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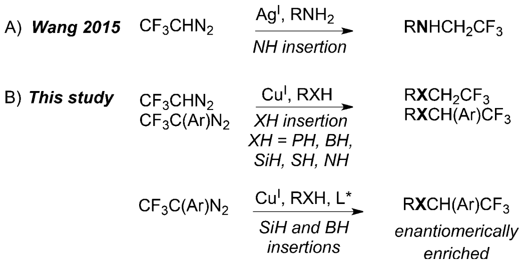
Copper-Catalyzed Insertion into Heteroatom–Hydrogen Bonds with Trifluorodiazoalkanes

*Stephen Hyde, Janis Veliks, Benoît Liégault, David Grassi, Marc Taillefer, and Véronique Gouverneur**

Abstract: *Copper-catalyzed Si−H, B−H, P−H, S−H, and N−H insertion reactions of 2,2,2-trifluoro-1-diazoethane and 1-aryl 2,2,2-trifluorodiazoethanes generated a large number of new fluorine-containing chemical entities for medicinal chemists. With selected Si−H and B−H insertion reactions, we demonstrate successful extension to asymmetric catalysis.*

The wide range of materials and biologically active molecules containing fluorine substitution has prompted much research on late-stage fluorination and trifluoromethylation.[1] The installation of a 1,1,1-trifluoro-2λ^3-ethane (CF_3CH_2) fragment onto arenes and heteroatoms has received less attention. Recent developments include cross-coupling reactions with CF_3CH_2I under Pd catalysis with aryl boronic acids,[2] or through CH arene functionalization.[3] More conventional approaches have been implemented for heteroatom trifluoroethylation: The N-trifluoroethylation of anilines with an electrophilic hypervalent iodine CH_2CF_3 reagent has been reported;[4] alternatively, trifluoroacetaldehyde has been subjected to reductive amination.[5] The installation of branched trifluoroalkyl fragments of the type CF_3CHR is more challenging, especially when enantioselectivity is required. With heteroatom functionalization as our primary objective, we opted to address this problem with a strategy based on heteroatom–hydrogen bond (X−H) insertion. Transition-metal-catalyzed X−H (X = O, N, S, Si, B) insertions of diazo compounds are a powerful approach for the construction of C−X bonds.[6] This methodology has been studied extensively with α-diazoesters and α-diazoketones, and extended to numerous asymmetric carbene-insertion reactions. The attractive synthetic route towards 2,2,2-trifluorodiazoethane (CF_3CHN_2) reported by Morandi and Carreira[7] led us to consider this class of CF_3-containing synthon in the context of X−H insertion. This choice was driven by the prospect of extending this methodology to asymmetric carbene insertion with 1-aryl 2,2,2-trifluorodiazoethanes.[8] Wang and co-workers recently reported the trifluoroethylation of anilines and amides with 2,2,2-trifluorodiazoethane under Ag^I catalysis; this catalytic system was applied exclusively to insertion reactions involving amines and amides, and does not offer a platform towards asymmetric catalysis since the products of trifluoroethylation are achiral (Scheme 1 A).[9] Herein, we report that Si−H, B−H, P−H, S−H, and N−H insertion reactions of trifluorodiazoalkanes are possible under Cu^I catalysis; asymmetric variants are reported for selected Si−H and B−H insertions. The insertion products expand the chemical space available to chemists (Scheme 1 B).



Scheme 1. Silver- and copper-catalyzed X−H bond insertion reactions with trifluorodiazoalkanes.

This study began with the preparation of 2,2,2-trifluoro-1-diazoethane (**1a**) from commercially available $CF_3CH_2NH_2 \cdot HCl$ by the procedure disclosed by Morandi and Carreira.[7] The body of work on copper-[10] and rhodium-catalyzed[11] X−H insertion with α-diazoesters prompted us to focus on these transition metals to probe the reactivity of 2,2,2-trifluoro-1-diazoethane with the model substrate dimethylphenylsilane (Table 1).

Optimization studies indicated that $[Cu(CH_3CN)_4]PF_6$ was superior to $[Rh_2(OAc)_4]$ for Si−H bond insertion in either dichloromethane or 2,2-dimethylbutane (DMB) as the reaction solvent (Table 1, entries 1–4). Slow addition (30 min) of the diazo reagent to a solution of the silane and catalyst led to significant improvement by suppressing the side reaction resulting from diazo dimerization (Table 1, entry 5). A catalyst loading of 2 mol % was effective, but the product was formed in lower yield when it was decreased to 1 mol % (Table 1, entries 7 and 9). With this slow-addition protocol in place, $[Cu(CH_3CN)_4]PF_6$ (2 mol %) was retained for further studies as superior to $Cu(OTf)_2$ (Table 1, entries 8). No reaction took place with $AgSbF_6$ (5 mol %) in 1,2-dichloroethane (DCE; Table 1, entry 10); these reaction conditions were identified as optimal for the N-trifluoroethylation of

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[*] S. Hyde, Dr. J. Veliks, Dr. B. Liégault, Dr. D. Grassi, Prof. V. Gouverneur
University of Oxford, Chemistry Research Laboratory
Mansfield Road, Oxford, OX1 3TA (UK)
E-mail: veronique.gouverneur@chem.ox.ac.uk

Dr. B. Liégault, Dr. M. Taillefer
Institut Charles Gerhardt Montpellier
UMR-CNRS 5253, AM2N, ENSCM
8 rue de l'Ecole Normale, 34296 Montpellier Cedex 5 (France)

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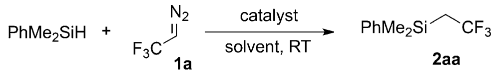
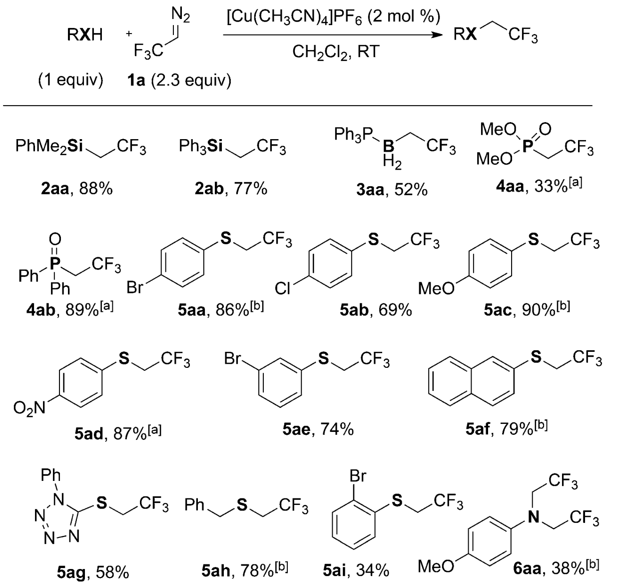
Table 1: Evaluation of reaction conditions for Si–H insertion.[a]



Entry	Catalyst (mol %)	Conditions[b]	Solvent	Yield [%][c]
1	$[Rh_2(OAc)_4]$ (5)	A	CH_2Cl_2	16
2	$[Rh_2(OAc)_4]$ (5)	A	DMB	15
3	$[Cu(CH_3CN)_4]PF_6$ (5)	A	CH_2Cl_2	44
4	$[Cu(CH_3CN)_4]PF_6$ (5)	A	DMB	34
5	$[Cu(CH_3CN)_4]PF_6$ (5)	B	CH_2Cl_2	87
6	$[Cu(CH_3CN)_4]PF_6$ (5)	B	toluene	61
7	$[Cu(CH_3CN)_4]PF_6$ (2)	B	CH_2Cl_2	(88)
8	$Cu(OTf)_2$ (2)	B	CH_2Cl_2	32
9	$[Cu(CH_3CN)_4]PF_6$ (1)	B	CH_2Cl_2	61
10[d]	$AgSbF_6$ (5)	B	DCE	0
11	–	B	CH_2Cl_2	0
12	$[Cu(CH_3CN)_4]PF_6$ (2)	B	CH_2Cl_2	(77)[e]

[a] Reaction conditions: $PhMe_2SiH$ (1.0 equiv), **1a** (2.3 equiv). [b] Conditions A: manual addition of **1a**; conditions B: slow addition of **1a** over 0.5 h with a syringe pump. [c] The yield was determined by ^{19}F NMR spectroscopy with trifluorotoluene as an internal reference. Values in parenthesis indicate the yield of the isolated product. [d] The reaction was performed at 60 °C. [e] The reaction was performed with triphenylsilane. The product is triphenyl(2,2,2-trifluoroethyl)silane (**2ab**).



Scheme 2. Copper-catalyzed Si–H, B–H, P–H, S–H, and N–H bond insertion with 2,2,2-trifluoro-1-diazoethane (**1a**). Reaction conditions: Slow addition of **1a**, then stirring for 18 h at room temperature. Yields given are for the isolated product. [a] The reaction was performed with $NaBAr_F$ (2.2 mol %). [b] $[Cu(CH_3CN)_4]PF_6$: 4 mol %.

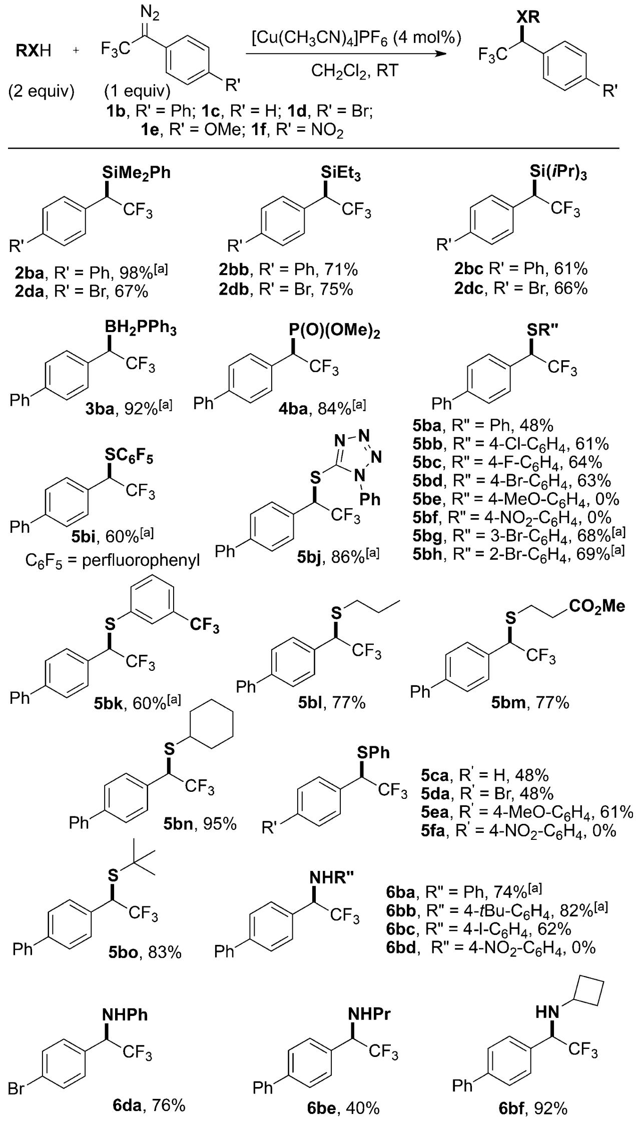
anilines and amides.[9] As expected, the catalyst was essential for Si–H insertion (Table 1, entry 11). The optimal reaction conditions therefore consist of treating dimethylphenylsilane with an excess of the diazo reagent (2.3 equiv) in dichloromethane at room temperature in the presence of $[Cu(CH_3CN)_4]PF_6$ (2 mol %) for 18 h. Under these conditions, the product of Si–H insertion **2aa** was isolated in 88 % yield (Table 1, entry 7). Pleasingly, Si–H insertion of more sterically demanding triphenylsilane was also successful and led to product **2ab** in 77 % yield (Table 1, entry 12).

After establishing these conditions for copper-catalyzed Si–H insertion with 2,2,2-trifluoro-1-diazoethane (**1a**), we examined the reactivity of triphenylphosphine-protected borane, dimethyl phosphonate, diphenylphosphine oxide, thiols, and 4-methoxyaniline, and found that the generality of the heteroatom–hydrogen insertion process is striking (Scheme 2). Triphenylphosphine borane is a suitable substrate and was converted into the B–H insertion product **3aa** in 52 % yield. Dimethyl phosphonate and diphenylphosphine oxide also reacted under Cu^I catalysis to afford **4aa** and **4ab** in 33 and 89 % yield, respectively, thereby establishing the feasibility of P–H insertion. The reaction tolerates a range of aryl, heteroaryl, and alkyl thiols, thus leading to the 2,2,2-trifluoroethyl-substituted sulfides **5aa–ah** in up to 90 % yield. Under the standard reaction conditions, the reaction of 2,2,2-trifluoro-1-diazoethane with 4-methoxyaniline led to the product of double insertion **6aa**. The product of the O–H insertion of phenol was not observed with either $[Cu(CH_3CN)_4]PF_6$ or $AgSbF_6$.

The broad scope of this method encouraged further studies on the installation of branched trifluoroalkyl fragments. We probed the reactivity of the model 1-aryl 2,2,2-trifluoro-1-diazoethanes **1b–f**[8] in a range of heteroatom–hydrogen insertion reactions. For this class of diazoethanes, the reaction was performed with an excess of the nucleophilic component, and the catalyst loading was typically increased to 4 mol % (Scheme 3).

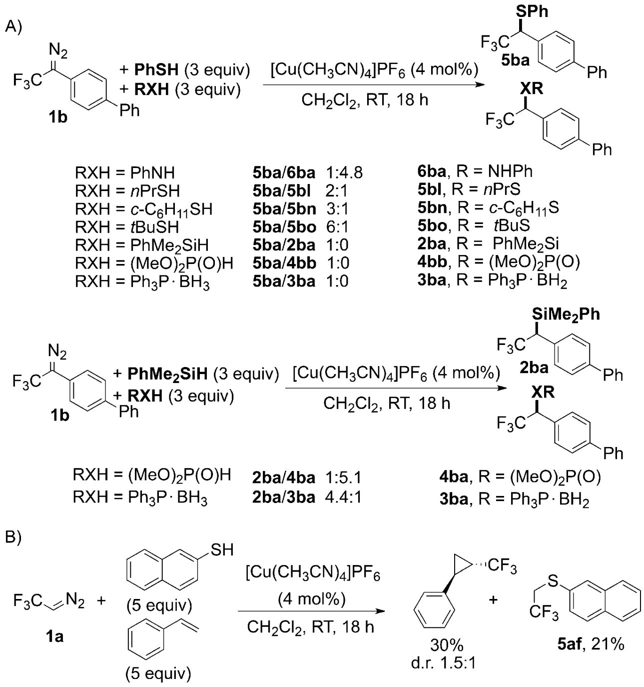
The reaction scope is very broad, and a large collection of novel chiral products with a CF_3 substituent located at the benzylic position were synthesized. Similarly to the reactions with 2,2,2-trifluoro-1-diazoethane (**1a**), Si–H, B–H, and P–H insertion reactions were feasible; the corresponding products were isolated in 61–98 % yield. A detailed investigation of S–H insertion reactions revealed that aryl, heteroaryl, primary, secondary, and tertiary alkyl groups are all tolerated on the sulfur atom. Only strongly electron donating (OMe) or electron withdrawing (NO_2) groups located in the *para* position of benzenethiol are not compatible. All 1-aryl 2,2,2-trifluoro-1-diazoethanes tested were competent substrates with the exception of the nitro-substituted derivative **1f**. For the parent benzenethiol, we found that $[Cu(CH_3CN)_4]PF_6$ was superior to $[Cu(CH_3CN)_4]BAr_F$, and $AgSbF_6$ was not effective. In contrast to the product outcome observed with 2,2,2-trifluoro-1-diazoethane (**1a**), aniline derivatives underwent monoinsertion with no detectable products resulting from undesired double insertion. Primary alkyl and cycloalkyl amines also reacted with **1b** as demonstrated with the synthesis of **6be** and **6bf**, which were isolated in 40 % and 92 % yield, respectively. For reactions with **1b** leading to lower yields, 1-[(1,1′-biphenyl)-4-yl]-2,2-difluoroethan-1-one was the main side product isolated after work-up; this observation indicates that hydrolysis of the unreacted diazo precursor occurs to afford 1-[(1,1′-biphenyl)-4-yl]-2,2,2-trifluoroethan-1-ol, an intermediate prone to HF elimination.

The ability of $[Cu(CH_3CN)_4]PF_6$ to catalyze efficiently a range of heteroatom–hydrogen insertion reactions led us to carry out a series of competition experiments with the diazo



Scheme 3. Copper-catalyzed Si–H, B–H, P–H, S–H, and N–H bond insertion reactions with 1-aryl 2,2,2-trifluoro-1-diazoethanes **1b–f**. Reaction conditions: Slow addition of **1b–f** over 1 h, then stirring for 18 h at room temperature. [a] $[Cu(CH_3CN)_4]PF_6$: 2 mol%. Yields given are for the isolated product.

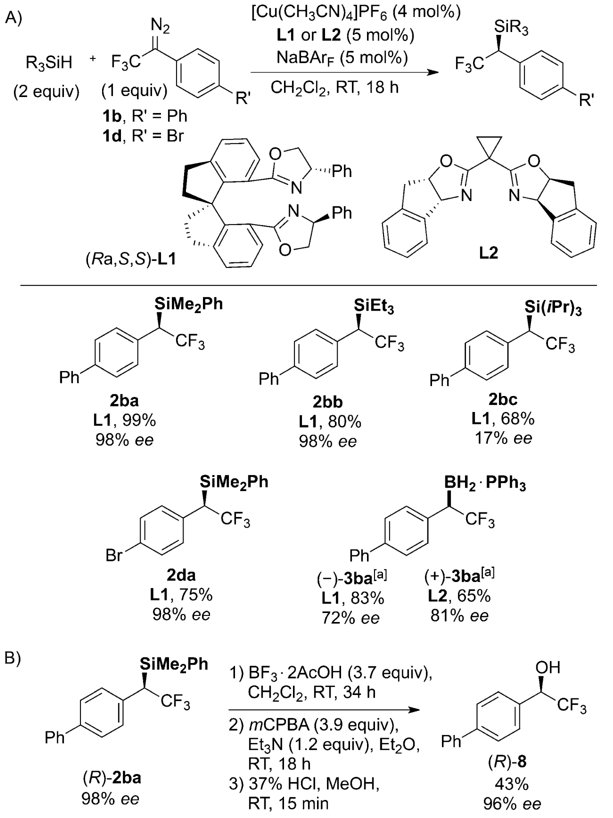
compound **1b** to provide an order of reactivity: $PhNH_2 > PhSH > n PrSH > \text{cyclohexylSH} > t BuSH > Ph_3P{\cdot}BH_3 > Me_2PhSiH > (MeO)_2P(O)H$. This ranking may serve as a predictive tool for insertion when substrates possessing two or more heteroatom–hydrogen functionalities are used (Scheme 4A). The reaction of 2,2,2-trifluoro-1-diazoethane (**1a**) with an excess of naphthalene-2-thiol and styrene under Cu^I catalysis gave products of cyclopropanation[7] and S–H insertion (Scheme 4B). In the absence of the thiol, the cyclopropane product was obtained in 96% yield; these experiments indicate the relevance of a donor–acceptor copper carbenoid species in the catalytic cycle. In contrast, the system reported by Wang and co-workers for silver-catalyzed N–H insertion with **1a**[9] afforded no product of cyclopropanation in the presence of styrene.



Scheme 4. Competition experiments. A) Copper-catalyzed Si–H, B–H, P–H, and N–H insertion versus PhS–H insertion with **1b**, and copper-catalyzed B–H and N–H insertion versus Si–H insertion with **1b**. The product ratio was determined by ^{19}F NMR spectroscopy. B) Cyclopropanation versus S–H bond insertion with **1a**. The yield was determined by ^{19}F NMR spectroscopy with 3-fluoronitrobenzene as an internal reference. Reaction conditions: Slow addition of **1a**,**b**, then stirring for 18 h at room temperature.

Asymmetric insertion reactions of diazoesters are well-documented,[12] and numerous reaction parameters as well as the nature of the ester group can influence enantioselectivity.[12c] To date, no catalytic enantioselective heteroatom–hydrogen insertion reactions are known for 2,2,2-trifluorodiazoethanes. The steric bulk of the trifluoromethyl group (A value: 2.1 $kcal\,mol^{-1}$) is similar to that of the isopropyl group (A value: 2.2) and larger than that of most ester functionalities (A value for CO_2Me: 1.3),[13] and the Hammett substituent constants[14] are in the same range as CF_3 ($\sigma_{meta} = 0.43$ and $\sigma_{para} = 0.54$) and CO_2Et ($\sigma_{meta} = 0.37$ and $\sigma_{para} = 0.45$); these trends encouraged exploratory studies with **1b** and **1d**, two diazo entities that are precursors of donor–acceptor-substituted metal carbenoids. The preference for copper complexes to remain bound to the substrate during protonation prompted the use of copper over rhodium complexes for asymmetric insertion reactions. Our research on the merging of organosilane and fluorine chemistry[15] led us to focus on Si–H insertion, as we anticipated that the nonpolar Si–H bond would favor a concerted mechanism for carbenoid insertion.[6,16] The resulting enantiomerically enriched products would be challenging to prepare by other routes (Scheme 5).

Experiments undertaken with a catalytic amount of $[Cu(CH_3CN)_4]PF_6$ (4 mol%) and the large noncoordinating ion tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (BAr_F^-,[17] 5 mol%) identified the chiral bisoxazoline Zhou ligand



Scheme 5. Copper-catalyzed enantioselective Si–H and B–H insertion reactions with **1b** and **1d**. Reaction conditions: Slow addition of **1b** or **1d**, then stirring for 18 h at room temperature. Yields given are for the isolated product. [a] The reaction was performed with $Ph_3P \cdot BH_3$ (2 equiv). *m*CPBA = *m*-chloroperbenzoic acid.

(*R*a,*S*,*S*)-**L1** (5 mol%) based on the spirobiindane scaffold as optimal for the induction of high enantioselectivity.[18] With this ligand, Si–H insertion in dichloromethane at 25 °C with dimethylphenylsilane and triethylsilane afforded enantiomerically enriched (−)-**2ba** and (−)-**2bb**, which were isolated in 99 and 80% yield, respectively, with 98% *ee*. The diazo precursor **1d** was converted into (−)-**2da** in 75% yield with 98% *ee*. The yield and enantioselectivity decreased significantly with bulkier triisopropylsilane. The bisoxazoline **L2** was superior to **L1** for B–H insertion as exemplified by the synthesis of enantiomerically enriched (+)-**3ba** (81% *ee*) (Scheme 5A). For completion, we assigned the absolute configuration of **2ba** as *R* by performing a stereoretentive Tamao–Fleming oxidation[19] and comparing the $[\alpha]_D$ value of the resulting enantiomerically enriched alcohol (*R*)-**8** ($ee >$ 96%) with a previously reported value (Scheme 5B).[20] The absolute configuration of other Si–H insertion products was tentatively assigned by analogy with (*R*)-**2ba**.

In summary, we have developed a catalytic insertion of 1-aryl 2,2,2-trifluoro-1-diazoalkanes into Si–H, B–H, P–H, S–H, and N–H bonds. These transformations enable the synthesis of a large collection of novel and valuable chiral CF_3-substituted molecules. Enantioselective Si–H and B–H insertion reactions catalyzed by Cu^I complexes derived from chiral bisoxazoline ligands proceeded in high yields with good to excellent enantioselectivity. Further study on the application of these novel reactions is ongoing in our laboratory.

Experimental Section

General procedure: $[Cu(CH_3CN)_4]PF_6$ (2–4 mol%) and the substrate (0.2 mmol, 2.0 equiv) were dissolved in degassed CH_2Cl_2 (0.5 mL). A solution of the $CF_3C(R)N_2$ reagent (0.1 mmol, 1.0 equiv) in CH_2Cl_2 (0.8 mL) was then added at room temperature over 1 h with a syringe pump, and the reaction mixture was stirred for 18 h. Once the reaction was complete (TLC), the solvent was evaporated, and the residue was purified by silica-gel column chromatography.

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