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Au(I) Fluorido Phosphine Complexes: Tools for the Hydrofluorination of Alkynes

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The reactivity of the Au(I) fluorido complex [Au(F)(SPhos)] (SPhos = dicyclohexyl(2′,6′-dimethoxy[1,1′-biphenyl]-2-yl)phosphine) (**1**) towards several alkynes was studied. The formation of fluorovinyl species by formal insertion of the alkyne in the metal-fluorine bond was observed. Addition of HCl to vinyl complexes resulted in protodeauration and elimination of the hydrofluorinated alkynes. Treatment of **1** with the terminal alkyne 1-hexyne resulted in clean formation of the alkynyl complex [Au(C≡CC_4H_9)(SPhos)] (**15**), whereas with an excess alkyne hydrofluorination was also observed. Various Au(I) phosphine complexes including **1** were then compared in their ability to catalyze hydrofluorination reactions of 1-phenyl-1-propyne with $Et_3N{\cdot}3HF$ as HF source. Model reactions suggested a reaction mechanism, which imparts a pre-coordination of an alkyne to a cationic gold center followed by nucleophilic addition of a fluoride. Mechanistic investigations included reactivity studies at [Au(SPhos)][$B(C_6F_5)_4$)] (**17**), which was treated with 4-phenyl-3-butyn-2-one and TMAF (TMAF = tetramethylammonium fluoride). The reaction led to the formation of the complex [Au(CH_3C(O)C=C(F)Ph)(SPhos)] (**13**), but not the fluorido complex **1**.

Introduction

The ability of Lewis-acidic gold(I) complexes to activate organic molecules in catalysis is well known.[1] A preference to react with alkynes over alkenes is well established and this "alkynophilicity"[1–2] has been used for the functionalization of alkynes.[3] The transformations include hydrofluorination reactions, which are of particular interest, because they open up routes to access fluorinated building blocks. The latter are of increasing interest in materials science as well as for pharmaceutical and agrochemical applications.[4]

While several research groups[3a,5] reported on catalytic hydrofluorination reactions with gold(I) complexes as catalysts, mechanistic insights are still scarce.[6] Transition metal catalyzed hydrofluorination reactions at alkynes usually give addition products with the fluorine and hydrogen atoms in a mutually *trans* position. Although some exceptions with a *cis* stereoselectivity do exist,[5c] *cis*-isomers are only observed as minor products. Transition metal free reactions, on the other hand, often result in *cis* addition products.[7] The addition of the fluoride is widely regarded to occur by an outer-sphere nucleophilic attack at the alkyne coordinated to the Au(I) complex.[8] To increase reaction rates, Brønsted acids are commonly added as cocatalysts to facilitate the protodeauration, which can be the rate limiting step.[8a,9] Commonly used acids include $KHSO_4$ or *para*-chlorobenzoic acid.

Isolated complexes, which might be intermediates of putative catalytic cycles include NHC (NHC = *N*-heterocyclic carbene) gold derivatives. Sadighi *et al.* characterized the alkyne complex [Au(3-hexyne)(SIPr)][BF_4] (SIPr = 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene) as well as the vinyl compounds [Au(R^1C=C(F)R^2)(SIPr)] (R^1=Ph, R^2=CH_3 as well as R^1=R^2=C_2H_5).[5a] In a recent contribution towards the hydrofluorination of terminal alkynes, the compound [{Au(SIPr)}$_2$μ-OH][FHF] as well as mono- and binuclear alkynyl species were identified as potential intermediates.[6b]

In this paper we will present reactivity studies at Au(I) fluorido phosphine complexes[10] towards alkynes. Studies on the formation of fluorovinyl complexes allowed for a further understanding of key-steps in hydrofluorination reactions with Au(I) catalysts.

Results and Discussion

Treatment of the fluorido complex [Au(F)(SPhos)] (SPhos = dicyclohexyl(2′,6′-dimethoxy[1,1′-biphenyl]-2-yl)phosphane) (**1**) with an excess of 1-phenyl-1-propyne yielded the vinyl compound [Au(PhC=C(F)CH_3)(SPhos)] (**2**). The observed regio- and stereoselectivity is similar to the previously reported one for a reaction of the carbene complex [Au(F)(SIPr)] with the same alkyne (Scheme 1).[5a] In the absence of any proton source, the vinyl complex **2** is quite stable. In the $^{31}P\{^1H\}$ NMR spectrum complex **2** exhibits a signal at 46.7 ppm with a coupling between the phosphorous and the fluorine atom of 40 Hz (Figure 1). This unusually large value is comparable to the value previously reported for the vinyl compound [Pt(PhC=C(F)Ph)(F)-{κ^2-(*P*,*P*)-$Cy_2PC_2H_4PCy_2$}] ($^4J_{FP}$ = 45 Hz).[11] Note that smaller $^4J_{FP}$

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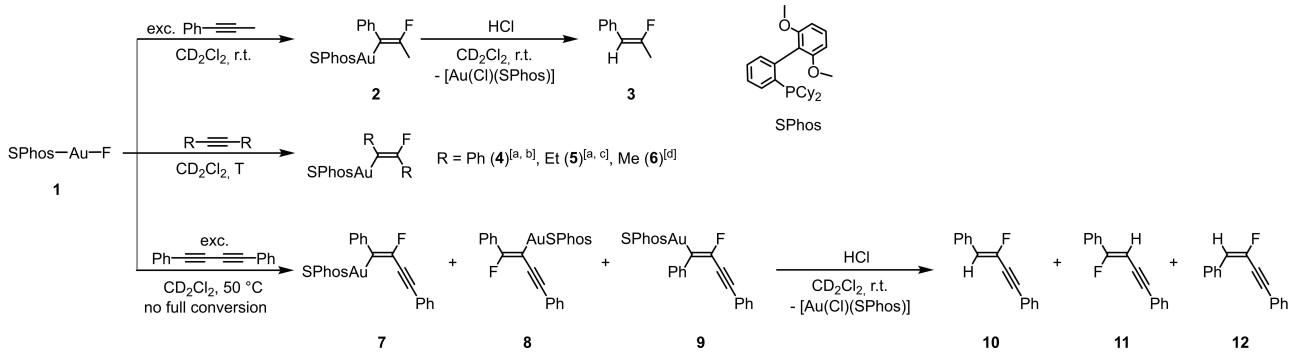

Scheme 1. Generation and reactivities of fluorovinyl complexes towards HCl. [a]only traces at T = 293 K, [b]full conversion at T = 323 K for 3 h, [c]50% conversion at T = 323 K, extended heating leads to decomposition, [d]full conversion at T = 293 K; ratio: **7**:**8**:**9**:**1**:1.4:1.0:0.1:3.2.

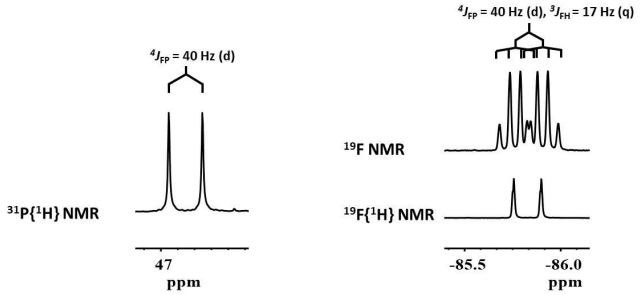

Figure 1. $^{31}P\{^1H\}$ (left), ^{19}F (right) and $^{19}F\{^1H\}$ NMR spectra of the vinyl complex [Au(PhC=C(F)CH_3)(SPhos)] (**2**).

coupling constants of about 20 Hz have also been reported, albeit for compounds with a *cis* configuration of the metal and fluorine atoms.[12] The ^{19}F NMR spectrum of **2** reveals a signal at -85.4 ppm, which appears as a doublet of quartets with a $^3J_{FH}$ coupling to the methyl group of 17 Hz (Figure 1) in addition to the coupling with the phosphorous atom.

When HCl was added to the vinyl complex [Au(PhC=C-(F)CH_3)(SPhos)] (**2**), protodeauration occurred and the hydrofluorinated product (*Z*)-2-fluoro-1-phenylpropene (**3**) was obtained as well as the respective gold complex [Au(Cl)(SPhos)] (Scheme 1). The proton in the fluorinated olefin **3** is found at the same position as the gold atom in the vinyl compound, indicating that regio- and stereoselectivity are retained. A reaction of the vinyl species **2** with various electrophilic fluorine sources such as 1-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate or Selectfluor did not result in the difluorinated olefin. Instead, no reaction was observed, although fluorodeauration has been proposed and demonstrated in other cases.[13]

With one exception, all literature reported gold(I) catalyzed hydrofluorination reactions show the same regioselectivity as in the reaction sequence of **1** into **3**, i.e. addition of the proton to the carbon atom with the more electron-withdrawing group to give the major product.[3a,5a,b,d–f,14] However, a directing group can reverse the regioselectivity by intramolecular interaction.[5c] Note that other gold(I) catalyzed reactions like hydration and hydroalkoxylation at internal alkynes are usually less regioselective.[7a] For recent transition metal free hydrofluorination reactions on using HBF_4 as fluoride source, the selective production of *E*- or *Z*-isomers by kinetic or thermodynamic control was reported. The best results were achieved on using 2,6-dichloropyridinium salts to mediate the conversions. The regioselectivity, however, was reverse to the one found for gold(I) catalyzed hydrofluorinations.[15] Note that for silver(I) promoted hydrofluorination reactions both regioselectivities were reported.[16]

The fluorido complex **1** was also treated with other alkynes. Diphenylacetylene requires an excess of alkyne and 50 °C to react with **1** to form the respective vinyl compound [Au(PhC=C-(F)Ph)(SPhos)] (**4**) (Scheme 1). A reaction of [Au(F)(SPhos)] (**1**) with 3-hexyne at room temperature only produced traces of the vinyl compound (Au(C_2H_5C=C(F)C_2H_5)(SPhos)] (**5**) which is in contrast to the reported conversion of [Au(F)(SIPr)] with 3-hexyne to give full conversion to [Au(C_2H_5C=C(F)C_2H_5)(SIPr)] within 30 minutes.[5a] Heating to 50 °C resulted in 50% conversion into **5**; further heating led to decomposition. With an excess of 2-butyne the vinyl complex [Au(CH_3C=C-(F)CH_3)(SPhos)] (**6**) was generated, but a vinyl complex from the reaction with 1,1,1,4,4,4-hexafluorobutyne was not observed, even not at elevated temperatures. In general, when compared to NHC complexes, phosphine complexes showed a diminished reactivity towards alkynes to generate vinyl compounds, although the electronic structures of complexes [Au(F)(L)] (L = NHC, phosphine) are comparable according to DFT calculations.[10] The obtained complexes **4**–**6** exhibit analogous spectroscopic data as found for the vinyl compound **2**, with $^4J_{FP}$ coupling constants of 40 Hz. As in the reaction with 1-phenyl-1-propyne, a huge excess of the alkynes is required to obtain notable conversions.

Furthermore, a reaction of [Au(F)(SPhos)] (**1**) with one equivalent of 4-phenyl-3-butyn-2-one was conducted to yield the vinyl species [Au(CH_3C(O)C=C(F)Ph)(SPhos)] (**13**) (Scheme 2). Complex **13** shows also $^4J_{FP}$ coupling constant of 40 Hz for the signals in the $^{31}P\{^1H\}$ and the ^{19}F NMR spectra. After treatment of **13** with HCl the olefin (*Z*)-4-fluoro-4-phenylbut-3-en-2-one (**14**) was obtained with the expected stereochemistry.

Interestingly, a reaction of a freshly prepared solution of the vinyl complex [Au(PhC=C(F)(CH_3)] (**2**) with an excess of 4-phenyl-3-butyn-2-one resulted also in formation of the vinyl

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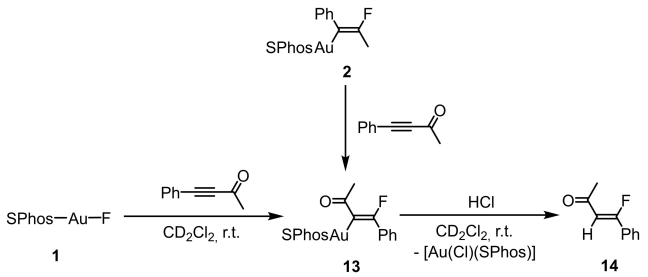


Scheme 2. Synthesis and reactivity of [Au($CH_3C(O)C{=}C(F)Ph$)(SPhos)] (**13**).

species **13** after several hours at room temperature (Scheme 2, Figure 2). It can be assumed that cationic alkyne complexes serve as intermediates, which are in equilibria with fluorovinyl complexes since a direct metal-mediated reaction from **2** to **13** would require an unprecedented fluorine shift from one organyl moiety to the other. Note that Sadighi *et al.* reported that the reaction to form [Au($C_2H_5C{=}C(F)C_2H_5$)(SIPr)] from [Au(F)(SIPr)] and 3-hexyne can be reverted by applying vacuum for 2.5 h.[5a] A consistent reactivity pattern for the vinyl complexes bearing SPhos as ligand was found, although in the latter cases only partial formation [Au(F)(SPhos)] (**1**) was observed. Thus, applying vacuum to the vinyl complex [Au($CH_3C{=}C(F)CH_3$)(SPhos)] (**6**) for 24 h lead to approximately 40% reversion to yield **1** and 2-butyne, which is the alkyne with the lowest boiling point. The other vinyl species showed a reverse reaction to yield only 0–5% **1**. When complex [Au(F)(SPhos)] (**1**) was added to a mixture containing one equivalent of 1-phenyl-1-propyne as well as one equivalent of 4-phenyl-3-butyn-2-one, the formation of both vinyl species **2** and **13** was observed with a ratio of 1:11 according to the ^{19}F NMR spectrum (Figure S2), again demonstrating the preference to form **13** over **2**. When compound **1** was added to a mixture containing ten equivalents of each of the alkynes, the sole formation of **13** was observed in agreement with the reaction of **2** to **13** described above.

In a next step, the behavior of a dialkyne was examined. Thus, treatment of [Au(F)(SPhos)] (**1**) with an excess of 1,4-diphenylbutadiyne resulted in the appearance of three sets of doublets in the ^{19}F as well as the $^{31}P\{^1H\}$ NMR spectra of the reaction solution upon heating to 50 °C for several hours (Scheme 1). However, complete conversion was not achieved, even after prolonged heating. The three signals could be assigned to the complexes **7**, **8** and **9** (ratio: 1.4 (**7**, 37 Hz): 1.0 (**8**, 36 Hz): 0.1 (**9**, 17 Hz): 3.2 (unreacted [Au(F)(SPhos)] (**1**)) (see Figures S3 and S4). There was no indication for the presence of any binuclear species. Treatment of the reaction mixture with HCl converted all of the compounds into [Au(Cl)(SPhos)]. In addition, three new sets of doublets were observed in the ^{19}F spectra again, with couplings of 35 Hz, 33 Hz and 17 Hz to a proton. The analytical data are in accordance with the data for the previously reported compounds **10**,[17] **11**[18] and **12**[19] (ratio 1.4:1:0.1, see Figure S5). No products of dihydrofluorination at both alkyne moieties were detected by GC/MS either, supporting the assignment of **7**–**9** further.

It was not possible to observe metal-bound vinyl compounds from reactions of **1** with terminal alkynes. Instead, treatment of **1** with one equivalent 1-hexyne resulted in clean formation of the alkynyl complex [Au($C{\equiv}CC_4H_9$)(SPhos)] (**15**) (Scheme 3). Note that it was reported that [Au(F)(SPhos)] (**1**) reacts with protic sources under HF elimination, and a reaction with phenylacetylene results in formation of the alkynyl complex [Au(C≡CPh)(SPhos)].[10] When an excess of the alkyne was used, the regioselective generation of the fluorinated olefin 2-fluoro-1-hexene (**16**) was also observed in addition to complex **15** (Scheme 3). The structure of the alkene **16** has been unambiguously determined by comparison with the literature.[20] The alkynyl complex **15** shows a singlet at 45.7 ppm in the $^{31}P\{^1H\}$ NMR spectrum as well as signals in the $^{13}C\{^1H\}$ NMR spectrum at 124.0 and 102.2 ppm for the alkynyl ligand, which is in good agreement with the signals reported for [Au($C{\equiv}CC_4H_9$)(JohnPhos)] (JohnPhos = ditertbutyl(2-biphenylyl)phosphane).[21]

To corroborate the above mentioned outer-sphere attack of fluoride at a cationic alkyne complex, the compound [Au(SPhos)][$B(C_6F_5)_4$)] (**17**) was treated with 4-phenyl-3-butyn-2-one and TMAF (TMAF = tetramethylammonium fluoride). Indeed, the reaction led to the formation of complex [Au($CH_3C(O)C{=}C(F)Ph$)(SPhos)] (**13**) but not the fluorido complex [Au(F)(SPhos)] (**1**) (Scheme 4, left). In contrast, Sadighi *et al.* reported that the

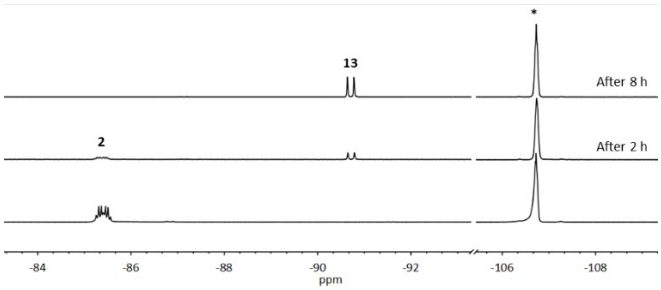
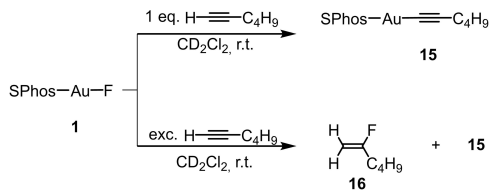
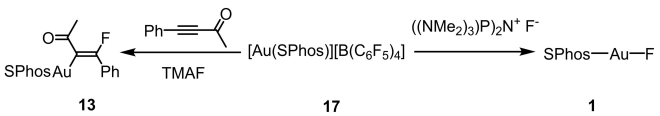


Figure 2. ^{19}F NMR spectra of the reaction of **2** to **13** in the presence of an excess 4-phenyl-3-butyn-2-one over the course of several hours (*internal standard OP(4-$C_6H_4F)_3$).



Scheme 3. Reactions of [Au(F)(SPhos)] (**1**) towards 1-hexyne.



Scheme 4. Formation of the vinyl species **13** as well as [Au(F)(SPhos)] (**1**) from [Au(SPhos)][$B(C_6F_5)_4$] (**17**).

complex [Au(3-hexyne)(SIPr)][BF_4] transforms into the respective fluorido complex [Au(F)(SIPr)] by reaction with $[(Me_2N)_3P]_2N^+F^-$ in CD_2Cl_2.[5a,22] [Au(SIPr)][BF_4] as well as [Au(SPhos)][$B(C_6F_5)_4$] did react with the same salt to produce the respective fluorido complexes as well (Scheme 4, right). However, any other source of nucleophilic fluoride such as TMAF, HF or MF (M=Ag, Cs) did not induce this reaction.

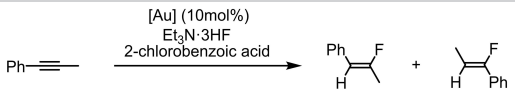
After confirming that the complex [Au(F)(SPhos)] (**1**) could form several vinyl complexes by formal insertion of alkynes into Au–F bonds, catalytic conversions for a hydrofluorination of an alkyne were studied (Table 1). Various Au(I) compounds were treated with 1-phenyl-1-propyne as the model substrate on using $Et_3N{\cdot}3HF$ as HF source. 2-Chlorobenzoic acid was added as additional proton source, because Brønsted acids have been used before to facilitate any protodeauration step in hydrofluorination.[5a,e] These experiments did aim for a comparison of various Au(I) catalytic precursors. The results and the respective yields for the formation of the two regioisomers **3** and **18** are depicted in Table 1.

Without the presence of any Au(I) gold complex, no hydrofluorination was observed (entry 1). The compounds [Au(F)(SPhos)] (**1**) and the respective vinyl species [Au(PhC=C(F)CH_3)(SPhos)] (**2**) yielded the hydrofluorination product **3** as the major product in agreement with the stereochemistry of the vinyl species **2** (entries 2 and 3), which holds for all tested catalysts. However, the best catalytic system under these non-optimized conditions consisted of the NHC complex [Au(Cl)(SIPr)] in the presence of $AgBF_4$ (entry 4), not only producing the highest yields but also the highest ratio of **3** to the regioisomer **18**. [Au(I)(SPhos)] (**19**) did not catalyze any hydrofluorination (entry 5), but addition of $AgBF_4$ enabled the transformation (entry 6). The use of the cationic Au(I) species [Au(SPhos)][$B(C_6F_5)_4$] (**17**) resulted in a similar yield (entry 7). We also tested the in situ generation of cationic species without the use of silver salts and the complex [Au(CH_3)(SPhos)] (**20**) was chosen since CH_4 formation in presence of acidic protons can be envisaged. Indeed, a gas evolution was observed and although the remaining cationic species did catalyze the hydrofluorination, the yield was slightly lower (entry 8). This catalyst was the only one for which an immediate red coloration of the reaction mixture was observed, indicating the formation of Au(0) nanoparticles. This suggest also that a stabilization of cationic gold species by the anions is of a certain importance.

Surprisingly, when all of the catalytic reactions were run without addition of 2-chlorobenzoic acid, the yields increased. This indicates that $Et_3N{\cdot}3HF$ itself is – in the presence of a $\{Au(SPhos)\}^+$ center – acidic enough to facilitate the protodeauration. The presence of a weakly coordinating anion might in addition avoid deactivation of the cationic catalytic species and allow for a protonation step with $Et_3N{\cdot}3HF$. Except for [Au(SPhos)][$B(C_6F_5)_4$] (**17**) (entry 7), for all catalyst an increase of the yields was found, but the ratio of **3** to **18** was comparable. However, no distinct anion influence was observed,[23] on using $AgSbF_6$ and AgOTf instead of $AgBF_4$ with [Au(Cl)(SIPr)] as well as [Au(I)(SPhos)] (**19**) as catalytic precursors (entries 9–12). The observed yields were mostly lower when compared the literature,[3a,5b,d,e,6b] but higher than reported for [Au(Cl)(PPh_3)]/$AgBF_4$, which showed only a stoichiometric conversion.[5a]

The preference to form the vinyl species [Au(CH_3C(O)C=C(F)Ph)(SPhos)] (**13**) over [Au(PhC=C(F)CH_3)(SPhos)] (**2**) from the reaction of the respective alkynes with [Au(F)(SPhos)] (**1**) was described above. Consequently, the competitive hydrofluorination between 1-phenyl-1-propyne and 4-phenyl-3-butyn-2-one was examined by treatment of **1** with a mixture consisting of equal amounts of the two alkynes on using the same amounts $Et_3N{\cdot}3HF$ as used before. As might be expected, hydrofluorination of 4-phenyl-3-butyn-2-one was observed to be the main reaction pathway (yielding olefin **14**), but hydrofluorination of 1-phenyl-1-propyne was also observed. No regioisomer of **14** was detected, although for the hydrofluorination of 1-phenyl-1-propyne only, both isomers were observed (Table 1, entry 4, see

Table 1. Catalytic hydrofluorination of 1-phenyl-1-propyne with $Et_3N{\cdot}3HF$ at various catalytic systems.[a]



3 **18**

Entry	Complex [Au]	Yield of **3**[b]	Yield of **18**[b]	Ratio (**3**:**18**)[b]	Yield of **3**[c]	Yield of **18**[c]	Ratio (**3**:**18**)[c]
	–	0%	0%	–	–	–	–
2	[Au(F)(SPhos)] (**1**)	37%	5%	7:1	54%	7%	8:1
3	[Au(PhC=C(F)CH_3)(SPhos)] (**2**)	37%	4%	9:1	49%	6%	8:1
4	[Au(Cl)(SIPr)]/$AgBF_4$	61%	2%	31:1	63%	1%	63:1
5	[Au(I)(SPhos)] (**19**)	0%	0%	–	–	–	–
6	[Au(I)(SPhos)] (**19**)/$AgBF_4$	43%	6%	7:1	61%	9%	7:1
7	[Au(SPhos)][$B(C_6F_5)_4$] (**17**)	44%	10%	4:1	26%	4%	7:1
8	[Au(CH_3)(SPhos)] (**20**)	30%	4%	8:1	33%	3%	11:1
9	[Au(Cl)(SIPr)]/$AgSbF_6$	–	–	–	54%	2%	27:1
10	[Au(I)(SPhos)] (**19**)/$AgSbF_6$	–	–	–	55%	8%	7:1
11	[Au(Cl)(SIPr)]/AgOTf	–	–	–	57%	1%	57:1
12	[Au(I)(SPhos)] (**19**)/AgOTf	–	–	–	61%	8%	8:1

[a] Yields are calculated by integration of the ^{19}F NMR spectra versus OP(4-$C_6H_4F)_3$. [b] Reaction conditions: 0.15 mmol $Et_3N{\cdot}3HF$, 0.3 mmol 2-chlorobenzoic acid, 0.03 mmol OP(4 $C_6H_4F)_3$, 0.3 mmol 1-phenyl-1-propyne, 0.03 mmol [Au], 0.045 mmol AgX (entries 7–12). [c] Reaction conditions: 0.15 mmol $Et_3N{\cdot}3HF$, 0.03 mmol OP(4-$C_6H_4F)_3$, 0.3 mmol 1-phenyl-1-propyne, 0.03 mmol [Au], 0.045 mmol AgX (entries 7–12).

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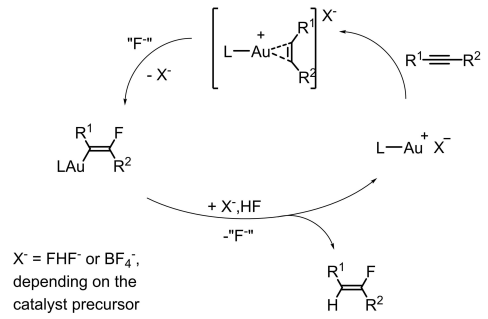

Scheme 5. Simplified mechanism for the hydrofluorination of internal alkynes.

Figure S6). This is in contrast to the previously reported hydrofluorination of 4-phenyl-3-butyn-2-one by [Au(IPr*Tol)(NEt$_3$)][FHF] (IPr*Tol = 1,3-bis(methyl-2,6-di(di-4-tolylmethane)-4-methylphenyl)imidazole-2-ylidene), for which a ratio for the two regiosiomers of 9:1 was obtained.[5d]

Mechanistic possibilities for the hydrofluorination reactions involve either insertion of the alkyne into the Au–F bond or outer-sphere fluorination of a coordinated alkyne, with literature suggesting the latter (Scheme 5),[8] resulting in an *anti*-addition of the nucleophile.[6a] The above mentioned fluoride attack at **17** in the presence of alkyne also supports the outer-sphere fluorination mechanisms (Scheme 4). After formation of the vinyl species, the protodeauration should provide the hydrofluorinated compound and the catalytic cycle is completed (Scheme 5). In a recent paper regarding the Au(I) catalyzed hydrofluorination of terminal alkynes with aqueous HF, cationic complexes have also been postulated as intermediates.[6b] In addition to mononuclear intermediates, binuclear species involving Au(I) alkynyl complexes, were proposed.

Conclusions

The formation of fluorovinyl Au phosphine complexes by addition of alkynes to the Au(I) fluorido complex [Au(F)(SPhos)] (**1**) has been demonstrated. A preference to react with 4-phenyl-3-butyn-2-one over 1-phenyl-1-propyne was established and demonstrated the importance of electronic properties of the alkynes. Model reactions for the mechanism of hydrofluorination reactions suggest an outer-sphere mechanism by pre-coordination of an alkyne to a cationic gold center followed by nucleophilic addition of a fluoride. The regioselectivity matched previously reported vinyl species bearing NHC ligands.[5a] Various Au(I) complexes including **1** were then compared in their ability to catalyze hydrofluorination reactions of 1-phenyl-1-propyne employing Et$_3$N·3HF as HF source. It is intriguing that the activity of the catalytic systems improved by omitting an additional proton source for protodeauration.

Experimental Section

All samples were prepared in a glovebox and the reactions performed using conventional Schlenk techniques. CH_2Cl_2 and CD_2Cl_2 were dried over CaH_2 and distilled or condensed before usage. Hexane and thf were dried over Solvona® and distilled before usage. All reagents were obtained from commercial sources. Solids were dried in high vacuum and liquids were degassed and stored over activated molecular sieves prior to usage. NMR spectra were acquired at a Bruker DPX 300 or Bruker AVANCE II 300 spectrometer at room temperature. ^{1}H NMR and ^{13}C{^{1}H} NMR chemical shifts (δ) were referenced to residual CD_2Cl_2 (δ = 5.32 ppm and δ = 53.84 ppm, respectively).[24] ^{19}F NMR spectra were calibrated externally to $CFCl_3$ and ^{31}P{^{1}H} NMR spectra to external 85% H_3PO_4. LIFDI-TOF-MS was measured with a Micromass Q-TOF-2 mass spectrometer, equipped with a Linden LIFDI source (Linden CMS GmbH). Elemental analyses (EA) were performed with a HEKAtech Euro EA Elemental Analyzer. OP(4-$C_6H_4F)_3$,[25] $[(Me_2N)_3P]_2N^+F^-$,[22] [Au(Cl)(SIPr)],[26] [Au(Cl)(SPhos)],[27] [Au(I)(SPhos)] (**19**),[10] [Au(SPhos)][$B(C_6F_5)_4$] (**17**)[28] and [Au(F)(SPhos)] (**1**)[10] were synthesized according to previously reported protocols.

Formation of the vinyl species [Au(PhC=C(F)CH$_3$)(SPhos)] (2), [Au(PhC=C(F)Ph)(SPhos)] (4), [Au(C_2H_5C=C(F)C_2H_5)(SPhos)] (5) and [Au(CH_3C=C(F)CH_3)(SPhos)] (6)

A CD_2Cl_2 solution containing 0.06 mmol [Au(F)(SPhos)] (**1**) was transferred to a PFA tube loaded with the respective alkyne (0.15 mL). The mixture was allowed to stand for 3 h at room temperature (**2** and **6**) or heated at 323 K for 3 h (**4** and **5**). No full conversion could be achieved for **5** (50% conversion, see Figures S11 and S12). Characterization was done in situ by NMR spectroscopy. The signals for the two vinyl carbon atoms were located with HMBC ^{1}H,^{13}C (**2**, **6**) or ^{19}F,^{13}C (**4**, **5**) NMR correlation experiments and identified by their coupling to ^{19}F. The $^2J_{FC}$ as well as the $^2J_{PC}$ coupling constants could not be determined reliably due to the low resolution in the ^{13}C domain.

Analytical data for [Au(PhC=C(F)CH$_3$)(SPhos)] (**2**): ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2, 298 K) $\delta = 46.7$ (d, $^4J_{FP} = 40$ Hz) ppm. ^{19}F NMR (282 MHz, CD_2Cl_2, 298 K) $\delta = -85.4$ (dq, $^4J_{FP} = 40$ Hz, $^3J_{FC} = 17$ Hz) ppm. ^{1}H,^{13}C HMBC (300/75 MHz, CD_2Cl_2, 298 K) $\delta = 2.30/153.7$ (dd/d, $^2J_{HC} = 8$ Hz, $^3J_{HF} = 17$ Hz/$^1J_{FC} = 255$ Hz, AuC=*C*), 2.30/143.2 (d/s, $^3J_{HF} = 17$ Hz, Au*C*=C) ppm.

Analytical data for [Au(PhC=C(F)Ph)(SPhos)] (**4**): ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2, 298 K) $\delta = 46.0$ (d, $^4J_{FP} = 39$ Hz) ppm. ^{19}F NMR (282 MHz, CD_2Cl_2, 298 K) $\delta = -98.1$ (d, $^4J_{FP} = 39$ Hz) ppm. ^{19}F,^{13}C HMBC (282/75 MHz, CD_2Cl_2, 298 K) $\delta = -98.1/155.1$ (dd/s, $^4J_{FP} = 39$ Hz, $^1J_{FC} = 264$ Hz, AuC=*C*), −98.1/138.2 (dd/s, $^4J_{FP} = 39$ Hz, $^2J_{FC} = 40$ Hz, Au*C*=C) ppm.

Analytical data for [Au(C_2H_5C=C(F)C_2H_5)(SPhos)] (**5**): ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2, 298 K) $\delta = 48.0$ (d, $^4J_{FP} = 40$ Hz) ppm. ^{19}F NMR (282 MHz, CD_2Cl_2, 298 K) $\delta = -99.5$ (dt, $^4J_{FP} = 40$ Hz, $^3J_{FH} = 20$ Hz) ppm. ^{19}F,^{13}C HMBC (282/75 MHz, CD_2Cl_2, 298 K) $\delta = -99.5/159.5$ (dd/s, $^4J_{FP} = 40$ Hz, $^1J_{FC} = 300$ Hz, AuC=*C*), −99.5/143.8 (dd/s, $^4J_{FP} = 40$ Hz, $^2J_{FC} = 20$ Hz, Au*C*=C) ppm.

Analytical data for [Au(CH_3C=C(F)CH_3)(SPhos)] (**6**): ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2, 298 K) $\delta = 47.1$ (d, $^4J_{FP} = 40$ Hz) ppm. ^{19}F NMR (282 MHz, CD_2Cl_2, 298 K) $\delta = -89.4$ (dq, $^4J_{FP} = 40$ Hz, $^3J_{FH} = 17$ Hz) ppm. ^{1}H,^{13}C HMBC (300/75 MHz, CD_2Cl_2, 298 K) $\delta = 1.89/154.7$ (dd/d, $^2J_{HC} = 7$ Hz, $^3J_{HF} = 17$ Hz/$^1J_{FC} = 257$ Hz, AuC=*C*), 1.89/136.6 (d/s, $^3J_{HF} = 17$ Hz, Au*C*=C) ppm.

Formation of the vinyl species [Au($CH_3C(O)C{=}C(F)Ph$)(SPhos)] (13)

A CD_2Cl_2 solution containing 0.06 mmol [Au(F)(SPhos)] (**1**) was transferred into a PFA tube loaded with 4-phenyl-3-butyn-2-one (0.06 mmol, 8 μL). The mixture was allowed to stand for 3 h at room temperature and the quantitative formation of **13** was observed by NMR spectroscopy.

Analytical data for [Au($CH_3C(O)C{=}C(F)Ph$)(SPhos)] (**13**): ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K) $\delta = 8.05–6.93$ (m, 10H, H_{ar}), 6.65–6.13 (m, 2H, H_{ar}), 3.53 (s, 6H, OCH_3), 2.68–0.95 (m, 22H, H_{Cy}), 2.22 (s, 3H, $C(O)CH_3$) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, 298 K) $\delta = 46.6$ (d, $^4J_{FP} = 40$ Hz) ppm. ^{19}F NMR (282 MHz, CD_2Cl_2, 298 K) $\delta = -91.3$ (d, $^4J_{FP} = 40$ Hz) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, 298 K) $\delta = 157.4$, 154.7 (d, $^1J_{CF} = 260$ Hz, Au*C*=C), 143.2 (d, $J_{CP} = 15$ Hz), 136.7 (d, $^2J_{CF} = 38$ Hz, Au*C*=C), 133.3 (d, $J_{CP} = 8$ Hz), 133.0, 130.9, 130.1, 129.0 (d, $J_{CP} = 46$ Hz), 129.0, 128.2, 127.8, 127.4 (d, $J_{CP} = 7$ Hz), 126.8 (d, $J_{CF} = 5$ Hz), 118.8, 104.8, 55.4, 36.5 (d, $J_{CP} = 30$ Hz), 31.9, 30.7 (d, $J_{CP} = 5$ Hz), 29.6, 27.2 (d, $J_{CP} = 12$ Hz), 27.1 (d, $J_{CP} = 14$ Hz), 26.4 ppm.

Exchange reaction between vinyl species [Au(PhC=C(F)CH_3)(SPhos)] (2) and [Au($CH_3C(O)C{=}C(F)Ph$)(SPhos)] (13)

The vinyl species [Au(PhC=C(F)CH_3)(SPhos)] (**2**) was prepared according to the procedure above and all volatiles were removed in high vacuum overnight. CD_2Cl_2 (0.3 mL) was added and the ^{1}H, $^{31}P\{^1H\}$ and ^{19}F NMR spectra recorded, indicating the formation of small amounts of [Au(F)(SPhos)] (**1**) and 1-phenyl-1-propyne. 4-Phenyl-3-butyn-2-one (0.15 mL) was added and NMR spectra recorded after 2 h and 8 h reaction time revealed the formation of the vinyl species [Au($CH_3C(O)C{=}C(F)Ph$)(SPhos)] (**13**).

Reactivity of the vinyl species [Au(PhC=C(F)CH_3)(SPhos)] (2) and [Au($CH_3C(O)C{=}C(F)Ph$)(SPhos)] (13) towards HCl

HCl (2 M in Et_2O, 0.1 mL) was added to a solution containing the vinyl species **2** or **13** in CD_2Cl_2 and allowed to stand at room temperature for several minutes. Characterization was done in situ. The spectroscopic data of the obtained products were in agreement with these previously reported in literature: [Au(Cl)(SPhos)];[27] from **2**: (*Z*)-2-fluoro-1-phenylpropene (**3**);[29] from **13**: (*Z*)-4-fluoro-4-phenylbut-3-en-2-one (**14**).[5d]

Reactivity of [Au(F)(SPhos)] (1) towards 1,4-diphenylbutadiyne

A CD_2Cl_2 solution containing 0.06 mmol [Au(F)(SPhos)] (**1**) was transferred into a PFA tube loaded with 1,4-diphenylbutadiene (80 mg, 0.4 mmol). The mixture was heated to 50 °C for 3 h and the formation of the vinyl species **7**, **8** and **9** was observed. **7**, **8** and **9** are present in a ratio of 1.4 (**7**) to 1 (**8**) to 0.1 (**9**) to 3.2 (unreacted starting material **1**) by integration of the ^{19}F NMR spectrum (see SI). No complete conversion was achieved by extended heating. HCl (2 M in Et_2O, 0.1 mL) was added after cooling down. The mixture was allowed to stand at room temperature for 1 h after which the formation of two products of monohydrofluorination, (*Z*)-1,4-diphenyl-2-fluoro-1-buten-3-yne (**10**),[17] (*Z*)-(1-fluorobut-1-en-3-yne-1,4-diyl)dibenzene (**11**)[18] and (*E*)-1,4-diphenyl-3-fluoro-3-buten-1-yne (**12**)[19] (also in ratio 1.4:1:0.1 according to the ^{19}F NMR spectrum, see SI), was observed.

Analytical data for (*E*)-[Au(PhC=C(F)C≡CPh)(SPhos)] (**7**): $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, 298 K) $\delta = 45.7$ (d, $^4J_{FP} = 37$ Hz) ppm. ^{19}F NMR (282 MHz, CD_2Cl_2, 298 K) $\delta = -88.9$ (d, $^4J_{FP} = 37$ Hz) ppm.

Analytical data for [Au((PhC≡C)C=C(F)Ph)(SPhos)] (**8**): $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, 298 K) $\delta = 44.9$ (d, $^4J_{FP} = 35$ Hz) ppm. ^{19}F NMR (282 MHz, CD_2Cl_2, 298 K) $\delta = -79.5$ (d, $^4J_{FP} = 35$ Hz) ppm.

Analytical data for (*Z*)-[Au(PhC=C(F)C≡CPh)(SPhos)] (**9**): $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, 298 K) $\delta = 44.3$ (d, $^4J_{FP} = 9$ Hz) ppm. ^{19}F NMR (282 MHz, CD_2Cl_2, 298 K) $\delta = -80.0$ (d, $^4J_{FP} = 9$ Hz) ppm.

Reactivity of [Au(F)(SPhos)] (1) towards excess 1-hexyne

A CD_2Cl_2 solution containing 0.06 mmol [Au(F)(SPhos)] (**1**) was transferred into a PFA tube loaded with 1-hexyne (0.15 mL, 1.3 mmol). The mixture was allowed to stand for 3 h at room temperature. The formation of 2-fluorohex-1-ene (**16**) was confirmed by comparison of the data with the literature[20] and all volatiles removed in vacuo over two days. The residue was washed with hexane (3×3 mL) and [Au(C≡CC_4H_9)(SPhos)] (**15**) obtained as a colourless solid.

Analytical data for [Au(C≡CC_4H_9)(SPhos)] (**15**): ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K) $\delta = 7.70–7.30$ (m, 4H, H_{ar}), 7.21–7.08 (m, 1H, H_{ar}), 6.67 (d, $J_{HH} = 8$ Hz, 2H, H_{ar}), 3.72 (s, 6H, OCH_3), 2.18–0.90 (m, 31H) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, 298 K) $\delta = 45.7$ ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, 298 K) $\delta = 157.7$, 143.1 (d, $J_{CP} = 15$ Hz), 133.4 (d, $J_{CP} = 8$ Hz), 133.3 (d, $J_{CP} = 3$ Hz), 130.8, 129.9, 129.0 (d, $J_{CP} = 47$ Hz), 127.3 (d, $J_{CP} = 8$ Hz), 124.0 (d, $J_{CP} = 132$ Hz), 119.0 (d, $J_{CP} = 6$ Hz), 104.8, 102.2 (d, $J_{CP} = 24$ Hz), 55.6, 36.4 (d, $J_{CP} = 31$ Hz), 32.7, 30.5 (d, $J_{CP} = 5$ Hz), 30.5 (d, $J_{CP} = 5$ Hz), 29.7, 27.2 (d, $J_{CP} = 12$ Hz), 27.1 (d, $J_{CP} = 14$ Hz), 26.3, 22.5, 20.0 ppm.

Reaction of [Au(F)(SPhos)] (1) with one equivalent 1-hexyne

A CD_2Cl_2 solution containing 0.06 mmol [Au(F)(SPhos)] (**1**) was transferred to a PFA tube loaded with 1-hexyne (7 μL, 0.06 mmol,). The mixture was allowed to stand for 3 h at room temperature and the formation of [Au(C≡CC_4H_9)(SPhos)] (**15**) was observed (for NMR data, see above).

Synthesis of [Au(CH_3)(SPhos)] (20)

CH_3Li (1.6 M, 0.7 mL, 1.1 eq.) was slowly added to a stirred solution of [Au(Cl)(SPhos)] (0.643 g, 1 mmol) in thf (30 mL) at −65 °C. After addition, the mixture was allowed to warm to room temperature and stirred for 1 h. All volatiles were removed in vacuo. Toluene (15 mL) was added to the residue and the mixture was filtered through a pad of celite. After removal of the solvent from the filtrate in high vacuum, [Au(CH_3)(SPhos)] (0.416 g, 68%) was obtained as a colourless powder.

Analytical data for [Au(CH_3)(SPhos)] (**20**): ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): $\delta = 7.63–7.30$ (m, 4H, H_{ar}), 7.13–7.09 (m, 1H, H_{ar}), 6.60 (d, $J_{HH} = 8$ Hz, 2H, H_{ar}), 3.69 (s, 6H, OCH_3), 2.30–2.15 (m, 2H, H_{Cy}), 2.05–1.90 (m, 2H, H_{Cy}), 1.84–1.11 (m, 18H, H_{Cy}), −0.31 (d, $^3J_{HP} = 8$ Hz, 3H, $AuCH_3$) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, 298 K): $\delta = 49.7$ ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, 298 K): $\delta = 157.9$, 143.3 (d, $J_{CP} = 16$ Hz), 133.6, 133.2 (d, $J_{CP} = 8$ Hz), 131.8 (d, $J_{CP} = 37$ Hz), 131.5, 130.4, 129.1, 127.2 (d, $J_{CP} = 5$ Hz), 120.4 (d, $J_{CP} = 5$ Hz), 104.4, 55.6, 36.7 (d, $J_{CP} = 26$ Hz), 30.4 (d, $J_{CP} = 6$ Hz), 29.5, 27.4 (d, $J_{CP} = 11$ Hz), 27.3 (d, $J_{CP} = 13$ Hz), 26.5, 9.1 (d, $^2J_{CP} = 96$ Hz) ppm. MS (LIFDI-TOF, CH_2Cl_2) for $C_{27}H_{38}AuO_2P$ $[M]^+$ calc. m/z = 622, found m/z = 622. EA for $C_{27}H_{38}AuO_2P$ calc. C 52.09, H 6.15; found C 52.10, H 6.08.

Catalytic hydrofluorination reaction of 1-phenyl-1-propyne

The respective gold complex (0.03 mmol) was loaded into a polypropylene vial. A CH_2Cl_2 solution containing $OP(4\text{-}C_6H_4F)_3$

(0.03 M), 1-phenyl-1-propyne (3 M), $Et_3N \cdot 3HF$ (1.5 M) and 2-chlorobenzoic acid (3 M, only for experiments [b] (Table 1)) was prepared and 1 mL added to each vial. The reaction solutions were stirred for 4 d at room temperature. An aliquot of 0.1 mL was taken from each vial and topped with CD_2Cl_2 (0.2 mL) and ^{19}F NMR spectra were recorded with 128 scans and a d1 time of 30 s to make sure that relaxation was complete. The integral of the signal for OP(4-$C_6H_4F)_3$ was set to 3.0 and the signals of the products integrated accordingly. The spectroscopic data for the products is in agreement with the literature ((*Z*)-2-fluoro-1-phenylpropene (**3**) (main regioisomer),[29] (*Z*)-α-fluoro-β-methylstyrene (**17**) (minor regioisomer)[30]).

Competing reactions of 1-phenyl-1-propyne and 4-phenyl-3-butyn-2-one with [Au(F)(SPhos)] (1)

a) A CD_2Cl_2 solution containing 0.03 mmol [Au(F)(SPhos)] (**1**) was transferred to a PFA tube loaded with 1-phenyl-1-propyne (3.8 μL, 0.03 mmol, 1 eq.) and 4-phenyl-3-butyn-2-one (4.4 μL, 0.03 mmol, 1 eq.) and allowed to stand for 3 h at room temperature after which the mixture was analysed by NMR spectroscopy. The same procedure was repeated with loadings of 10 eq. of both alkynes.

b) A CH_2Cl_2 solution containing 0.03 mmol [Au(F)(SPhos)] (**1**) and OP(4-$C_6H_4F)_3$ (0.03 mmol) was added to a polypropylene vial. A CH_2Cl_2 solution containing 1-phenyl-1-propyne (0.30 mmol, 38 μL, 10 eq.), 4-phenyl-3-butyn-2-one (44 μL, 0.3 mmol, 10 eq.) and $Et_3N \cdot 3HF$ (0.15 mmol, 25 μL, 15 eq. HF) was prepared and added to the vial. The vial was stirred for 4 d at room temperature. An aliquot of 0.1 mL was taken from the vial, topped with CD_2Cl_2 (0.2 mL) and ^{19}F NMR spectra were recorded with 128 scans and a d1 time of 30 s to make sure that relaxation was complete. The integral of the signal for OP(4-$C_6H_4F)_3$ was set to 3.0 and the signals of the products integrated accordingly. The spectroscopic data for the hydrofluorination product of 4-phenyl-3-butyn-2-one agrees with the literature ((*Z*)-4-fluoro-4-phenylbut-3-en-2-one (**14**),[5d] the other regioisomer[31] was not observed).

Reactions of [Au(L)][BR_4] with [$(Me_2N)_3P]_2N^+F^-$

[$(Me_2N)_3P]_2N^+F^-$ (0.5 mmol, 180 mg) was prepared freshly.[22] A CD_2Cl_2 solution containing [Au(SPhos)][$B(C_6F_5)_4$] (**19**) (0.03 mmol, 38.6 mg) or [Au(SIPr)][BF_4] (0.03 mmol, 20.2 mg) was added to a PFA tube. [$(Me_2N)_3P]_2N^+F^-$ (0.1 mmol) was added to the solutions, resulting in immediate black coloration as well as precipitation. ^{19}F NMR spectra confirmed the formation of [Au(F)(SPhos)] (**1**)[10] as well as of [Au(F)(SIPr)],[26] albeit in low yields.

Reaction of [Au(SPhos)][$B(C_6F_5)_4$] (17) with 4-phenyl-3-butyn-2-one and TMAF

4-Phenyl-3-butyn-2-one (0.15 mL, 1.07 mmol, 36 eq.) was added to a PFA tube containing [Au(SPhos)][$B(C_6F_5)_4$] (**17**) (0.03 mmol, 38.6 mg) and TMAF (0.60 mmol, 56 mg, 20 eq.). CD_2Cl_2 (0.3 mL) was added and the tube flame-sealed. Sonication for 1 h afforded the vinyl species [Au($CH_3C(O)C{=}C(F)Ph$)(SPhos)] (**13**) (for analytical data see above).

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Fluorido complexes · Fluoroalkenes · Gold · Hydrofluorination · Phosphine complexes

[1] a) A. Fürstner, P. W. Davies, *Angew. Chem. Int. Ed.* **2007**, *46*, 3410–3449; *Angew. Chem.* **2007**, *119*, 3478–3519; b) D. J. Gorin, F. D. Toste, *Nature* **2007**, *446*, 395–403.
[2] a) A. Fürstner, *Chem. Soc. Rev.* **2009**, *38*, 3208–3221; b) B. Ranieri, I. Escofet, A. M. Echavarren, *Org. Biomol. Chem.* **2015**, *13*, 7103–7118; c) M. Garcia-Mota, N. Cabello, F. Maseras, A. M. Echavarren, J. Perez-Ramirez, N. Lopez, *ChemPhysChem* **2008**, *9*, 1624–1629.
[3] a) O. E. Okoromoba, J. Han, G. B. Hammond, B. Xu, *J. Am. Chem. Soc.* **2014**, *136*, 14381–14384; b) A. S. Hashmi, G. J. Hutchings, *Angew. Chem. Int. Ed.* **2006**, *45*, 7896–7936; *Angew. Chem.* **2006**, *118*, 8064–8105; c) H. G. Raubenheimer, H. Schmidbaur, *J. Chem. Educ.* **2014**, *91*, 2024–2036; d) A. S. Hashmi, *Chem. Rev.* **2007**, *107*, 3180–3211; e) J.-F. Paquin, M. Drouin, J.-D. Hamel, *Synthesis* **2018**, *50*, 881–955; f) S. Hara, *Top. Curr. Chem.* **2012**, *327*, 59–86.
[4] a) K. Müller, C. Faeh, F. Diederich, *Science* **2007**, *317*, 1881–1886; b) P. Jeschke, *ChemBioChem* **2004**, *5*, 571–589; c) D. E. Yerien, S. Bonesi, A. Postigo, *Org. Biomol. Chem.* **2016**, *14*, 8398–8427.
[5] a) J. A. Akana, K. X. Bhattacharyya, P. Müller, J. P. Sadighi, *J. Am. Chem. Soc.* **2007**, *129*, 7736–7737; b) R. Gauthier, M. Mamone, J. F. Paquin, *Org. Lett.* **2019**, *21*, 9024–9027; c) B. C. Gorske, C. T. Mbofana, S. J. Miller, *Org. Lett.* **2009**, *11*, 4318–4321; d) F. Nahra, S. R. Patrick, D. Bello, M. Brill, A. Obled, D. B. Cordes, A. M. Slawin, D. O'Hagan, S. P. Nolan, *ChemCatChem* **2015**, *7*, 240–244; e) T. J. O'Connor, F. D. Toste, *ACS Catal.* **2018**, *8*, 5947–5951; f) A. Gómez-Herrera, F. Nahra, M. Brill, S. P. Nolan, C. S. J. Cazin, *ChemCatChem* **2016**, *8*, 3381–3388.
[6] a) A. S. Hashmi, *Angew. Chem. Int. Ed.* **2010**, *49*, 5232–5241; *Angew. Chem.* **2010**, *122*, 5360–5369; b) R. Gauthier, N. V. Tzouras, Z. Zhang, S. Bedard, M. Saab, L. Falivene, K. Van Hecke, L. Cavallo, S. P. Nolan, J. F. Paquin, *Chem. Eur. J.* **2022**, *28*, e202103886.
[7] a) J. A. Goodwin, A. Aponick, *Chem. Commun.* **2015**, *51*, 8730–8741; b) G. Compain, K. Jouvin, A. Martin-Mingot, G. Evano, J. Marrot, S. Thibaudeau, *Chem. Commun.* **2012**, *48*, 5196–5198.
[8] a) W. Wang, G. B. Hammond, B. Xu, *J. Am. Chem. Soc.* **2012**, *134*, 5697–5705; b) C. J. Halliday, J. M. Lynam, *Dalton Trans.* **2016**, *45*, 12611–12626; c) R. E. Brooner, R. A. Widenhoefer, *Angew. Chem. Int. Ed.* **2013**, *52*, 11714–11724; *Angew. Chem.* **2013**, *125*, 11930–11941; d) W. Zi, F. Dean Toste, *Chem. Soc. Rev.* **2016**, *45*, 4567–4589.
[9] Z. Lu, G. B. Hammond, B. Xu, *Acc. Chem. Res.* **2019**, *52*, 1275–1288.
[10] S. G. Rachor, R. Müller, P. Wittwer, M. Kaupp, T. Braun, *Inorg. Chem.* **2022**, *61*, 357–367.
[11] J. Berger, T. Braun, T. Ahrens, P. Klaring, R. Laubenstein, B. Braun-Cula, *Chem. Eur. J.* **2017**, *23*, 8886–8900.
[12] a) L. M. Milner, L. M. Hall, N. E. Pridmore, M. K. Skeats, A. C. Whitwood, J. M. Lynam, J. M. Slattery, *Dalton Trans.* **2016**, *45*, 1717–1726; b) M. Hofer, A. Genoux, R. Kumar, C. Nevado, *Angew. Chem. Int. Ed.* **2017**, *56*, 1021–1025; *Angew. Chem.* **2017**, *129*, 1041–1045; c) N. A. Barnes, A. K. Brisdon, W. I. Cross, J. G. Fay, J. A. Greenall, R. G. Pritchard, J. Sherrington, *J. Organomet. Chem.* **2000**, *616*, 96–105.

[13] a) T. de Haro, C. Nevado, *Chem. Commun.* **2011**, *47*, 248–249; b) V. Gouverneur, M. Hopkinson, G. Giuffredi, A. Gee, *Synlett* **2010**, *2010*, 2737–2742.
[14] X. Zeng, S. Liu, G. B. Hammond, B. Xu, *Chem. Eur. J.* **2017**, *23*, 11977–11981.
[15] R. Guo, X. Qi, H. Xiang, P. Geaneotes, R. Wang, P. Liu, Y. M. Wang, *Angew. Chem. Int. Ed.* **2020**, *59*, 16651–16660; *Angew. Chem.* **2020**, *132*, 16794–16803.
[16] a) J. Che, Y. Li, F. Zhang, R. Zheng, Y. Bai, G. Zhu, *Tetrahedron Lett.* **2014**, *55*, 6240–6242; b) Y. Li, X. Liu, D. Ma, B. Liu, H. Jiang, *Adv. Synth. Catal.* **2012**, *354*, 2683–2688.
[17] C. Chen, K. Wilcoxen, C. Q. Huang, N. Strack, J. R. McCarthy, *J. Fluorine Chem.* **2000**, *101*, 285–290.
[18] A. Jayaraman, S. Lee, *Org. Lett.* **2019**, *21*, 7923–7927.
[19] X. Zhang, D. J. Burton, *J. Fluorine Chem.* **2001**, *112*, 317–324.
[20] W. R. Dolbier Jr, X. X. Rong, M. D. Bartberger, H. Koroniak, B. E. Smart, Z.-Y. Yang, *J. Chem. Soc. Perkin Trans. 2* **1998**, 219–232.
[21] G. F. Manbeck, M. C. Kohler, M. R. Porter, R. A. Stockland Jr., *Dalton Trans.* **2011**, *40*, 12595–12606.
[22] a) R. Schwesinger, R. Link, G. Thiele, H. Rotter, D. Honert, H.-H. Limbach, F. Männle, *Angew. Chem. Int. Ed.* **1991**, *30*, 1372–1375; *Angew. Chem.* **1991**, *103*, 1376–1378; b) R. Schwesinger, R. Link, P. Wenzl, S. Kossek, *Chem. Eur. J.* **2005**, *12*, 438–445.
[23] J. Schießl, J. Schulmeister, A. Doppiu, E. Wörner, M. Rudolph, R. Karch, A. S. K. Hashmi, *Adv. Synth. Catal.* **2018**, *360*, 2493–2502.
[24] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176–2179.
[25] A. J. Stepen, M. Bursch, S. Grimme, D. W. Stephan, J. Paradies, *Angew. Chem. Int. Ed.* **2018**, *57*, 15253–15256; *Angew. Chem.* **2018**, *130*, 15473–15476.
[26] D. S. Laitar, P. Müller, T. G. Gray, J. P. Sadighi, *Organometallics* **2005**, *24*, 4503–4505.
[27] C. Nieto-Oberhuber, S. Lopez, A. M. Echavarren, *J. Am. Chem. Soc.* **2005**, *127*, 6178–6179.
[28] J. Schießl, J. Schulmeister, A. Doppiu, E. Wörner, M. Rudolph, R. Karch, A. S. K. Hashmi, *Adv. Synth. Catal.* **2018**, *360*, 3949–3959.
[29] K. Isogai, N. Nishizawa, T. Saito, J.-I. Sakai, *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1555–1556.
[30] O. A. Wong, Y. Shi, *J. Org. Chem.* **2009**, *74*, 8377–8380.
[31] T. B. Patrick, T. Y. Agboka, K. Gorrell, *J. Fluorine Chem.* **2008**, *129*, 983–985.

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