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J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/jacs.0c04690 • Publication Date (Web): 24 Jul 2020

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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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Supporting Information Placeholder

ABSTRACT: *A new mode of bond activation involving M→Z interactions is disclosed. Coordination to transition metals as σ-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 $MgBr_2$. 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→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 π(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→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→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 ligands[8] 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→σ*(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]

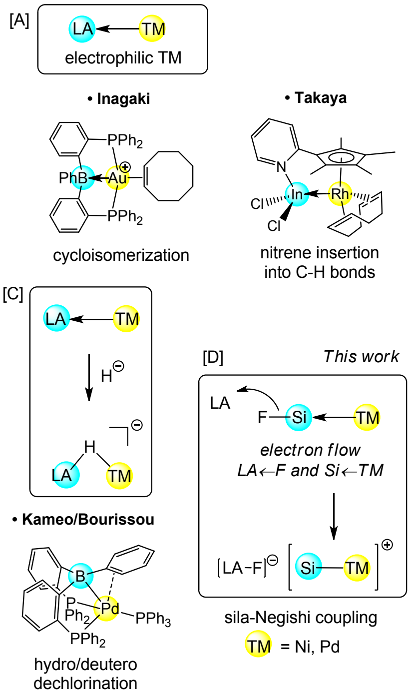
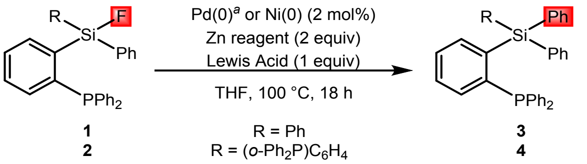


Figure 1. Representative modes of bond activation involving M→Z interactions, with selected examples of complexes applied in catalysis.

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 interactions[8] prompted us to use fluoro silanes **1-2** as substrates (Table 1). Under typical conditions for Negishi-type coupling, using $ZnPh_2$, 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 $ZnAr_2$),[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 $MgBr_2$ or MgI_2 (Entries 7 and 8). The addition of $B(C_6F_5)_3$ also enables the catalysis to proceed (Entry 9),[17] while no reaction was observed with BPh_3 (Entry 10). Even magnesium salts generated *in situ* upon formation of $ZnPh_2$ (by reacting $ZnCl_2$ 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 $ZnCl_2$ + 2 PhMgBr) and the use of $B(C_6F_5)_3$ 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 Ph_3SiF 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.

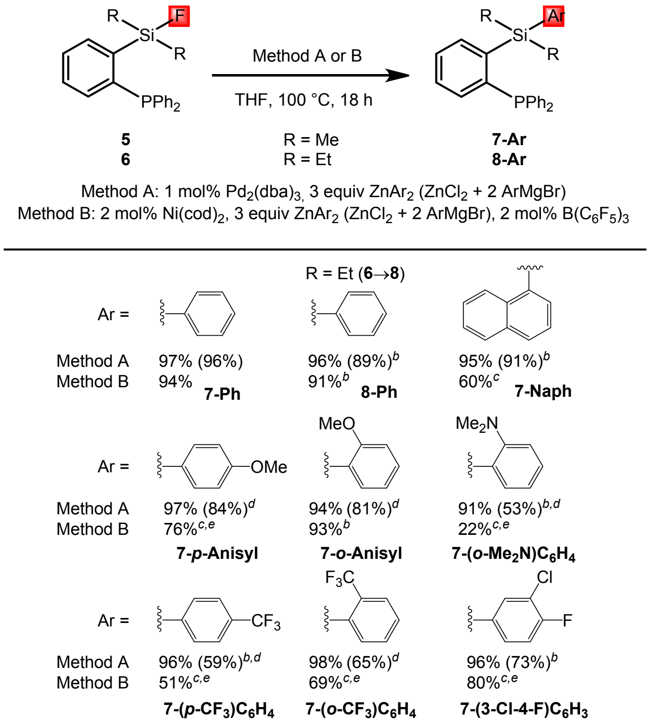


Entry	Substrate	Catalyst[a]	Zn reagent, LA additive	Yield[b]
1	**1**	$Pd_2(dba)_3$	$ZnPh_2$, none	0
2	**1**	$Pd_2(dba)_3$	$ZnPh_2$, LiCl	7
3	**1**	$Pd_2(dba)_3$	$ZnPh_2$, LiBr	7
4	**1**	$Pd_2(dba)_3$	$ZnPh_2$, LiI	29
5	**1**	$Pd_2(dba)_3$	$ZnPh_2$, Li(OTf)	3
6	**1**	$Pd_2(dba)_3$	$ZnPh_2$, $MgCl_2$	4
7	**1**	$Pd_2(dba)_3$	$ZnPh_2$, $MgBr_2$	99
8	**1**	$Pd_2(dba)_3$	$ZnPh_2$, MgI_2	99
9	**1**	$Pd_2(dba)_3$	$ZnPh_2$, $B(C_6F_5)_3$	82
10	**1**	$Pd_2(dba)_3$	$ZnPh_2$, BPh_3	0
11	**1**	$Pd_2(dba)_3$	$ZnCl_2$ + 2 PhMgBr	99[c]
12	**1**	$Ni(COD)_2$	$ZnCl_2$ + 2 PhMgBr	65
13	**1**	$Ni(COD)_2$	$ZnCl_2$ + 2 PhMgBr, $B(C_6F_5)_3$	96
14	**2**	$Pd_2(dba)_3$	$ZnCl_2$ + 2 PhMgBr	97
15	**2**	$Pd(PPh_3)_4$	$ZnCl_2$ + 2 PhMgBr	76
16	**2**	$Ni(COD)_2$	$ZnCl_2$ + 2 PhMgBr	25
17	**2**	$Ni(COD)_2$	$ZnCl_2$ + 2 PhMgBr, $B(C_6F_5)_3$	21
18	**2**	**9**	$ZnCl_2$ + 2 PhMgBr	66
19	**2**	**11^{Pd}-Br**	$ZnCl_2$ + 2 PhMgBr	84

[a] 1 mol% catalyst for $Pd_2(dba)_3$. [b] Determined by ^{31}P NMR. [c] 93% 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 substitutents at silicon (R = Me, Et). The reaction works with a variety of diaryl zinc reagents. It proceeds smoothly with electron-withdrawing (CF_3, F, Cl) as well as electron-donating substituents (OMe, NMe_2), 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*-Me_2N substituent.

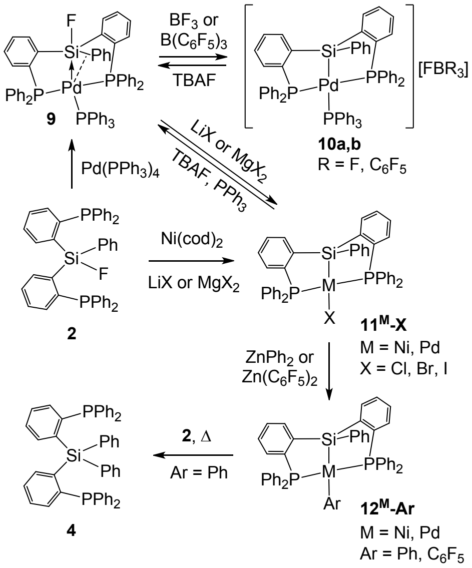
TABLE 2. Scope of zinc reagents for the sila-Negishi coupling of fluoro silanes 5-6.[a]



[a] R = Me (**5**→**7**), unless otherwise stated; spectroscopic yields, as determined by ^{31}P NMR spectroscopy (isolated yields are given in parentheses). [b] 5 equiv ZnR_2. [c] 10 equiv ZnR_2. [d] 2 mol% $Pd_2(dba)_3$. [e] 5 mol% $Ni(cod)_2$, 5 mol% $B(C_6F_5)_3$.

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 diphosphine 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 $Pd(PPh_3)_4$.[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 Å[19]], the elongation of the Si–F bond [1.6339(17) *vs* 1.606(2) Å in $\{(o\text{-}Ph_2P)C_6H_4\}_3SiF$] 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 ^{29}Si NMR spectroscopy[20] and DFT calculations.[16]

Remarkably, addition of LiX (X = Cl, Br, I) and MgX$_2$ (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 BF$_3$ and B(C$_6$F$_5$)$_3$[21] at room temperature rapidly and cleanly led to the cationic silyl complex [(PSiP)Pd(PPh$_3$)][FBX$_3$] **10a,b**, whose structure was authenticated by X-ray diffraction after counter-anion exchange (complex **10c**, Figure 2c, BPh$_4$ salt). Of note, complexes **11^{Pd}-Cl** and **10c** readily react with MgBr$_2$ 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 PPh$_3$ regenerated the silane complex **9**.



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

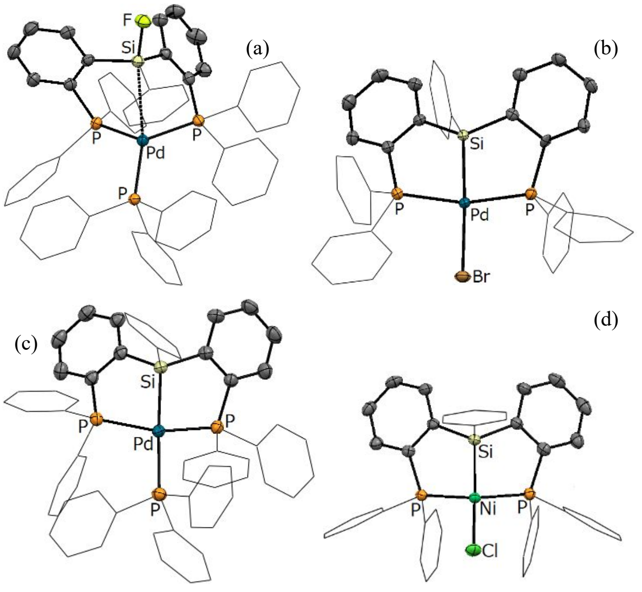
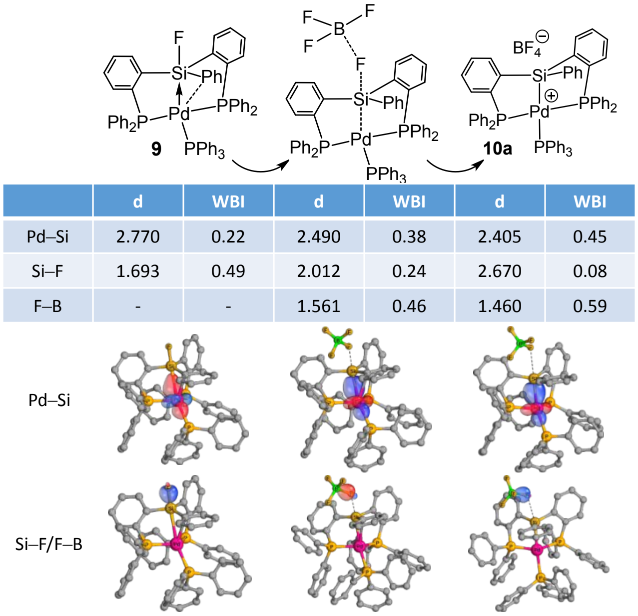


Figure 2. Molecular structures of complexes **9** (a), **11^{Pd}-Br** (b), **10c** (c) and **11^{Ni}-Cl** (d). Thermal ellipsoids at 40% probability. The BPh$_4$ anion and hydrogen atoms are omitted, the phenyl groups at P and Si are simplified for clarity.

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 BF$_3$ was studied computationally.[16] The key structures are depicted in Figure 3 for Pd. The Si–F bond significantly elongates upon interaction with BF$_3$ (from 1.693 to 2.012 Å) while the Pd–Si distance substantially shortens (from 2.770 to 2.490 Å). Ultimately, BF$_3$ abstracts the fluoride. The electron flow associated with the M→Si–F→BF$_3$ interaction is clearly apparent from the NBO analyses[16] and the intrinsic bond orbitals (IBOs). The Pd→silane dative interaction turns into a covalent Pd–silyl bond while the σ(Si–F) bond evolves into a σ(B–F) bond. Despite the strength of the Si–F bond, the concomitant participation of Pd / Ni and BF$_3$ makes its cleavage very easy, with an activation barrier of only 3–5 kcal/mol.[16]



	d	WBI	d	WBI	d	WBI
Pd–Si	2.770	0.22	2.490	0.38	2.405	0.45
Si–F	1.693	0.49	2.012	0.24	2.670	0.08
F–B	-	-	1.561	0.46	1.460	0.59

Figure 3. Key structures computed for the Si–F bond cleavage mediated by Pd and BF$_3$. 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 ZnPh$_2$ 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 ZnPh$_2$ (1:3 ratio with 3 equiv. of ZnPh$_2$). The structure of the analogous pentafluorophenyl complex **12^{Pd}-C$_6$F$_5$** prepared with Zn(C$_6$F$_5$)$_2$ 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 ZnPh$_2$. 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]

Based on all experimental and computational data, the sila-Negishi coupling is proposed to occur following the 4-step catalytic cycle disclosed in Figure 4 for the diphosphine fluoro silane **2**: (*i*) P-directed coordination of the fluoro-silane to Pd as a σ-acceptor ligand, (*ii*) Si–F bond cleavage by cooperation between Pd and the Lewis acid, (*iii*) transmetalation by $ZnPh_2$; (*iv*) reductive elimination and ligand exchange at Pd to release the coupling product **4** and turnover. Of note, the isolated Pd complexes **9** and **11^{Pd}-Br** showed catalytic activities comparable to $Pd(PPh_3)_4$ (Table 1, Entries 18-19), supporting their relevance. In addition, direct transmetalation from Zn to Si, once the fluoro-silane is coordinated to Pd as a Z-type ligand, seems unlikely. Indeed, no reaction was observed between complex **9** and $ZnPh_2$. The presence of a Lewis acid and activation of the Si–F bond are required. Note also that ^{31}P NMR monitoring a catalytic reaction performed with the fluoro silane **2** as substrate and $Pd(PPh_3)_4$ as catalyst (reaction conditions of entry 15, Table 1) showed the presence of complexes **11^{Pd}-Br** and **12^{Pd}-Ph** in about 3:1 ratio as resting states.

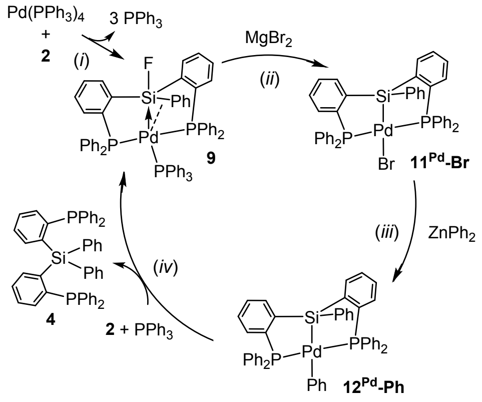


Figure 4. Plausible catalytic cycle for the Si–F bond activation / arylation of **2** co-catalyzed by $Pd(PPh_3)_4$ and $MgBr_2$ (as representative examples).

In conclusion, the coordination of fluoro silanes as σ-acceptor ligands was shown to enable Si–F bond activation under mild conditions. When combined with external Lewis acids such as $MgBr_2$, palladium and nickel are able to readily cleave Si–F bonds thanks to Pd/Ni→Si–F→LA interactions. The process was turned to catalysis and sila-Negishi cross-coupling starting from fluoro silanes was actually achieved for the first time. The activation of Si–F bonds is of major interest because many transformations involving silicon derivatives end in fluoro silanes (the strength of the Si–F bond being used as a driving force). Developing catalytic Si–C cross-couplings from fluoro silanes may enable to recycle Si by-products and contribute to circular silicon chemistry.[22]

The new mode of activation evidenced here for Si–F bonds expands further the chemistry arising from M→Z interactions and may be generalized to other directing groups and other strong polar bonds.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental methods and DFT calculations (PDF)
Crystallographic data (CIF)

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ACKNOWLEDGMENT

This work was supported by Grant-in-Aid for Scientific Research (C) (No. 18K05151 and 18K05152) of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. H.K. acknowledges the financial support from the Tonen general sekiyu research/development encouragement & scholarship foundation. The Centre National de la Recherche Scientifique (CNRS), the Université Paul Sabatier (UPS) and the Agence Nationale de la Recherche (ANR-15-CE07-0003) are acknowledged for financial support of this work. The "Direction du Numérique" of the Université de Pau et des Pays de l'Adour and CINES under allocation A007080045 made by Grand Equipement National de Calcul Intensif (GENCI) are acknowledged for computational facilities.

REFERENCES

(1) (a) Amgoune, A.; Bourissou, D. σ-Acceptor, Z-type Ligands for Transition Metals. *Chem. Commun.* **2011**, *47*, 859–871. (b) Bouhadir, G.; Bourissou, D. Coordination of Lewis Acids to Transition Metals: Z-type Ligands. In the *Structure and Bonding* book entitled "*The Chemical Bond III - 100 years old and getting stronger*" (Ed.: Mingos, D. M. P.) **2017**, *171*, pp. 141–201.

(2) (a) Bouhadir, G.; Bourissou, D. Complexes of Ambiphilic Ligands: Reactivity and Catalytic Applications. *Chem. Soc. Rev.* **2016**, *45*, 1065–1079. (b) You, F.; Gabbaï, F. P. Tunable σ-accepting, Z-type Ligands for Organometallic Catalysis. *Trend in Chem.* **2019**, *1*, 485–496.

(3) (a) Devillard, M.; Nicolas, E.; Appelt, C.; Backs, J.; Mallet-Ladeira, S.; Bouhadir, G.; Slootweg, J. C.; Uhl, W.; Bourissou, D. Novel Zwitterionic Complexes Arising from the Coordination of an Ambiphilic Phosphorus-Aluminum Ligand to Gold. *Chem Commun.* **2014**, *50*, 14805–14808. (b) Inagaki, F.; Matsumoto, C.; Okada, Y.; Maruyama, N.; Mukai, C. Air-Stable Cationic Gold(I) Catalyst Featuring a Z-Type Ligand: Promoting Enyne Cyclizations *Angew. Chem. Int. Ed.* **2015**, *54*, 818–822. (c) Yang, H.; Gabbaï, F. P. Activation of a Hydroamination Gold Catalyst by Oxidation of a Redox-Noninnocent Chlorostibine Z-Ligand *J. Am. Chem. Soc.* **2015**, *137*, 13425–13432. (d) You, D.; Gabbai, F. P. Activation of a Hydroamination Gold Catalyst by Oxidation of a Redox-Noninnocent Chlorostibine Z-Ligand *J. Am. Chem. Soc.* **2017**, *139*, 6843–6846. (e) Cammarota, R. C.; Vollmer, M. V.; Xie, J.; Ye, J.; Linehan, J. C.; Burgess, S. A.; Appel, A. M.; Gagliardi, L.; Lu, C. C. A Bimetallic Nickel–Gallium Complex Catalyzes CO_2 Hydrogenation via the Intermediacy of an Anionic d^{10} Nickel Hydride. *J. Am. Chem. Soc.* **2017**, *139*, 14244–14250. (f) Ueno, A.; Watanabe, K.; Daniliuc, C. G.; Kehr, G.; Erker, G. Unsaturated Vicinal Frustrated Phosphane/borane Lewis Pairs as Ligands in Gold(I) Chemistry. *Chem. Commun.* **2019**, 55, 4367–4370.

(4) Yamada, R.; Iwasawa, N.; Takaya, J. Rhodium-Catalyzed C-H Activation Enabled by an Indium Metalloligand. *Angew. Chem. Int. Ed.* **2019**, *58*, 17251–17254.

(5) (a) Harman, W. H.; Peters, J. C. Reversible H_2 Addition across a Nickel-borane Unit as a Promising Strategy for Catalysis. *J. Am. Chem. Soc.* **2012**, *134*, 5080–5082. (b) Harman, W. H.; Lin, T.-P.; Peters, J. C. A d^{10}

Ni–(H_2) Adduct as an Intermediate in H–H Oxidative Addition across a Ni–B Bond. *Angew. Chem. Int. Ed.* **2014**, *53*, 1081–1086. (c) MacMillan, S. N.; Harman, W. H.; Peters, J. C. Facile Si–H Bond Activation and Hydrosilylation Catalysis Mediated by a Nickel–borane Complex. *Chem. Sci.* **2014**, *5*, 590–597. (d) Cowie, B. E.; Emslie, D. J. H. Platinum Complexes of a Borane-Appended Analogue of 1,1'-Bis(diphenylphosphino)ferrocene: Flexible Borane Coordination Modes and in situ Vinylborane Formation. *Chem. Eur. J.* **2014**, *20*, 16899–16912. (e) Barnett, B. R.; Moore, C. E.; Rheingold, A. L.; Figueroa, J. S. Cooperative Transition Metal/Lewis Acid Bond-Activation Reactions by a Bidentate (Boryl)iminomethane Complex: A Significant Metal–Borane Interaction Promoted by a Small Bite-Angle LZ Chelate. *J. Am. Chem. Soc.* **2014**, *136*, 10262–10265. (f) Devillard, M.; Declercq, R.; Nicolas, E.; Ehlers, A. W.; Backs, J.; Saffon-Merceron, N.; Bouhadir, G.; Slootweg, J. C.; Uhl, W.; Bourissou, D. A Significant but Constrained Geometry Pt→Al Interaction: Fixation of CO_2 and CS_2, Activation of H_2 and $PhCONH_2$. *J. Am. Chem. Soc.* **2016**, *138*, 4917–4926. (g) Li, Y.; Hou, C.; Jiang, J.; Zhang, Z.; Zhao, C.; Page, A. J.; Ke, Z. General H_2 Activation Modes for Lewis Acid-Transition Metal Bifunctional Catalysts. *ACS Catal.* **2016**, *6*, 1655–1662. (h) Cammarota, R. C.; Lu, C. C. Tuning Nickel with Lewis Acidic Group 13 Metalloligands for Catalytic Olefin Hydrogenation. *J. Am. Chem. Soc.* **2015**, *137*, 12486–12489. (i) Ramirez, B. L.; Lu, C. C. Rare-Earth Supported Nickel Catalysts for Alkyne Semihydrogenation: Chemo- and Regioselectivity Impacted by the Lewis Acidity and Size of the Support. *J. Am. Chem. Soc.* **2020**, *142*, 5396−5407.

(6) Devillard, M.; Bouhadir, G.; Bourissou, D. Cooperation between Transition Metals and Lewis Acids: a New Way to Activate H_2 and H–E bonds. *Angew. Chem. Int. Ed.* **2015**, *54*, 730–732.

(7) Kameo, H.; Yamamoto, J.; Asada, A.; Nakazawa, H.; Bourissou, D. Palladium-Borane Cooperation: Evidence for an Anionic Pathway and its Application to Catalytic Hydro- / Deutero-dechlorination. *Angew. Chem. Int. Ed.* **2019**, *58*, 18783–18787.

(8) (a) Gualco, P.; Lin, T.-P.; Sircoglou, M.; Ladeira, S.; Bouhadir, G.; Pérez, L. M.; Amgoune, A.; Maron, L.; Gabbaï, F. P.; Bourissou, D. Gold→Silane and Gold→Stannane Complexes: Coordination of Saturated Molecules as σ-Acceptor Ligands. *Angew. Chem. Int. Ed.* **2009**, *48*, 9892–9895. (b) Gualco, P.; Mercy, M.; Ladeira, S.; Coppel, Y.; Maron, L.; Amgoune, A.; Bourissou, D. Hypervalent Silicon Compounds upon Coordination of Diphosphine-silanes to Gold. *Chem. Eur. J.* **2010**, *16*, 10808–10817. (c) Kameo, H.; Nakazawa, H. Saturated Heavier Group 14 Compounds as *σ*-Electron-Acceptor (Z-Type) Ligands. *Chem. Rec.* **2017**, *17*, 268–286.

(9) For transition metal-mediated Si–F activations involving Z-type coordination, see: (a) Kameo, H.; Sakaki, S. Activation of Strong Boron–Fluorine and Silicon–Fluorine *σ*-Bonds: Theoretical Understanding and Prediction. *Chem. Eur. J.* **2015**, *21*, 13588–13597. (b) Kameo, H.; Kawamoto, T.; Sakaki, S.; Bourissou, D.; Nakazawa, H. Transition-Metal-Mediated Cleavage of Fluoro-Silanes under Mild Conditions. *Chem. Eur. J.* **2016**, *22*, 2370–2375.

(10) For stoichiometric activations of B–F, P–F, Sb–F bonds at transition metals involving Z-type coordination, see: (a) Bauer, J.; Braunschweig, H.; Kraft, K.; Radacki, K. Oxidative Addition of Boron Trifluoride to a Transition Metal *Angew. Chem. Int. Ed.* **2011**, *50*, 10457–10460. (b) Bauer, J.; Braunschweig, H.; Dewhurst, R. D.; Radacki, K. Reactivity of Lewis Basic Platinum Complexes Towards Fluoroboranes *Chem. Eur. J.* **2013**, *19*, 8797–8805. (c) Arnold, N.; Bertermann, R.; Bickelhaupt, F. M.; Braunschweig, H.; Drisch, M.; Finze, M.; Hupp, F.; Poater, J.; Sprenger, J. A. P. Formation of a Trifluorophosphane Platinum(II) Complex by P−F Bond Activation of Phosphorus Pentafluoride with a Pt^0 Complex. *Chem. Eur. J.* **2017**, *23*, 5948–5952. (d) You, D.; Yang, H.; Sen, S.; Gabbaï, F. P. Modulating the σ-Accepting Properties of an Antimony Z-type Ligand via Anion Abstraction: Remote-Controlled Reactivity of the Coordinated Platinum Atom. *J. Am. Chem. Soc.* **2018**, *140*, 9644–9651.

(11) For reversible atom/group transfer between transition metals and silicon involving silyl and silane moieties, see also: (a) Takaya, J.; Iwasawa, N. Bis(*o*-phosphinophenyl)silane as a Scaffold for Dynamic Behavior of H–Si and C–Si Bonds with Palladium(0). *Organometallics* **2009**, *28*, 6636–6638. (b) Kirai, N.; Takaya, J.; Iwasawa, N. Two Reversible σ-Bond Metathesis Pathways for Boron−Palladium Bond Formation: Selective Synthesis of Isomeric Five-Coordinate Borylpalladium Complexes. *J. Am. Chem. Soc.* **2013**, *135*, 2493−2496. (c) Takaya, J.; Iwasawa, N. Silyl Ligand Mediated Reversible β-Hydrogen Elimination and Hydrometalation at Palladium *Chem. Eur. J.* **2014**, *20*, 1181 –11819. (d) Kim, J.; Kim, Y.-E.; Park, K.; Lee, Y. A Silyl-Nickel Moiety as a Metal–Ligand Cooperative Site. *Inorg. Chem.* **2019**, *58*, 11534–11545.

(12) (a) Ke, I.-S.; Jones, J. S.; Gabbaï, F. P. Anion-Controlled Switching of an X Ligand into a Z Ligand: Coordination Non-Innocence of a Stiboranyl Ligand. *Angew. Chem. Int. Ed.* **2014**, *53*, 2633–2637. (b) Jones, J. S.; Wade, C. R.; Gabbaï, F. P. Redox and Anion Exchange Chemistry of a Stibine Nickel Complex: Writing the L, X, Z Ligand Alphabet with a Single Element. *Angew. Chem. Int. Ed.* **2014**, *53*, 8876–8879.

(13) (a) Korch, K. M.; Watson, D. A. Cross-Coupling of Heteroatomic Electrophiles. *Chem. Rev.* **2019**, *119*, 8192–8228. (b) Terao, J.; Torii, K.; Saito, K.; Kambe, N.; Baba, A.; Sonoda, N. Zirconocene-Catalyzed Silylation of Alkenes with Chlorosilanes. *Angew. Chem. Int. Ed* **1998**, *37*, 2653–2656. (c) McAtee, J. R.; Martin, S. E. S.; Ahneman, D. T.; Johnson, K. A.; Watson, D. A. Preparation of Allyl and Vinyl Silanes by the Palladium - Catalyzed Silylation of Terminal Olefins: A Silyl-Heck Reaction. *Angew. Chem. Int. Ed.* **2012**, *51*, 3663–3667. (d) Martin, S. E. S.; Watson, D. A. Preparation of Vinyl Silyl Ethers and Disiloxanes via the Silyl-Heck Reaction of Silyl Ditriflates. *J. Am. Chem. Soc.* **2013**, *135*, 13330–13333. (e) Cinderella, A. P.; Vulovic, B.; Watson, D. A. Palladium-Catalyzed Cross-Coupling of Silyl Electrophiles with Alkylzinc Halides: A Silyl-Negishi Reaction. *J. Am. Chem. Soc.* **2017**, *139*, 7741–7744. (f) Vulovic, B.; Cinderella, A. P.; Watson, D. A. Palladium-Catalyzed Cross-Coupling of Monochlorosilanes and Grignard Reagents. *ACS Catal.* **2017**, *7*, 8113–8117. (g) Matsumoto, K.; Huang, J.; Naganawa, Y.; Guo, H.; Beppu, T.; Sato, K.; Shimada, S.; Nakajima, Y. Direct Silyl-Heck Reaction of Chlorosilanes. *Org. Lett.* **2018**, *20*, 2481–2484.

(14) Bond dissociation energies for R_3Si–F bonds > 150 kcal/mol, see Y.-R. Luo, *Handbook of bond dissociation energies in organic compounds*, CRC press, *2002*.

(15) Ohashi, M.; Kambara, T.; Hatanaka, T.; Saijo, H.; Doi, R.; Ogoshi, S. Palladium-Catalyzed Coupling Reactions of Tetrafluoroethylene with Arylzinc Compounds. *J. Am. Chem. Soc.* **2011**, *133*, 3256–3259.

(16) See Supporting Information for details.

(17) Abstraction of the fluoride at Si was supported in this case by the characterization of the fluoroborate $[FB(C_6F_5)_3]^-$ upon monitoring the reaction by $^{19}F\{^1H\}$ NMR spectroscopy (Figure S1A).[16]

(18) Analogous η^2-coordination is known for aryl-boranes, see: Emslie, D. J. H.; Cowie, B. E.; Kolpin, K. B. Acyclic Boron-Containing π-Ligand Complexes: η^2- and η^3-Coordination Modes. *Dalton Trans.* **2012**, *41*, 1101–1117.

(19) Batsanov, S. S. Van der Waals Radii of Elements. *Inorg. Mater.* **2001**, *37*, 871–885.

(20) The ^{29}Si 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 $B(C_6F_5)_3$, see ref. 10d.

(22) (a) Withers, P. J. A.; Elser, J. J.; Hilton, J.; Ohtake, H.; J. Schipper, W. J.; van Dijk, K. C. Greening the Global Phosphorus Cycle: How Green Chemistry can Help Achieve Planetary P Sustainability. *Green Chem.* **2015**, *17*, 2087–2099. (b) Keijer, T.; Bakker. V.; Slootweg, J. C. Circular Chemistry to Enable a Circular Economy. *Nat. Chem.* **2019**, *11*, 190–195.

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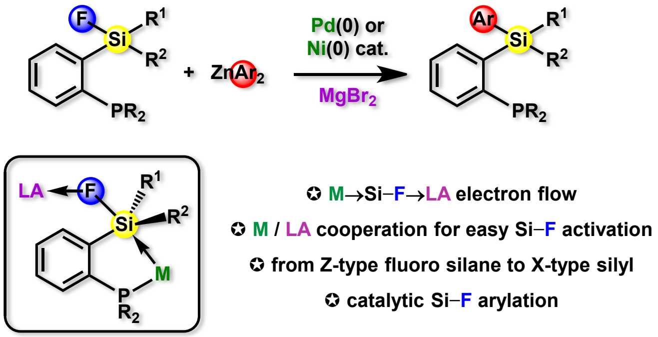

✪ M→Si–F→LA electron flow

✪ M / LA cooperation for easy Si–F activation

✪ from Z-type fluoro silane to X-type silyl

✪ catalytic Si–F arylation