2\text{I}(\text{PMe}_3)]$ (prepared from $[\text{Au}(\text{CF}_3)(\text{PMe}_3)]$ and ICF_3) with $\text{Cd}(\text{CF}_3)_2 \cdot \text{DME}$ gave $[\text{Au}(\text{CF}_3)_3(\text{PMe}_3)]$ in high yield (Scheme 15), although the reaction had to be carried out under an ICF_3 atmosphere, because otherwise $[\text{Au}(\text{CF}_3)(\text{PMe}_3)]$ and ICF_3 could also be formed.⁸⁸ The tris(trifluoromethyl) complex is a thermally, air and moisture stable crystalline solid, which can be purified by sublimation.^{58,88} The complexes *cis*- $[\text{Au}(\text{CF}_3)(\text{Me})_2\text{L}]$ ($\text{L} = \text{PMe}_3, \text{PEt}_3, \text{PMe}_2\text{Ph}$ or PMePh_2) have been also obtained by Komiya and coworkers in the reaction of *cis*- $[\text{Au}(\text{OPh})(\text{Me})_2\text{L}]$ with Me_3SiCF_3 (Scheme 15).⁹⁸

$[\text{Au}(\text{CF}_3)_4]^-$ was firstly prepared by Neumann and coworkers as its PPN^+ salt, although the synthetic method was not reported.¹²² Recently, Menjón and coworkers described the synthesis of this complex by the reaction of AuCl_3 , Me_3SiCF_3 and CsF (Scheme 16).⁶¹ During the reaction, partial reduction



Scheme 15 Synthesis of Au(III) trifluoromethyl complexes by transmetalation.^{88,98}



Scheme 16 Synthesis of complexes $[\text{Au}(\text{CF}_3)_x]^-$ ($x = 2, 4$) from AuCl_3 . The PPh_4^+ salts were separated by crystallization.⁶¹



of the metal took place to give a mixture of $[\text{Au}(\text{CF}_3)_2]^-$ and $[\text{Au}(\text{CF}_3)_4]^-$. Fortunately, the mixture could be separated by using PPh_4^+ as the counteranion due to the different solubilities of the Au(I) and Au(III) salts. $(\text{PPh}_4)[\text{Au}(\text{CF}_3)_4]$ is remarkably stable, because it melts at 125 °C and does not show significant weight loss until it is heated at 370 °C. In addition, delocalization of the negative charge over 12 fluorine atoms, makes $[\text{Au}(\text{CF}_3)_4]^-$ an uncommon weakly coordinating anion with a flat shape,¹²³ which has been used as a component of organic superconductors.^{122,124–127}

Finally, the reaction of $[\text{N}^t\text{Bu}_4][\text{Au}(\text{CN})_4]$ with ClF afforded a mixture of complexes of the type $[\text{AuF}_x\text{Cl}_y(\text{CF}_3)_{4-x-y}]^-$ ($x = 0-4$, $y = 0-2$). Metathesis of this mixture with Me_3SiX ($X = \text{Cl}$ or CN) gave Me_3SiF and new mixtures of the composition $[\text{AuX}_x(\text{CF}_3)_{4-x}]^-$ ($x = 0-4$). The components of these mixtures were identified by NMR spectroscopy but could not be separated.¹²⁸

Summary and outlook

Au(I), Au(II) and Au(III) trifluoromethyl complexes have been reported being, in general, more thermally stable than their methyl analogues. All known Au(I) complexes are of the $[\text{Au}(\text{CF}_3)_2\text{L}]$ type, except $[\text{Au}(\text{CF}_3)_2]^-$ and $[\text{Au}(\text{CF}_3)(\text{C}_6\text{F}_5)]^-$. Most of them have been obtained by using Me_3SiCF_3 as the nucleophilic trifluoromethylating agent in the presence of fluoride salts as activators of the silane. Among all the methodologies tested, the combination of Me_3SiCF_3 and AgF is the most versatile one. Only two Au(II) trifluoromethyl complexes have been described, both displaying an Au–Au bond. Au(III) complexes containing 1, 2, 3 or 4 trifluoromethyl ligands have been reported. Most of them have been prepared by the oxidative addition of ICF_3 or halogens to Au(I) complexes.

Overall, the available synthetic methods still suffer from important drawbacks, such as the use of expensive reagents, the low yields in selected cases and the narrow scope. Thus, the development of efficient methodologies for the introduction of trifluoromethyl and, specially, higher perfluoroalkyl groups in the coordination sphere of gold is highly desirable, and it should boost the application of these compounds in different fields.

Potentially interesting applications may emerge from the singular structural properties and reactivity of these compounds. Thus, the observation of unusually fast reductive eliminations of trifluoromethylated compounds in the Au(III) trifluoromethyl complexes could be applied in the catalytic trifluoromethylation of organic compounds. Other opportunities for the application of these compounds in homogeneous catalysis may arise from the strong electron-withdrawing ability of the trifluoromethyl groups, which enhances the Lewis acidity of the metal center, or from the α -fluoride abstraction reactions, which generate highly reactive difluorocarbene intermediates. In addition, the development of efficient methods for the synthesis of the anions $[\text{Au}(\text{C}_n\text{F}_{2n+1})_4]^-$ would improve their use as flat, weakly

coordinating, fluorophilic anions in synthesis and materials science.

Note added in proof

After submission of this review, Toste and coworkers have reported a study of the reductive elimination of ArX and ArCF_3 in complexes $[\text{Au}(\text{CF}_3)(\text{Ar})\text{X}(\text{PPh}_3)]$ ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$). See M. S. Winston, W. J. Wolf, F. D. Toste *J. Am. Chem. Soc.* 2015, **137**, 7921.

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Notes and references

- 1 F. G. A. Stone, *J. Fluorine Chem.*, 1999, **100**, 227.
- 2 M. I. Bruce and F. G. A. Stone, in *Prep. Inorg. React.*, ed. W. L. Jolly, Interscience Publishers, Bristol, 1968, vol. 4, p. 177.
- 3 A. G. Algarra, V. V. Grushin and S. A. MacGregor, *Organometallics*, 2012, **31**, 1467.
- 4 R. P. Hughes, *Adv. Organomet. Chem.*, 1990, **31**, 183.
- 5 J. A. Morrison, *Adv. Organomet. Chem.*, 1993, **35**, 211.
- 6 K. L. Kirk, *Org. Process Res. Dev.*, 2008, **12**, 305.
- 7 G. W. Gribble, *Acc. Chem. Res.*, 1998, **31**, 141.
- 8 D. O'Hagan, C. Schaffrath, S. L. Cobb, J. T. G. Hamilton and C. D. Murphy, *Nature*, 2002, **416**, 279.
- 9 T. Hiyama, in *Organofluorine Compounds: Chemistry and Applications*, Springer-Verlag, Berlin, 2000.
- 10 R. C. Chambers, in *Fluorine in Organic Chemistry*, Blackwell, Oxford, UK, 2004.
- 11 P. Kirsch, in *Modern Fluoroorganic Chemistry*, Wiley-VCH, Weinheim, 2004.
- 12 P. M. Murphy, C. S. Baldwin and R. C. Buck, *J. Fluorine Chem.*, 2012, **138**, 3.
- 13 I. T. Horváth, *Acc. Chem. Res.*, 1998, **31**, 641.
- 14 L. P. Barthel-Rosa and J. A. Gladysz, *Coord. Chem. Rev.*, 1999, **190–192**, 587.
- 15 M. A. Úbeda and R. Dembinski, *J. Chem. Educ.*, 2006, **83**, 84.
- 16 W. Zhang and C. Cai, *Chem. Commun.*, 2008, 5686.
- 17 W. Zhang, *Tetrahedron*, 2003, **59**, 4475.
- 18 S. Purser, P. R. Moore, S. Swallow and V. Gouverneur, *Chem. Soc. Rev.*, 2008, **37**, 320.
- 19 J. Wang, M. Sánchez-Roselló, J. L. Aceña, C. del Pozo, A. E. Sorochinsky, S. Fustero, V. A. Soloshonok and H. Liu, *Chem. Rev.*, 2014, **114**, 2432.
- 20 R. J. Lundgren and M. Stradiotto, *Angew. Chem., Int. Ed.*, 2010, **49**, 9322.



- 21 T. Furuya, A. S. Kamlet and T. Ritter, *Nature*, 2011, **473**, 470.
- 22 O. A. Tomashenko and V. V. Grushin, *Chem. Rev.*, 2011, **111**, 4475.
- 23 Z. Jin, G. Hammond and B. Xu, *Aldrichimica Acta*, 2012, **45**, 6783.
- 24 C. Alonso, E. Martínez de Marigorta, G. Rubiales and F. Palacios, *Chem. Rev.*, 2015, **115**, 1847.
- 25 T. Besset, T. Poisson and X. Pannecoucke, *Chem. – Eur. J.*, 2014, **20**, 16830.
- 26 B. Lantaño, M. R. Torviso, S. M. Bonesi, S. Barata-Vallejo and A. Postigo, *Coord. Chem. Rev.*, 2015, **285**, 76.
- 27 T. Besset, C. Schneider and D. Cahard, *Angew. Chem., Int. Ed.*, 2012, **51**, 5048.
- 28 J.-J. Dai, C. Fang, B. Xiao, J. Yi, J. Xu, Z.-J. Liu, X. Lu, L. Liu and Y. Fu, *J. Am. Chem. Soc.*, 2013, **135**, 8436.
- 29 H. Serizawa, K. Aikawa and K. Mikami, *Chem. – Eur. J.*, 2013, **19**, 17692.
- 30 N. O. Ilchenko, P. G. Janson and K. J. Szabó, *Chem. Commun.*, 2013, **49**, 6614.
- 31 M. Chen and S. L. Buchwald, *Angew. Chem., Int. Ed.*, 2013, **52**, 11628.
- 32 D. M. Wiemers and D. J. Burton, *J. Am. Chem. Soc.*, 1986, **108**, 832.
- 33 D. J. Burton and L. Lu, *Top. Curr. Chem.*, 1997, **193**, 45.
- 34 Y. Ye and M. Sandford, *Synlett*, 2012, 2005.
- 35 Y. Zeng, L. Zhang, Y. Zhao, C. Ni, J. Zhao and J. Hu, *J. Am. Chem. Soc.*, 2013, **135**, 2955.
- 36 X. Wang, Y. Xu, F. Mo, G. Ji, D. Qiu, J. Feng, Y. Ye, S. Zhang, Y. Zhang and J. Wang, *J. Am. Chem. Soc.*, 2013, **135**, 10330.
- 37 S. Seo, J. B. Taylor and M. F. Greaney, *Chem. Commun.*, 2013, **49**, 6385.
- 38 A. Hafner and S. Bräse, *Angew. Chem., Int. Ed.*, 2012, **51**, 3713.
- 39 M. M. Kremlev, A. I. Mushta, W. Tyrre, D. Naumann, H. T. M. Fischer and Y. L. Yagupolskii, *J. Fluorine Chem.*, 2007, **128**, 1385.
- 40 N. D. Ball, J. B. Gary, Y. Ye and M. S. Sanford, *J. Am. Chem. Soc.*, 2011, **133**, 7577.
- 41 E. J. Cho, T. D. Senecal, T. Kinzel, Y. Zhang, D. A. Watson and S. L. Buchwald, *Science*, 2010, **328**, 1679.
- 42 V. V. Grushin and W. J. Marshall, *J. Am. Chem. Soc.*, 2006, **128**, 12644.
- 43 A. Maleckis and M. S. Sanford, *Organometallics*, 2014, **33**, 2653.
- 44 R. N. Loy and M. S. Sanford, *Org. Lett.*, 2011, **13**, 2548.
- 45 N. D. Ball, J. W. Kampf and M. S. Sanford, *J. Am. Chem. Soc.*, 2010, **132**, 2878.
- 46 Y. Ye, N. D. Ball, J. W. Kampf and M. S. Sanford, *J. Am. Chem. Soc.*, 2010, **132**, 14682.
- 47 X. Mu, S. Chen, X. Zhen and G. Liu, *Chem. – Eur. J.*, 2011, **17**, 6039.
- 48 T. C. Boorman and I. Larrosa, *Chem. Soc. Rev.*, 2011, **40**, 1910.
- 49 L.-P. Liu and G. B. Hammond, *Chem. Soc. Rev.*, 2012, **41**, 3129.
- 50 Z. Li, C. Brouwer and C. He, *Chem. Rev.*, 2008, **108**, 3239.
- 51 A. S. K. Hashmi, *Chem. Rev.*, 2007, **107**, 3180.
- 52 A. Arcadi, *Chem. Rev.*, 2008, **108**, 3266.
- 53 A. Corma, A. Leyva-Pérez and M. J. Sabater, *Chem. Rev.*, 2011, **111**, 1657.
- 54 A. S. K. Hashmi, *Angew. Chem., Int. Ed.*, 2012, **51**, 12935.
- 55 H. G. Raubenheimer and H. Schmidbaur, *J. Chem. Educ.*, 2014, **91**, 2024.
- 56 A. Johnson and R. J. Puddephatt, *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 1175.
- 57 A. Johnson and R. J. Puddephatt, *J. Chem. Soc., Dalton Trans.*, 1976, 1360.
- 58 H. K. Nair and J. A. Morrison, *J. Organomet. Chem.*, 1989, **376**, 149.
- 59 S. Martínez-Salvador, J. Forniés, A. Martín and B. Menjón, *Angew. Chem., Int. Ed.*, 2011, **50**, 6571.
- 60 D. Zopes, S. Kremer, H. Scherer, L. Belkoura, I. Pantenburg, W. Tyrre and S. Mathur, *Eur. J. Inorg. Chem.*, 2011, 273.
- 61 S. Martínez-Salvador, L. R. Falvello, A. Martín and B. Menjón, *Chem. – Eur. J.*, 2013, **19**, 14540.
- 62 W. J. Wolf, M. S. Winston and F. D. Toste, *Nat. Chem.*, 2014, **6**, 159.
- 63 J. Vicente, M. D. Bermúdez, J. Escribano, M. P. Carrillo and P. G. Jones, *J. Chem. Soc., Dalton Trans.*, 1990, 3083.
- 64 J. Vicente, M. D. Bermúdez and F. J. Carrión, *Inorg. Chim. Acta*, 1994, **220**, 1.
- 65 J. Vicente, M. D. Bermúdez, F. J. Carrión and P. G. Jones, *Chem. Ber.*, 1996, **129**, 1395.
- 66 J. Vicente, M. D. Bermúdez and J. Escribano, *Organometallics*, 1991, **10**, 3380.
- 67 M. S. Winston, W. J. Wolf and F. D. Toste, *J. Am. Chem. Soc.*, 2014, **136**, 7777.
- 68 D. A. Culkin and J. F. Hartwig, *Organometallics*, 2004, **23**, 3398.
- 69 P. M. Treichel and F. G. A. Stone, *Adv. Organomet. Chem.*, 1964, **1**, 143.
- 70 M. A. García-Monforte, S. Martínez-Salvador and B. Menjón, *Eur. J. Inorg. Chem.*, 2012, 4945.
- 71 N. H. Dryden, J. G. Shapter, L. L. Coatsworth, P. R. Norton and R. J. Puddephatt, *Chem. Mater.*, 1992, **4**, 979.
- 72 R. J. Puddephatt and I. Treurnicht, *J. Organomet. Chem.*, 1987, **319**, 129.
- 73 S. Komiya, T. A. Albright, R. Hoffmann and J. K. Kochi, *J. Am. Chem. Soc.*, 1977, **99**, 8440.
- 74 S. Komiya, S. Ochiai and Y. Ishizaki, *Inorg. Chem.*, 1992, **31**, 3168.
- 75 The mean C–F distances in Au(I), Au(II) and Au(III) compounds are 1.368, 1.306 and 1.323 Å, respectively, whereas the mean XF₂C–F (X ≠ metal) distance is 1.33 Å (see A. Yokozeki and S. H. Bauer, *Top. Curr. Chem.*, 1973, **53**, 71–119 and F. H. Allen, O. Kennard, D. G. Watson,



- L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1–S19).
- 76 The mean Au–C–F and F–C–F angles are 115.4° and 102.9° (Au(I)), 116.4° and 101.6° (Au(II)), 113.6° and 105.1° (Au(III)).
- 77 P. D. Gavens, J. J. Guy, M. J. Mays and G. M. Sheldrick, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1977, **33**, 137.
- 78 P. Tasker, A. Parkin, D. Coventry, S. Parsons and D. Messenger, personal communication.
- 79 U. Florke, H.-J. Haupt and P. G. Jones, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1996, **52**, 609.
- 80 M. T. Johnson, J. M. J. van Rensburg, M. Axelsson, M. S. G. Ahlquist and O. F. Wendt, *Chem. Sci.*, 2011, **2**, 2373.
- 81 M. Blaya, D. Bautista, J. Gil-Rubio and J. Vicente, *Organometallics*, 2014, **33**, 6358.
- 82 D. Zhu, S. V. Lindeman and J. K. Kochi, *Organometallics*, 1999, **18**, 2241.
- 83 M. Hall and R. F. Fenske, *Inorg. Chem.*, 1972, **11**, 768.
- 84 W. A. G. Graham, *Inorg. Chem.*, 1968, **7**, 315.
- 85 T. Leyssens, D. Peeters, A. G. Orpen and J. N. Harvey, *Organometallics*, 2007, **26**, 2637.
- 86 G. K. S. Prakash, F. Wang, Z. Zhang, R. Haiges, M. Rahm, K. O. Christe, T. Mathew and G. A. Olah, *Angew. Chem., Int. Ed.*, 2014, **53**, 11575.
- 87 W. B. Farnham, *Chem. Rev.*, 1996, **96**, 1633.
- 88 R. D. Sanner, J. H. Satcher Jr. and M. W. Droegge, *Organometallics*, 1989, **8**, 1498.
- 89 G. K. S. Prakash and A. K. Yudin, *Chem. Rev.*, 1997, **97**, 757.
- 90 X. Liu, C. Xu, M. Wang and Q. Liu, *Chem. Rev.*, 2015, **115**, 683.
- 91 N. Maggiorosa, W. Tyrra, D. Naumann, N. V. Kirij and Y. L. Yagupolskii, *Angew. Chem., Int. Ed.*, 1999, **38**, 2252.
- 92 W. Tyrra, M. M. Kremlev, D. Naumann, H. Scherer, H. Schmidt, B. Hoge, I. Pantenburg and Y. L. Yagupolskii, *Chem. – Eur. J.*, 2005, **11**, 6514.
- 93 J. Vicente, J. Gil-Rubio and D. Bautista, *Inorg. Chem.*, 2001, **40**, 2636.
- 94 J. Vicente, J. Gil-Rubio, J. Guerrero-Leal and D. Bautista, *Organometallics*, 2004, **23**, 4871.
- 95 F. L. Taw, B. L. Scott and J. L. Kiplinger, *J. Am. Chem. Soc.*, 2003, **125**, 14712.
- 96 J. Vicente, J. Gil-Rubio, J. Guerrero-Leal and D. Bautista, *Organometallics*, 2005, **24**, 5634.
- 97 G. G. Dubinina, H. Furutachi and D. A. Vicic, *J. Am. Chem. Soc.*, 2008, **130**, 8600.
- 98 Y. Usui, J. Noma, M. Hirano and S. Komiya, *Inorg. Chim. Acta*, 2000, **309**, 151.
- 99 D. Naumann, W. Wessel, J. Hahn and W. Tyrra, *J. Organomet. Chem.*, 1997, **547**, 79.
- 100 W. Tyrra, *J. Fluorine Chem.*, 2001, **112**, 149.
- 101 W. Tyrra and D. Naumann, *J. Fluorine Chem.*, 2004, **125**, 823.
- 102 C. Hegemann, W. Tyrra, J.-M. Neudörfl and S. Mathur, *Organometallics*, 2013, **32**, 1654.
- 103 W. Wessel, W. Tyrra and D. Naumann, *Z. Anorg. Allg. Chem.*, 2001, **627**, 1264.
- 104 K. J. Klabunde, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 287.
- 105 F. Glockling and V. B. Mahale, *J. Chem. Res.*, 1978, 170.
- 106 A. Graefe and T. Kruck, *J. Organomet. Chem.*, 1996, **506**, 31.
- 107 S. Gaillard, A. M. Z. Slawin and S. P. Nolan, *Chem. Commun.*, 2010, **46**, 2742.
- 108 M. Blaya, J. Gil-Rubio and J. Vicente, unpublished work.
- 109 P. J. Brothers and W. R. Roper, *Chem. Rev.*, 1988, **88**, 1293.
- 110 R. Usón, A. Laguna and J. Vicente, *J. Chem. Soc., Chem. Commun.*, 1976, 353.
- 111 R. Usón, A. Laguna and J. Vicente, *J. Organomet. Chem.*, 1977, **131**, 471.
- 112 R. Usón, A. Laguna, J. Vicente, J. García, B. Bergareche and P. Brun, *Inorg. Chim. Acta*, 1978, **28**, 237.
- 113 R. Usón, A. Laguna, J. Vicente, J. García, P. G. Jones and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1981, 655.
- 114 J. Vicente, M. T. Chicote, J.-A. Cayuelas, J. Fernández-Baeza, P. G. Jones, G. M. Sheldrick and P. Espinet, *J. Chem. Soc., Dalton Trans.*, 1985, 1163.
- 115 N. J. Rijs and R. A. J. O'Hair, *Dalton Trans.*, 2012, **41**, 3395.
- 116 H.-G. Cho and L. Andrews, *Organometallics*, 2014, **33**, 4315.
- 117 H. H. Murray, J. P. Fackler Jr., L. C. Porter, D. A. Briggs, M. A. Guerra and R. J. Lagow, *Inorg. Chem.*, 1987, **26**, 357.
- 118 D. Zopes, C. Hegemann, W. Tyrra and S. Mathur, *Chem. Commun.*, 2012, **48**, 8805.
- 119 X.-G. Xiong and P. Pyykkö, *Chem. Commun.*, 2013, **49**, 2103.
- 120 J. L. Margrave, K. H. Whitmire, R. H. Hauge and N. T. Norem, *Inorg. Chem.*, 1990, **29**, 3252.
- 121 M. A. Guerra, T. R. Bierschenk and R. J. Lagow, *J. Organomet. Chem.*, 1986, **307**, C58.
- 122 J. A. Schlueter, J. M. Williams, U. Geiser, J. D. Dudek, S. A. Sirchio, M. E. Kelly, J. S. Gregar, W. H. Kwok, J. A. Fendrich, *et al.*, *J. Chem. Soc., Chem. Commun.*, 1995, 1311.
- 123 U. Preiss and I. Krossing, *Z. Anorg. Allg. Chem.*, 2007, **633**, 1639.
- 124 J. A. Schlueter, U. Geiser, A. M. Kini, H. H. Wang, J. M. Williams, D. Naumann, T. Roy, B. Hoge and R. Eujen, *Coord. Chem. Rev.*, 1999, **190–192**, 781.
- 125 J. A. Schlueter, U. Geiser, H. H. Wang, M. E. Kelly, J. D. Dudek, J. M. Williams, D. Naumann and T. Roy, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A*, 1996, **284**, 195.
- 126 J. A. Schlueter, J. M. Williams, U. Geiser, H. H. Wang, A. M. Kini, M. E. Kelly, J. D. Dudek, D. Naumann and T. Roy, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A*, 1996, **285**, 43.
- 127 J. A. Schlueter, U. Geiser, J. M. Williams, J. D. Dudek, M. E. Kelly, J. P. Flynn, R. R. Wilson, H. I. Zakowicz, P. P. Sche, D. Naumann, T. Roy, P. G. Nixon, R. W. Winter and G. L. Gard, *Synth. Met.*, 1997, **85**, 1453.
- 128 E. Bernhardt, M. Finze and H. Willner, *J. Fluorine Chem.*, 2004, **125**, 967.

