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Fluoro Silane Activation by Pd/Ni→Si–F→Lewis Acid Interaction: an Entry to Catalytic Sila-Negishi Coupling

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Abstract:

A new mode of bond activation involving M→Z interactions is disclosed. Coordination to transition metals as π -acceptor ligands was found to enable the activation of fluoro silanes, opening the way to the first transition metal-catalyzed Si–F bond activation. Using phosphines as directing groups, sila-Negishi couplings were developed by combining Pd and Ni complexes with external Lewis acids such as MgBr₂. Several key catalytic intermediates have been authenticated spectroscopically and crystallographically. Combined with DFT calculations, all data support cooperative activation of the fluoro silane via Pd/Ni→Si–F→Lewis acid interaction with conversion of the Z-type fluoro silane ligand into an X-type silyl moiety.

The recent discovery that main-group based Lewis acids are able to act as σ -acceptor Z-type ligands for transition metals has opened new avenues in organometallic chemistry.¹ The resulting $M \rightarrow Z$ interactions offer new ways to tune the properties of metal centers and the Lewis acid moiety can actively participate in bond activation *via* so-called metal-ligand cooperation.² To date, Z-type ligands have been mostly used to modulate the Lewis acidity of electrophilic metal centers (Figure 1A). This approach has been employed to activate $\sigma(C=C)$ bonds towards cycloisomerization and nucleophilic addition.³ Recently, it was further extended to C–H activation and applied in catalysis to the amidation of arenes featuring *N* directing groups.⁴ Addition of E–H bonds across $M \rightarrow Z$ interactions also attracts much interest and offers interesting perspectives in catalysis (Figure 1B).^{5,6} Besides the development of these two scenarios, efforts are made to discover new modes of cooperation between transition metals and Lewis acids, such as the one involving hydride insertion into a $Pd \rightarrow B$ interaction we recently reported and applied to the catalytic hydro/deutero-dechlorination of arenes (Figure 1C).⁷

In this work, we reasoned that the ability of fluoro silanes to coordinate as Z-type ligands⁸ may open a new approach of bond activation (Figure 1D).^{9,10} In this case, the transition metal acts as a Lewis base and $M \rightarrow \sigma^*(Si-F)$ donation weakens the Si–F bond. Synergistic action of an external Lewis acid was envisioned to enable bond cleavage and converts the Z-type fluoro silane ligand into an X-type silyl moiety which may then be engaged in Si–C cross-coupling.¹¹ Note that the conversion of Z-type ligands into X and L-type ligands has been previously reported by Gabbaï with antimony.¹²

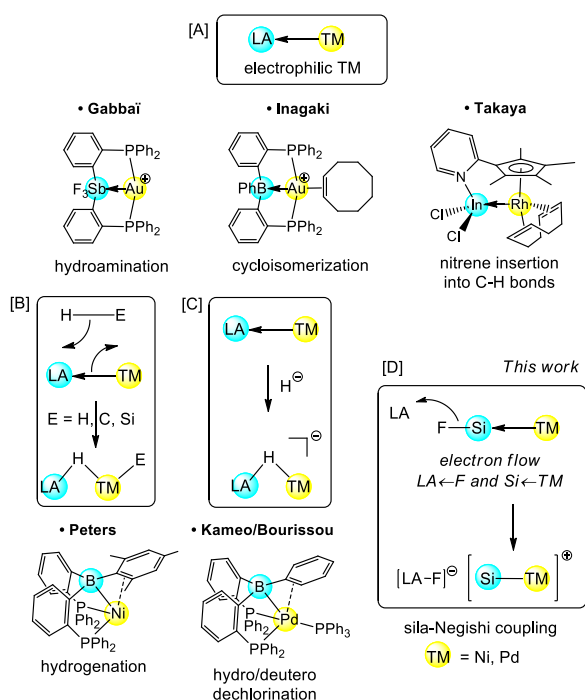
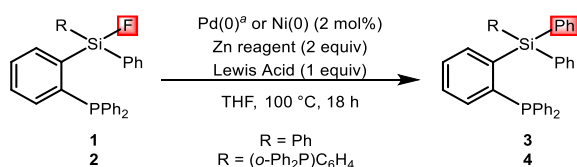


Figure 1. Representative modes of bond activation involving $M \rightarrow Z$ interactions, with selected examples of complexes applied in catalysis.

Here, we demonstrate the feasibility and catalytic applicability of such an approach. It enables to achieve for the first time catalytic cross-coupling from fluoro silanes. The use of Si-based electrophiles in Si–C cross-couplings has recently witnessed an upsurge of interest, and spectacular achievements have been reported with Si–I, Si–OTf and Si–Cl substrates.¹³ The activation of Si–F bonds is more challenging due to their very high bond strengths.¹⁴

The known ability of phosphines to support M→Si–F interactions⁸ prompted us to use fluoro silanes **1-2** as substrates (Table 1). Under typical conditions for Negishi-type coupling, using ZnPh₂, no reaction occurred from **1** (Entry 1). Inspired by the positive influence of lithium iodide noticed by Ohashi and Ogoshi in the Pd-catalyzed arylation of tetrafluoroethylene (C–F bond activation and coupling with ZnAr₂),¹⁵ the addition of various lithium and magnesium salts was tested.¹⁶ Gratifyingly, the desired coupling product **3** was formed in 29% yield in the presence of LiI (Entry 4) and quantitative reactions were observed using MgBr₂ or MgI₂ (Entries 7 and 8). The addition of B(C₆F₅)₃ also enables the catalysis to proceed (Entry 9),¹⁷ while no reaction was observed with BPh₃ (Entry 10). Even magnesium salts generated *in situ* upon formation of ZnPh₂ (by reacting ZnCl₂ with PhMgBr) proved efficient (Entry 11). Nickel catalysis was also possible under the same conditions, with Ni(cod)₂ as precursor. *In situ* generation of the aryl zinc species (from ZnCl₂ + 2 PhMgBr) and the use of B(C₆F₅)₃ gave the best result in this case (Entry 13). The diphosphine fluoro silane **2** was found to undergo Si–F activation and Si–Ph coupling too (Entries 14–17). It is worth noting that the catalysis worked as well (Pd) or even better (Ni) with only one phosphine anchoring group. Conversely, no Si–C coupling was observed starting from Ph₃SiF under the same conditions, substantiating the crucial influence of the phosphine directing groups.

TABLE 1. Screening of conditions for the sila-Negishi coupling of fluoro silanes 1-2.



Entry	Substrate	Catalyst ^a	Zn	Yield ^b
1	1	Pd ₂ (dba) ₃	ZnPh ₂	0
2	1	Pd ₂ (dba) ₃	ZnPh ₂	7
3	1	Pd ₂ (dba) ₃	ZnPh ₂	7
4	1	Pd ₂ (dba) ₃	ZnPh ₂	29
5	1	Pd ₂ (dba) ₃	ZnPh ₂	3
6	1	Pd ₂ (dba) ₃	ZnPh ₂	4
7	1	Pd ₂ (dba) ₃	ZnPh ₂	99
8	1	Pd ₂ (dba) ₃	ZnPh ₂	99
9	1	Pd ₂ (dba) ₃	ZnPh ₂	82
10	1	Pd ₂ (dba) ₃	ZnPh ₂	0
11	1	Pd ₂ (dba) ₃	ZnCl ₂ + 2	99 ^c
12	1	Ni(COD) ₂	ZnCl ₂ + 2	65
13	1	Ni(COD) ₂	ZnCl ₂ + 2	96
14	2	Pd ₂ (dba) ₃	ZnCl ₂ + 2	97
15	2	Pd(PPh ₃) ₄	ZnCl ₂ + 2	76
16	2	Ni(COD) ₂	ZnCl ₂ + 2	25
17	2	Ni(COD) ₂	ZnCl ₂ + 2	21
18	2	9	ZnCl ₂ + 2	66
19	2	11 ^{Pd-Br}	ZnCl ₂ + 2	84

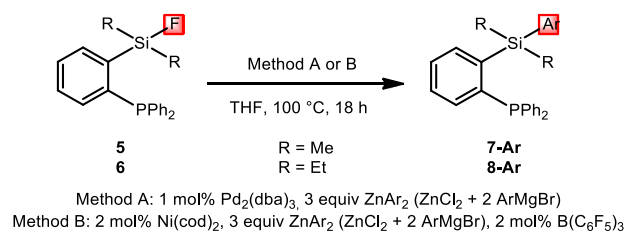
^a1 mol% catalyst for Pd₂(dba)₃. ^bDetermined by ³¹P NMR.

^c93% isolated yield.

Next, the scope of the Pd- and Ni-catalyzed reactions was explored employing the optimal conditions determined before (Table 1, Entries 11 and 13).¹⁶ As shown in Table 2, very high conversions were achieved with the fluoro silanes **5** and **6** featuring alkyl substituents at silicon (R = Me, Et). The reaction works with a variety of diaryl zinc reagents. It proceeds smoothly with electron-withdrawing (CF₃, F, Cl) as well as electron-donating substituents (OMe, NMe₂), and *ortho*-substituents are tolerated. In all cases, very high yields were observed with 2–4 mol% Pd (>90%).

Comparatively, nickel catalysis was less effective but nevertheless gave the coupling products in moderate to excellent yields (51-94%), except for the zinc reagent bearing an *o*-Me₂N substituent.

TABLE 2. Scope of zinc reagents for the sila-Negishi coupling of fluoro silanes 5-6.^a



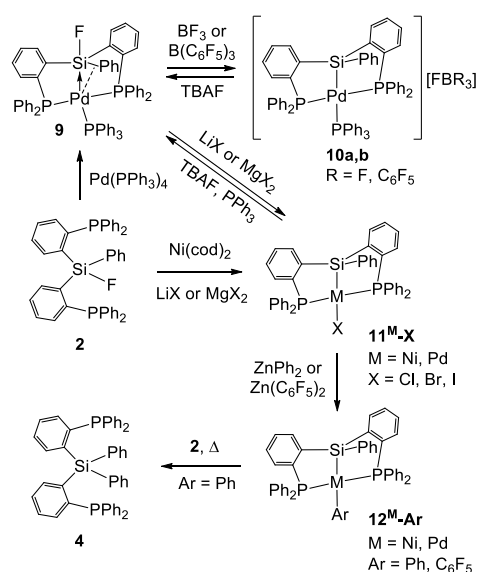
Ar =	R = Et (6→8)	
 Method A 97% (96%) Method B 94% 7-Ph	 96% (89%) ^b 91% ^b 8-Ph	 95% (91%) ^b 60% ^c 7-Naph
 Method A 97% (84%) ^d Method B 76% ^{c,e} 7-p-Anisyl	 94% (81%) ^d 93% ^b 7-o-Anisyl	 91% (53%) ^{b,d} 22% ^{c,e} 7-(o-Me₂N)C₆H₄
 Method A 96% (59%) ^{b,d} Method B 51% ^{c,e} 7-(p-CF₃)C₆H₄	 98% (65%) ^d 69% ^{c,e} 7-(o-CF₃)C₆H₄	 96% (73%) ^b 80% ^{c,e} 7-(3-Cl-4-F)C₆H₃

^aR = Me (5→7), unless otherwise stated; spectroscopic yields, as determined by ³¹P NMR spectroscopy (isolated yields are given in parentheses). ^b5 equiv ZnR₂. ^c10 equiv ZnR₂. ^d2 mol% Pd₂(dba)₃. ^e5 mol% Ni(cod)₂, 5 mol% B(C₆F₅)₃.

To shed light into the involved catalytic cycle and decipher the way the Si–F bond is activated, a series of stoichiometric reactions were performed with the diposphine fluoro silane **2** (Scheme 1). The two coordinating arms were hoped to stabilize some reactive intermediates and facilitate their characterization. First, complex **9** was obtained in excellent yield (91%) by phosphine exchange from Pd(PPh₃)₄.¹⁶ As shown by X-ray diffraction analysis (Figure 2a), the Pd center adopts a tetrahedral arrangement with the fluoro silane moiety coordinated *via* weak Pd⋯Si and Pd⋯C_{*ipso*} contacts.¹⁸ Most diagnostic are the relatively short Pd–Si distance [2.9770(8) Å, as to compared with the sum of van der Waals radii at 4.15 Å¹⁹], the elongation of the Si–F bond [1.6339(17) vs 1.606(2) Å in {(*o*-Ph₂P)C₆H₄}₃SiF] and the trigonal pyramidal environment around Si [the sum of C–Si–C angles = 352.36(21)°, Pd→Si–F bond angle = 161.67(8)°]. The presence of substantial Pd→Si–F interaction in **9** was further supported by ²⁹Si NMR spectroscopy²⁰ and DFT calculations.¹⁶

Remarkably, addition of LiX (X = Cl, Br, I) and MgX₂ (X = Cl, Br) salts at room temperature spontaneously induced Si–F bond cleavage and afforded the corresponding square-planar (diphosphine-silyl)(halogeno)palladium(II) complexes **11**^{Pd}-X (X = Cl, Br, I), all authenticated crystallographically (Figure 2b).¹⁶ Similarly, reacting **9** with the boranes BF₃ and B(C₆F₅)₃²¹ at room temperature rapidly and cleanly led to the cationic silyl complex [(PSiP)Pd(PPh₃)]⁺[FBX₃]⁻ **10a,b**, whose structure was authenticated by X-ray diffraction after counter-anion exchange (complex **10c**, Figure 2c, BPh₄ salt). Of note, complexes **11**^{Pd}-Cl and **10c** readily react with MgBr₂ to afford **11**^{Pd}-Br, making the latter complex a likely intermediate of the catalytic coupling. Interestingly, the conversion

between the Z-type fluoro silane and X-type silyl moieties is reversible. Treatment of **11**^{Pd}-Br with tetrabutylammonium fluoride (TBAF) in the presence of PPh₃ regenerated the silane complex **9**.



Scheme 1. Pd and Ni complexes deriving from the diphosphine fluoro silane **2**.

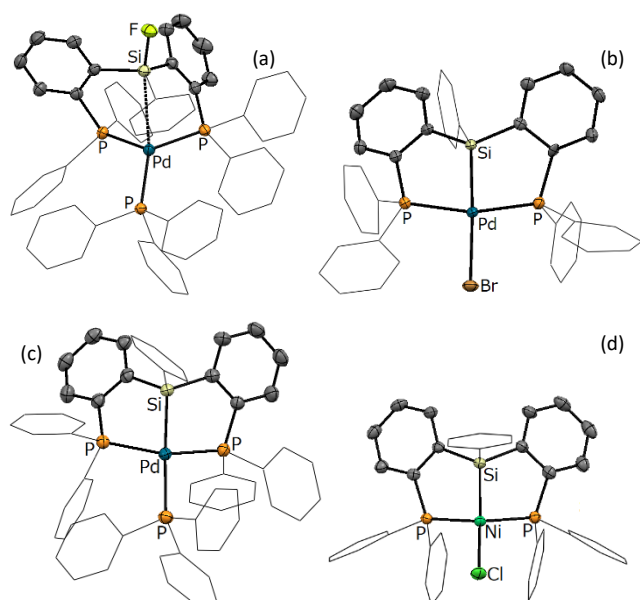


Figure 2. Molecular structures of complexes **9** (a), **11**^{Pd}-Br (b), **10c** (c) and **11**^{Ni}-Cl (d). Thermal ellipsoids at 40% probability. The BPh₄ anion and hydrogen atoms are omitted, the phenyl groups at P and Si are simplified for clarity.

Not surprisingly, related Ni species were more difficult to study. A complex akin to **9** could be detected by NMR spectroscopy upon reacting **2** with Ni(COD)₂ in the presence of DMAP.¹⁶ The feasibility and easiness of Si–F cleavage by cooperation between nickel and Lewis acids could also be substantiated. Indeed, addition of lithium or magnesium salts to a 1:1 mixture of **2** and Ni(COD)₂ resulted in the fast and selective formation of the corresponding (diphosphine-silyl)(halogeno)nickel(II) complexes **11**^{Ni}-X (X = Cl, Br, I). The structure and square-planar arrangement of complex **11**^{Ni}-Cl were confirmed crystallographically (Figure 2d).¹⁶

The Si–F bond cleavage at Pd / Ni assisted by BF₃ was studied computationally.¹⁶ The key structures are depicted in Figure 3 for Pd. The Si–F bond significantly elongates upon interaction with BF₃ (from

1.693 to 2.012 Å) while the Pd–Si distance substantially shortens (from 2.770 to 2.490 Å). Ultimately, BF₃ abstracts the fluoride. The electron flow associated with the M→Si–F→BF₃ interaction is clearly apparent from the NBO analyses¹⁶ and the intrinsic bond orbitals (IBOs). The Pd→silane dative interaction turns into a covalent Pd–silyl bond while the $\sigma(\text{Si–F})$ bond evolves into a $\sigma(\text{B–F})$ bond. Despite the strength of the Si–F bond, the concomitant participation of Pd / Ni and BF₃ makes its cleavage very easy, with an activation barrier of only 3–5 kcal/mol.¹⁶

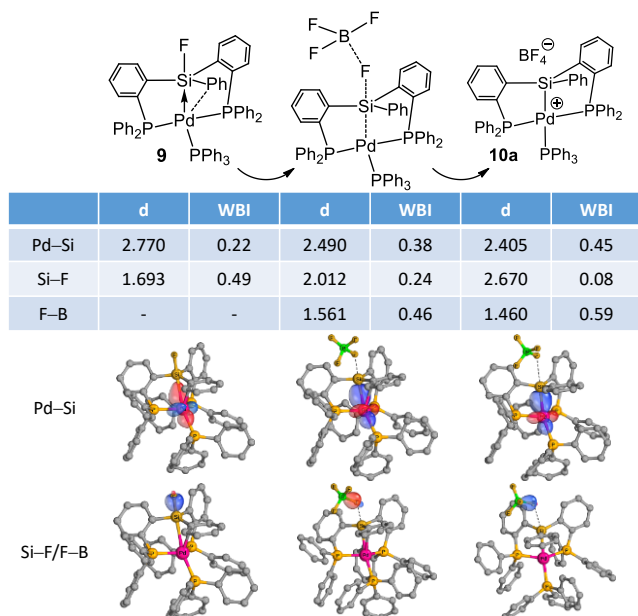


Figure 3. Key structures computed for the Si–F bond cleavage mediated by Pd and BF₃. Selected distances (in Å), Wiberg bond indexes (WBI) and intrinsic bond orbitals (IBOs).¹⁶

The transmetalation and reductive elimination steps were studied then. Complex **11^{Pd}-Br** was found to react smoothly with ZnPh₂ to give the corresponding phenyl complex (PSiP)Pd(Ph) **12^{Pd}-Ph**, obtained as a 2:1 mixture with **11^{Pd}-Br** using 10 equiv. of ZnPh₂ (1:3 ratio with 3 equiv. of ZnPh₂). The structure of the analogous pentafluorophenyl complex **12^{Pd}-C₆F₅** prepared with Zn(C₆F₅)₂ was unambiguously authenticated by X-ray diffraction analysis.¹⁶ The nickel complex **11^{Ni}-Br** also readily undergoes transmetalation when reacted with 10 equiv. of ZnPh₂. The phenyl complex (PSiP)Ni(Ph) **12^{Ni}-Ph** was obtained quantitatively in this case.¹⁶ Finally, thermolysis of both complexes **12^{Pd}-Ph** and **12^{Ni}-Ph** at 60–80 °C in the presence of **2** afforded the Si–Ph coupling product **4** within 2–16 hours. In line with the rather forcing conditions required to achieve these reductive eliminations (compared to the Si–F bond cleavage), the activation barriers computed by DFT are relatively large (20–23 kcal/mol).¹⁶

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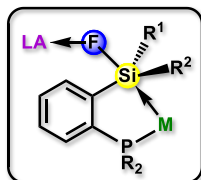
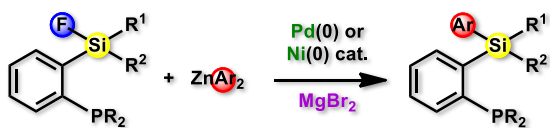
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(20) The ²⁹Si NMR signal is shifted to higher field and the *J*_{Si-F} coupling constant is reduced upon coordination of **2** to Pd, in line with that reported previously for related gold complexes.^{8a,b}

(21) For fluoride abstraction from a Pt→Sb–F complex with B(C₆F₅)₃, see ref. 10d.

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Entry for the Table of Contents



- ⊗ $\text{M} \rightarrow \text{Si}-\text{F} \rightarrow \text{LA}$ electron flow
- ⊗ M / LA cooperation for easy $\text{Si}-\text{F}$ activation
- ⊗ from Z-type fluoro silane to X-type silyl
- ⊗ catalytic $\text{Si}-\text{F}$ arylation

