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A copper(I)-catalyzed sulfonylative Hiyama cross-coupling

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Abstract

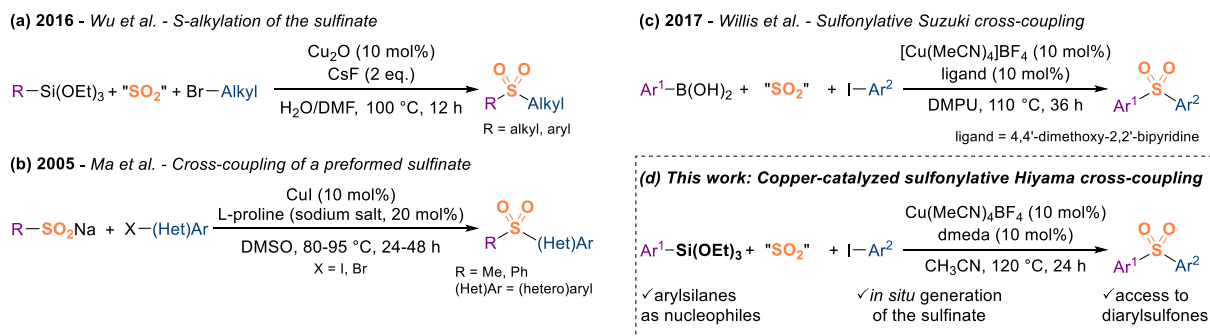
An air-tolerant Cu-catalyzed sulfonylative Hiyama cross-coupling reaction enabling the formation of diaryl sulfones is described. Starting from aryl silanes, DABSO and aryl iodides, the reaction tolerates a large variety of polar functional groups (amines, ketones, esters, aldehydes). Control experiments coupled with DFT calculations shed light on the mechanism, where the reductive elimination showcases an usual high energy barrier for a Cu(III)/Cu(I) process.

Introduction

Transition metal-catalyzed cross-coupling reactions of organometallic reagents with electrophilic coupling partners represent one of the most powerful methods to generate carbon–carbon and carbon–heteroatom bonds, and therefore, stand out as key methods in organic synthesis over the past decades.¹ Besides, three-component coupling reactions in which a small molecule is inserted between the nucleophile and the electrophile partners permit to increase the molecular complexity of products in an atom-economical way. While the insertion of carbon monoxide has been extensively exploited to prepare carbonyl derivatives,² much less attention has been given to sulfur dioxide.³ Yet, the resulting sulfones are known to have a prominent biological activity as well as an important synthetic utility, making sulfonylative couplings particularly attractive.^{4, 5}

From all commonly used organometallic reagents, organosilanes are presumably among the most appealing ones. In addition to being readily available, air-stable and relatively non-toxic, they display an improved functional-group tolerance compared to organolithium or -magnesium, thanks to their low nucleophilicity.⁶ Recently, we described the first Pd-catalyzed sulfonylative Hiyama cross-coupling with sp²-hybridized electrophiles.⁷ Surprisingly, only allylsilanes were found to react with sulfur dioxide, arylsilanes being inert under the reaction conditions. A careful mechanistic study unveiled that the organosilane was not involved in a transmetalation step, but instead reacting through a S_E2' mechanism, restricting the scope to the formation of allyl aryl sulfones. We therefore sought to develop a system able to unlock the conversion of arylsilanes to diaryl sulfones through a sulfonylative Hiyama coupling, for the first time.

Wu et al. reported in 2016 that both alkyl- and aryl(trialkoxysilanes were able to transmetalate with a Cu(I)-catalyst and thereafter insert sulfur dioxide in the newly formed Cu–C bond (Scheme 1a).⁸ However, the resulting sulfinate was only able to react with aliphatic electrophiles through an S-alkylation reaction. Meanwhile, Cu(I)-catalysts were shown to promote the coupling of sulfonates, either preformed or *in situ* synthesized from arylboronic acids, with aryl halides (Scheme 1b and 1c, respectively).^{3, 9} These encouraging precedents, added to the low price and toxicity of copper, have prompted us to investigate and disclose herein a Cu(I)-catalyzed sulfonylative Hiyama cross-coupling enabling the formation of diaryl sulfones (Scheme 1d).



Scheme 1. Sulfonates formation from organosilanes (a) and coupling with aryl iodides (b and c) under copper-catalyzed reaction conditions. DABSO = 1,4-diazabicyclo[2.2.2]octane bis(sulfur dioxide); dmeda = 1,2-dimethyl ethylenediamine.

Results and Discussion

We began our investigation by exploring the coupling of triethoxy(aryl)silane (**1a**), 4-iodotoluene (**2a**), and DABCO(SO₂)₂ (named DABSO), a commercial surrogate of sulfur dioxide, popularized by Willis and co-workers.¹⁰⁻¹² In the presence of a catalytic amount of Cu(MeCN)₄BF₄, 2,2'-bipyridine and tetrabutylammonium fluoride (TBAF, 1 M solution in THF) as an anhydrous fluoride source to activate organosilane **1a**, the reaction gave the desired sulfone **3a** in 55% yield after 6 h at 120 °C under inert atmosphere (Table 1, entry 1).

Table 1. Influence of the reaction conditions on the sulfonylative Hiyama cross-coupling of phenyl(triethoxy)silane (**1a**) with 4-iodotoluene (**2a**) (see ESI for a more exhaustive table).^[a]

$$\text{Ph-Si(OEt)}_3 + \text{"SO}_2\text{"} + \text{I-Tol} \xrightarrow[\text{CH}_3\text{CN, 120 }^\circ\text{C, 6 h}]{[\text{Cu} \text{ (10 mol\%)} \\ \text{ligand (10 mol\%)} \\ \text{F}^- \text{ (1 eq.)}]} \text{Ph-SO}_2\text{-Tol}$$

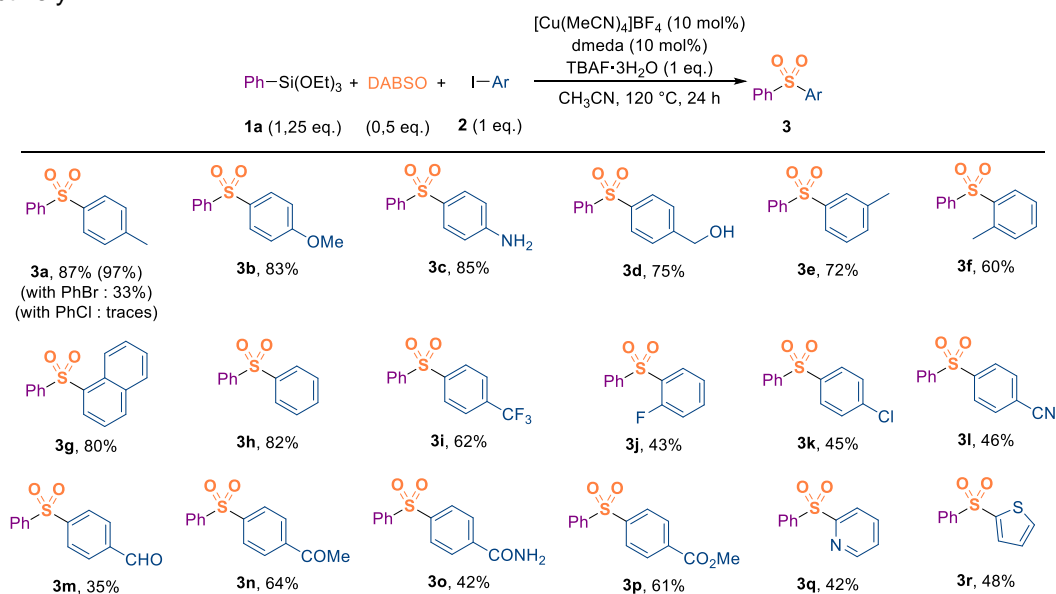
1a (2 eq.) (1 eq.) **2a** (1 eq.) **3a**

Entry	"SO ₂ "	F ⁻ source	[Cu]	Ligand	Yield ^a
1	DABSO	TBAF (1 M in THF)	[Cu(MeCN) ₄]BF ₄	bipy	55%
2	SO ₂	TBAF (1 M in THF)	[Cu(MeCN) ₄]BF ₄	bipy	27%
3	DABSO	TBAF·3H ₂ O	[Cu(MeCN) ₄]BF ₄	bipy	55%
4 ^b	DABSO	TBAF·3H ₂ O	[Cu(MeCN) ₄]BF ₄	bipy	54%
5	DABSO	TBAF·3H ₂ O	CuI	bipy	31%
6	DABSO	TBAF·3H ₂ O	Cu(OAc) ₂	bipy	18%
7	DABSO	TBAF·3H ₂ O	[Cu(MeCN) ₄]BF ₄	acac ⁻	48%
8	DABSO	TBAF·3H ₂ O	[Cu(MeCN) ₄]BF ₄	phen	65%
9	DABSO	TBAF·3H ₂ O	[Cu(MeCN) ₄]BF ₄	dmeda	69%
10 ^c	DABSO	TBAF·3H ₂ O	[Cu(MeCN) ₄]BF ₄	dmeda	98%
11 ^{c,d}	DABSO	TBAF·3H ₂ O	[Cu(MeCN) ₄]BF ₄	dmeda	97% (87%)
12	DABSO	TBAF·3H ₂ O	—	—	0%

[a] Standard reaction conditions: **1a** (0.2 mmol, 2 eq.), "SO₂" (0.1 mmol, 1 eq.), **2a** (0.1 mmol, 1 eq.), fluoride source (0.1 mmol, 1 eq.), [Cu] (0.01 mmol, 10 mol%), ligand (0.01 mmol, 10 mol%), CD₃CN (0.4 mL), Ar atmosphere, 120 °C, 6 h. Yields were measured by ¹H NMR (internal standard: mesitylene). The number within parentheses is the isolated yield from a 1.0 mmol scale reaction. [b] Air atmosphere was used instead of Ar. [c] Reaction was left for 24 h instead of 6 h. [d] Only 1.25 eq. of **1a** were used. bipy = 2,2'-bipyridine, acac⁻ = acetylacetonate anion, phen = 1,10-phenanthroline, dmeda = *N,N*-dimethyl ethylenediamine.

By contrast, gaseous sulfur dioxide, generated by thermal decomposition of $K_2S_2O_5$ in a two-chamber apparatus, led to a lower yield (27%, Table 1, entry 2) under the same conditions. When the bench-stable TBAF·3H₂O was used instead of the anhydrous THF solution, no change was observed in the yield, demonstrating some tolerance of the reaction towards water (Table 1, entry 3). Besides, the reaction was also shown to be air-tolerant (Table 1, entry 4). No better results were obtained with another source of copper (including Cu(II) salts, Table 1, entries 5 and 6), probably because of a greater solubility of $Cu(MeCN)_4BF_4$. A variety of different ligands employed in Cu-catalyzed C-heteroatom bond formation¹³⁻¹⁵ were explored, mainly bidentate *N,N*-, *N,O*- and *O,O*-ligands (Table 1, entries 7, 8, 9 and Table S5). *N,N'*-dimethylethylenediamine (dmeda) gave the best results, yielding the desired sulfone in 98% yield after 24 h at 120 °C (Table 1, entry 10). Using only 1.25 equivalent of the silane led to the same yield (97%, Table 1, entry 11). No product was observed without the catalyst (Table 1, entry 12) and a decrease in temperature (100 °C) led to lower yields, the ESI provides full details of the optimization study (see ESI 1.2). Interestingly, no formation of the direct C–C cross-coupling product was observed under these conditions.

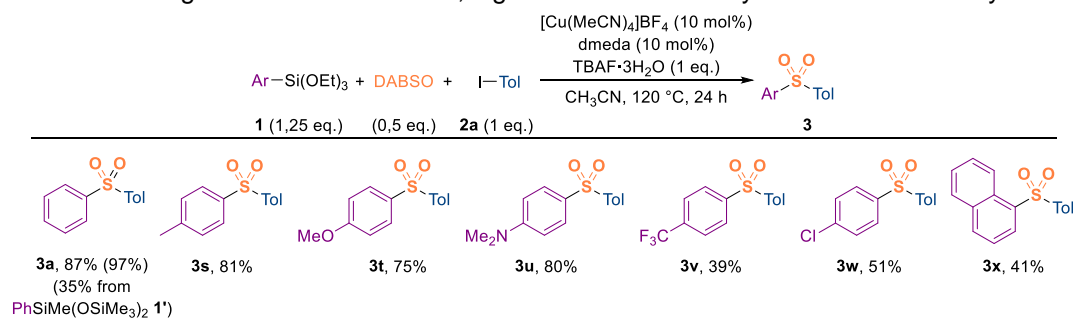
With the optimized reaction conditions in hand, we next explored the scope of the sulfonylation of various organic halides (Scheme 2). First, one can notice a good tolerance of the reaction to electron-donating groups (**3a–h**, 60–87%). Interestingly, halides **2c** and **2d** bearing either an unprotected amine or an alcohol group provided the desired products with good yields (85% and 75%, respectively), without observation of any side C–N or C–O coupling. Besides, variation of the position of the methyl group on iodotoluene (**2a**, **2e** and **2f**) as well as the use of a bicyclic halide (**3g**) show a moderate influence of steric hindrance on the reaction outcome (isolated yields 60–87%). In addition, electron-withdrawing groups could also be incorporated, leading to compounds **3i–p** in moderate yields (35–62%). It is noteworthy that a broad range of useful functionalities could be introduced, including fluorides and chlorides (**3i–k**, 43–62%) and some sensitive carbonyl moieties such as aldehyde (**3m**, 35%), ketone (**3n**, 64%), amide (**3o**, 42%), or ester (**3p**, 61%). Finally, heterocyclic electrophiles featuring pyridyl (**2q**) and thiophenyl (**2r**) moieties have also been used successfully, giving product yields of 42 and 48%, respectively.



Scheme 2. Substrate scope in organohalides. Reaction conditions: phenyl(triethoxy)silane (**1a**, 1.25 mmol, 1.25 eq.), electrophile (1.0 mmol, 1.0 eq.), DABSO (0.50 mmol, 0.50 eq.), TBAF·3H₂O (1.0 mmol, 1.0 eq.), $Cu(MeCN)_4BF_4$ (0.10 mmol, 10 mol%), dmeda (0.10 mmol, 10 mol%), CH₃CN (4 mL), 120 °C, 24 h. Isolated yields. Yields within parentheses were measured by ¹H NMR on 0.1 mmol scale (internal standard: mesitylene)

A range of aryl(triethoxy)silanes **1** was examined (Scheme 3), showing that the reaction tolerates electron-donating groups (**3s–u**, 75–81%) and, to a lesser extent, electron-withdrawing ones (**3v** and **3w**,

39 and 51%, respectively). More hindered substrates such as 1-naphtyl(triethoxy)silane also proceeded to give the desired sulfone **3x** in 41% yield. Siloxane **1'**, synthesized by direct silylation of benzene with an hydrosilane through C–H bond activation,¹⁶ gave the desired diaryl sulfone **3a** in 35% yield.

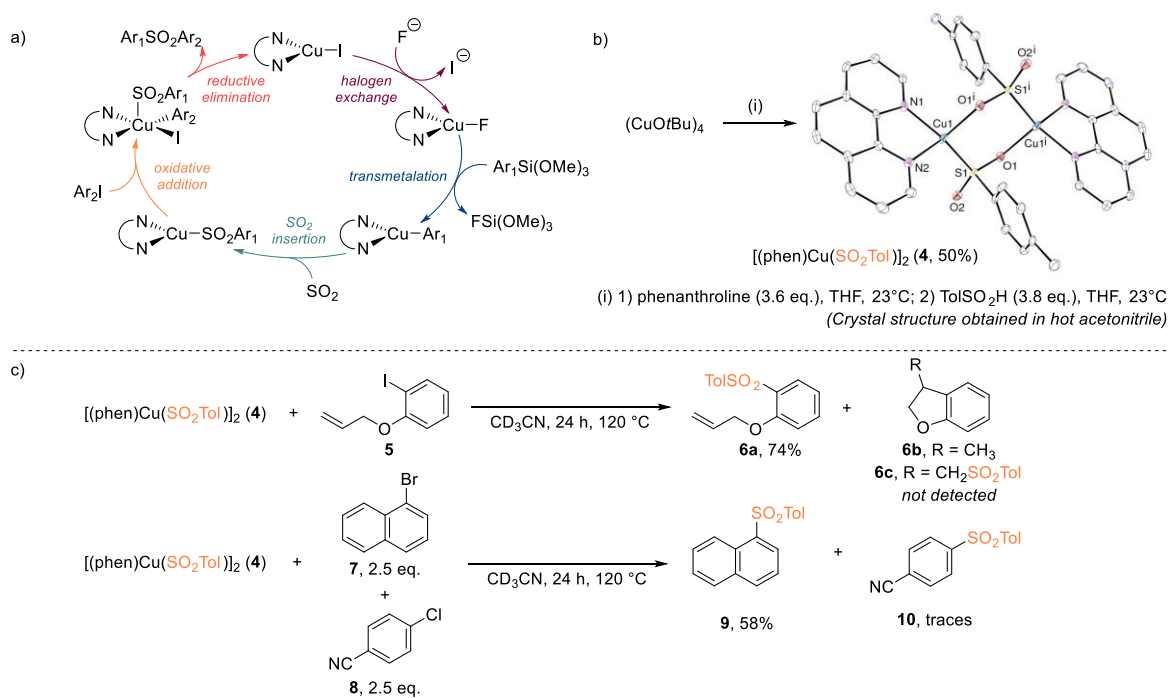


Scheme 3. Substrate scope in organohalides. Reaction conditions: organosilane (1.25 mmol, 1.25 eq.), 4-iodotoluene (**2a**, 1.0 mmol, 1.0 eq.), DABSO (0.50 mmol, 0.50 eq.), TBAF·3H₂O (1.0 mmol, 1.0 eq.), Cu(MeCN)₄BF₄ (0.10 mmol, 10 mol%), dmeda (0.10 mmol, 10 mol%), CH₃CN (4 mL), 120 °C, 24 h. Isolated yields. Yields within parentheses were measured by ¹H NMR on 0.1 mmol scale (internal standard: mesitylene).

To unravel the key features of the reaction, and in particular to understand the formation of both C–S bonds, the activation of the electrophile and disclose the rate-determining process, we carried out both experimental and computational mechanistic studies. The formation of the first C–S bond was supposed to occur after a halogen exchange on the metal to furnish a Cu–F intermediate, which, upon transmetalation with the nucleophile, followed by SO₂ insertion, yields a copper(I) sulfinate intermediate (Scheme 4a), as described by the group of Wu (Scheme 1a).⁸ Oxidative addition of the latter in the electrophile ArI, followed by reductive elimination would lead to the formation of the second C–S bond, release of the diarylsulfone and regeneration of the catalyst.

Different mechanisms have been reported for the activation of the aryl halide with Cu-complexes, featuring a one- or two-electron process. Although the Cu(I)/Cu(III) cycle through oxidative addition/reductive elimination is the most commonly reported mechanism for the modified Ullmann reaction,¹⁷ experimental and computational data do not converge into a single mechanism and the radical pathway has also shown to be viable.¹⁸ Here, the dependence of the reaction efficiency on the nature of the leaving halogen for the formation of compound **3a** on 0.1 mmol scale from aryl-iodide (97%), bromide (33%) and chloride (traces) hinted at an ionic mechanism (Scheme 2). To confirm this statement, we decided to explore the formation of a sulfone product by reaction between a copper(I)-sulfinate complex and an electrophile.

To avoid solubility issues, the study was performed with 1,10-phenanthroline (phen) as a ligand. The sulfinate dimer [(phen)Cu(SO₂Tol)]₂ (**4**) was synthesized from (CuOtBu)₄, treated with 1,10-phenanthroline, followed by 4-toluenesulfonic acid in THF at room temperature (Scheme 4b). Complex **4** crystallized in hot acetonitrile in the form of a dimer with (μ-SO₂Ar-κO:κS')-coordination, in accordance with its infrared spectrum, and as already observed for some Pd(II)-¹⁹ and Cu(II)-sulfinate²⁰ complexes. The stoichiometric coupling of **4** with 2-(allyloxy)iodobenzene (**5**) led to the exclusive formation of sulfone **6a** in 79% yield (Scheme 4c), providing further evidence for an ionic mechanism. In the case of a radical mechanism, the fast cyclization of the putative aryl radical intermediate would indeed have generated cyclized products such as **6b** or **6c**.²¹⁻²³



Scheme 4. (a) Proposed pathway for the mechanism of the reaction. (b) Synthesis of $[(\text{phen})\text{Cu}(\text{SO}_2\text{-C}_6\text{H}_4\text{-CH}_3)]_2$ (**4**). (c) Mechanistic control experiments: radical clock experiment with 2-(allyloxy)iodobenzene and substrate-competition study between 1-bromonaphthalene and 4-chlorobenzonitrile. Yields measured by ¹H NMR (internal standard: mesitylene).

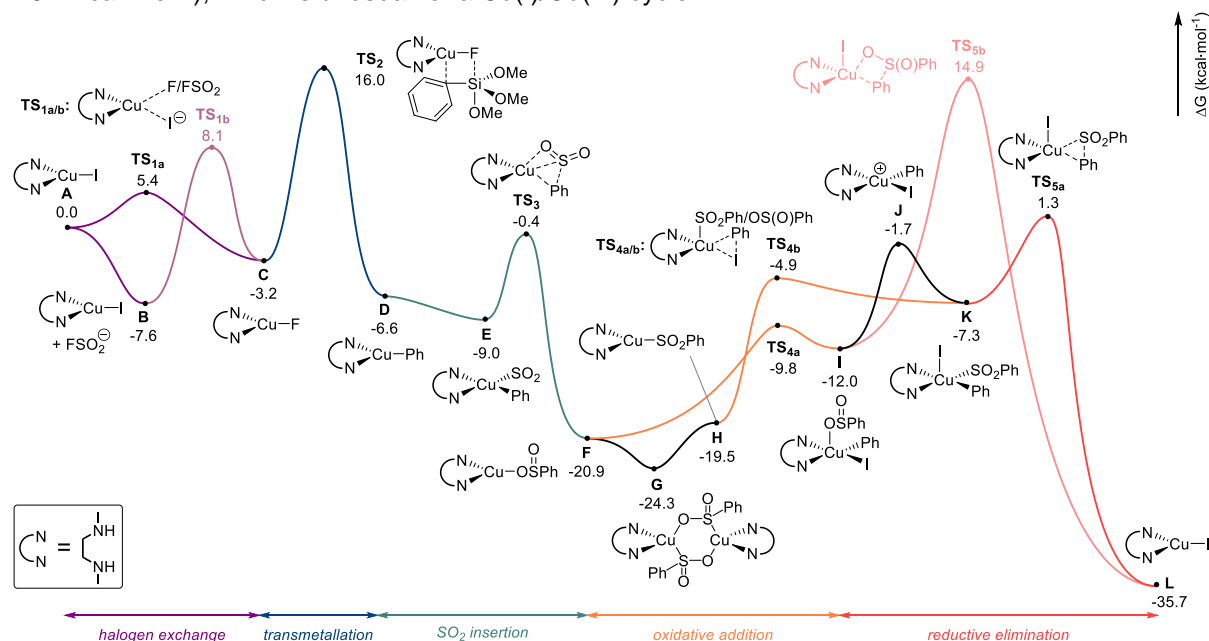
A last control experiment withstanding a concerted cleavage of the electrophile is the competition coupling between copper–sulfinate **4** and two electrophiles: 1-bromonaphthalene (**7**) and 4-chlorobenzonitrile (**8**) (Scheme 4c). Naphthalene **9** is expected to be the major product in the case of an ionic mechanism. In contrast, if the reaction occurs *via* a one-electron process, the predominant product should be **10**, since **8** has a higher reduction potential (-2.03 V against -2.17 V for **7** versus SCE in DMF).^{23, 24} The near exclusive formation of 1-(phenylsulfonyl)naphthalene (**9**, 51%) further supports a two-electron mechanism.

These first experimental observations also validate the possible involvement of a Cu(I) sulfinate complex. To propose a complete plausible mechanism for the formation of diarylsulfones and understand which step is controlling its kinetics, DFT calculations were carried out (Scheme 5).

In presence of one equivalent of fluoride anions, a fluoride copper species is likely to be formed (**A**→**C**, $\Delta G = -3.2$ kcal·mol⁻¹) to then proceed to the transmetalation with the organosilane.²⁵ Although it has already been reported and experimentally evidenced that a stable FSO₂⁻ anion is formed from DABSO and fluoride anions,^{7, 26} this adduct can also serve as a fluoride transfer agent to generate a copper(I) fluoride complex. As regards the transmetalation between the silane and the Cu–F species, computational results show a more favored transition state when the fluoride anion is in axial position on the silicon center (**C**→**D**, $\Delta G^\ddagger(\text{TS}_2) = 19.2$ kcal·mol⁻¹ vs $\Delta G^\ddagger(\text{TS}_2') = 24.9$ kcal·mol⁻¹ for the equatorial position, see ESI). After coordination to the metallic center (**D**→**E**, $\Delta G = -3.4$ kcal·mol⁻¹), SO₂ undergoes an exergonic 1,2-insertion in the Cu–C bond, in accordance with the S_E2 mechanism reported in the literature (**E**→**F**, $\Delta G = -11.9$ kcal·mol⁻¹; $\Delta G^\ddagger(\text{TS}_3) = 8.6$ kcal·mol⁻¹).^{27–30} While usually an apparent 1,1-insertion is observed because of the rearrangement to the more thermodynamically favored S-sulfinate,^{31, 32} the O-sulfinate is here found to be lower in energy. However, the dimer with S,O-coordination **G** is the lowest energy isomer, in agreement with the obtained crystal structure of compound **4** (see SI for details). The coupling with the electrophile can then take place from both O- or S-coordinated species. As experimental studies suggested, the ionic mechanism was considered for this step. The oxidative addition is more favored with an O-coordination of the sulfinate (From **G**, $\Delta G^\ddagger(\text{TS}_{4a}) = 14.5$ kcal·mol⁻¹ against $\Delta G^\ddagger(\text{TS}_{4b}) = 19.4$ kcal·mol⁻¹ for the S-coordination). However, by contrast, the 4-center reductive elimination resulting from O-coordination lies at $+39.2$ kcal·mol⁻¹ (**TS_{5b}**)

with respect to the copper-sulfinate dimer **G** and has to be discarded in favor of **TS_{5a}** associated with S-coordination.

From this mechanism, the reductive elimination step seems to be kinetically determining ($\Delta G^\ddagger(\text{TS}_{5a}) = 25.6 \text{ kcal}\cdot\text{mol}^{-1}$ with respect to **G**), which could explain the higher yields obtained with electrophiles bearing electron-donating groups (**3a–g**, 87–60%) than with withdrawing one (**3i–p**, 64–35%). Besides, the low barrier associated with the insertion of sulfur dioxide justifies the absence of any direct C–C cross-coupling and the efficient conversion of stoichiometric quantities of DABSO. Finally, it is noteworthy that the reductive elimination lies somewhat higher than the oxidative addition (here $\Delta\Delta G^\ddagger = 6.4 \text{ kcal}\cdot\text{mol}^{-1}$), which is unusual for a Cu(I)/Cu(III) cycle.¹⁵



Scheme 5. DFT-calculated energy profile for the reaction. Level of theory: B3LYP-D3/6-311+G(d) (C, H, O, N, F), 6-311++G(d,p) (S, Si), SDD for Cu and def2-TZVP for I, PCM was used for CH_3CN solvation. Given values correspond to Gibbs free energies (in $\text{kcal}\cdot\text{mol}^{-1}$). Since SO_2 decoordinates from DABCO without any transition state, free SO_2 was considered to compute transition states.

Conclusion

In conclusion, we have described an efficient route to diaryl sulfones from readily available and easy to handle organosilanes, aryl halides and DABSO. This air-tolerant process is attractive as it involves inexpensive $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$ and dmeda, and is compatible with a variety of functional groups on both coupling partners. Both experimental and theoretical studies support the mechanistic hypotheses for this process of a non-radical Hiyama cross-coupling with fast insertion of SO_2 into a Cu(I)–Ar intermediate.

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