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Cobalt-catalyzed Selective C—F Bond Activation and Alkylation of Polyfluoroaryl Imines

Faguan Lu, Hongjian Sun, and Xiaoyan Li*

School of Chemistry and Chemical Engineering, Key Laboratory of Special Functional Aggregated Materials,
Ministry of Education, Shandong University, Jinan, 250100 Shandong, China

In this paper the C—F bond activation of polyfluoroaryl imines is explored at cobalt(0) center with an imine-N atom as an anchoring group. The reaction of F_5C_6-CH=N-(2'-ClC_6H_4) (**2**) and F_5C_6-CH=N-C_6H_5 (**3**) with $Co(PMe_3)_4$ afforded the C—F bond activation products (*ortho*-F_4C_6-CH=N-(2'-ClC_6H_4))Co(I)$(PMe_3)_3$ (**5**) and (*ortho*-F_4C_6-CH=N-C_6H_5)Co(II)(F)$(PMe_3)_2$ (**6**), while only π-(C=N) coordinated cobalt(0) complex (2,4,5-$F_3C_6H_2$-CH=N-(4'-ClC_6H_4))Co(0)$(PMe_3)_3$ (**4**) was obtained from 2,4,5-$F_3C_6H_2$-CH=N-(4'-ClC_6H_4) (**1**) without C—F bond activation. Complexes **4**—**6** were characterized through X-ray single crystal diffraction. It was also found that dialkylation of *N*-(perfluorobenzylidene)benzenamine with organozinc reagents could be catalyzed by $Co(PMe_3)_4$ via C,C-coupling reaction under mild conditions.

Keywords C—F bond activation, cobalt, imine, organozinc reagent, C,C-coupling

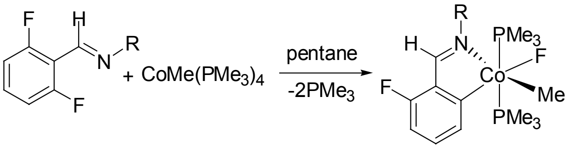
Introduction

Activation of C—F bonds is very meaningful and remains a significant challenge. How to design transition metal complexes as catalysts for selective activation and functionalization of C—F bonds under mild conditions is attracting more and more attention.[1-6]

There have been some reports on activation of C—F bonds of fluorinated compounds by the first-row transition metals.[7-11] Love published her review on cross coupling reactions of polyfluoroarenes via C—F activation.[12] However publications on C—F activation by cobalt complexes are rare. Klein disclosed the C—F bond activation by $Co(PMe_3)_4Me$ with the hard donor atom oxygen as anchoring group. The reaction is promoted by the release of CH_3F.[13]

In 2006 we reported our first example about cobalt(III) complex containing a [C-Co-F] fragment through cyclometalation reaction involving C—F bond activation at a cobalt(I) center with an aldazine-N atom as an anchoring group.[14] After that a series of cobalt complexes involved C—F bond activation were synthesized.[15-18]

Recently we have found that the C—F bonds of 2,6-difluorinated imines were activated by $Co(PMe_3)_4$-Me (Eq. 1).[16] But in the case of tetrakis(trimethylphosphine)cobalt(0), the expected C—F activation did not occur. Only a π-coordinated cobalt(0) complex was isolated (Eq. 2).



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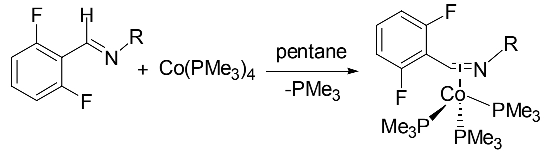

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As our continuation to study C—F bond activation of fluorinated imines, the substrates in this investigation were extended from the 2,6-difluorinated imines in our early study to the 2,4,5-trifluorinated imine and perfluorinated imine in order to increase the opportunity of C—F bond activation by $Co(PMe_3)_4$. As 2,6-difluorinated imines, similar π-coordinated cobalt(0) complex **4** was obtained from the reaction of 2,4,5-trifluorinated imine with $Co(PMe_3)_4$. Under similar reaction conditions the reaction of $Co(PMe_3)_4$ with perfluorinated imines afforded the C—F bond activation products, cobalt(I) complexes **5** and cobalt(II) complex **6** containing [C-Co-F] fragment. To our knowledge, complex **6** is the first covalent organocobalt(II) fluoride.[19] The structures of complexes **4**, **5** and **6** were determined by X-ray single crystal diffraction. Based on these research re-

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* E-mail: xli63@sdu.edu.cn; Tel.: 0086-0531-88361350; Fax: 0086-0531-88564464
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sults, the alkylation of perfluorinated imines catalyzed by $Co(PMe_3)_4$ was explored involving C—F bond activation via C,C-coupling reaction.

Experimental

General procedures and materials

Standard vacuum techniques were used in manipulations of volatile and air-sensitive materials. Solvents were dried by known procedures and distilled under nitrogen before use. Literature methods were used in the preparation of $Co(PMe_3)_4$.[20,21] Schiff bases were obtained by condensation of polyfluorobenzaldehyde with amines by refluxing in alcohol solution. Infrared spectra (4000—400 cm^{-1}), as obtained from Nujol mulls between KBr disks, were recorded on a Bruker ALPHA FT-IR. ^{1}H, ^{19}F and ^{31}P NMR (300, 282 and 121 MHz, respectively) spectra were recorded on a Bruker Avance 300 spectrometer. ^{19}F and ^{31}P NMR resonances were obtained with broadband proton decoupling. X-ray crystallography was performed with a Bruker Smart 1000 diffractometer. Elemental analyses were carried out on an Elementar Vario EL III. Melting points were measured in capillaries sealed under nitrogen and were uncorrected.

Synthesis of complex 4

A solution of **1** (0.54 g, 2.00 mmol) in 30 mL of pentane was added to a solution of $Co(PMe_3)_4$ (0.91 g, 2.50 mmol) in 30 mL of pentane at −80 ℃ dropwise within 5 min under N_2 atmosphere. The reaction mixture was allowed to warm to ambient temperature and stirred for 24 h. During this period, the reaction mixture turned brown in color. After filtering, crystallization from pentane solution at 4 ℃ yielded brown single crystals suitable for X-ray structure analysis. Yield 0.53 g (46%). Dec.＞119 ℃. IR (KBr) ν: 1626 (C=N), 1575 (C=C), 935 (PMe_3) cm^{-1}. Anal. calcd for $C_{22}H_{34}ClCoF_3NP_3$ (556.79 g•mol^{-1}): C 47.45, H 6.16, N 2.52; found C 47.52, H 6.48, N 2.46.

Complexes **5** and **6** were synthesized according to the method given above for **4**.

Complex 5 Yield 0.59 g (50%). Dec.＞88 ℃. ^{1}H NMR (300 MHz, C_6D_6, 296 K) δ: 0.85—1.12 (m, 27H, PCH_3), 6.91—7.16 (m, 4H, Ar*H*), 9.28 (s, 1H, C*H*=N); ^{31}P NMR (121 MHz, C_6D_6, 296K) δ: −15.9 (s, 1P, *P*Me$_3$), −13.6 (s, 1P, *P*Me$_3$), −0.8 (s, 1P, *P*Me$_3$); ^{19}F NMR (282 MHz, 296 K) δ: −112.1 (s, 1F), −145.5 (s, 1F), −163.4 (s, 1F), −167.9 (s, 1F); IR ν: 1624 (C=N), 1582 (C=C), 944 (PMe_3). Anal. calcd for $C_{22}H_{32}ClCoF_4NP_3$ (573.78 g•mol^{-1}): C 46.05, H 5.62, N 2.44; found C 46.22, H 5.48, N 2.54.

Complex 6 Yield 0.38 g (41%). Dec.＞280 ℃. IR ν: 1624 (C=N), 1591, 1541 (C=C), 942 (PMe_3). Anal. calcd for $C_{19}H_{24}CoF_5NP_2$ (482.26 g•mol^{-1}): C 47.32, H 5.02, N 2.90; found C 47.18, H 5.28, N 2.79.

X-ray structure determination

Table 1 Crystallographic data for complexes **4**, **5** and **6**

	4	5	6
Formula	$C_{22}H_{34}ClCoF_3NP_3$	$C_{22}H_{32}ClCoF_4NP_3$	$C_{19}H_{24}CoF_5NP_2$
Size/mm^3	0.22×0.2×0.19	0.21×0.19×0.15	0.32×0.24×0.22
Formula weight/(g•mol^{-1})	556.79	573.78	482.26
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	$P2_12_12_1$	$P2_1/c$
a/Å	15.102(3)	1156.80(10)	868.20(7)
b/Å	9.7154(19)	1298.10(10)	1402.10(18)
c/Å	19.236(4)	1633.5(2)	1771.5(2)
α/(°)	90	90	90
β/(°)	102.35(3)	90	96.823(9)
γ/(°)	90	90	90
V/Å^3	2757.0(9)	2452.9(4)	2141.2(4)
Z	4	4	4
Calculated density/(mg•cm^{-3})	1.341	1.554	1.496
Absorption coefficient/mm^{-1}	0.924	1.046	0.998
Reflections collected	15675	18973	15702
Indep Rflns	6089	5172	4502
R(int)	0.0431	0.0930	0.0270
Parameters	289	417	349
R_1 (all data)	0.0790	0.0492	0.0402
wR_2 (all data)	0.1215	0.1350	0.1023
R_1 [$I>2\sigma(I)$]	0.0479	0.0482	0.0343
wR_2 [$I>2\sigma(I)$]	0.1070	0.1321	0.0971
Goodness of fit on F^2	1.054	1.077	0.863

Catalytic study

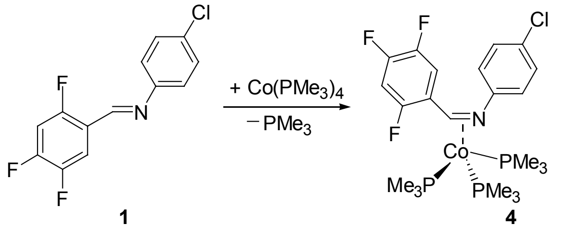
Compound **3** (0.0542 g, 0.2 mmol) with $Co(PMe_3)_4$ (0.02 mmol) and 1.5 equiv. of ZnR_2 were dissolved in 3 mL of DME. The reaction mixture was heated to the given temperature and stirred for the given hours. After cooled to ambient temperature, the solution was characterized by *in situ* ^{19}F NMR spectra.

Results and Discussion

Reaction of $Co(PMe_3)_4$ with fluorinated benzalimine

In our early study we found that increasing the number of fluorine atoms on the aromatic rings benefits the C—F bond cleavage. At first we explored the reaction of trifluoroaryl imine with $Co(PMe_3)_4$. The reaction of compound **1** with $Co(PMe_3)_4$ afforded a π-(C=N) coordinated cobalt(0) complex **4** as brown crystals in the yield of 46%. The expected C—F bond activation product could not be found. The molecular structure of complex **4** was identified by X-ray diffraction (Figure 1).

Complex **4** has a tetrahedral coordination geometry with a π-coordinated imine group [C(7)—N(1)] and three σ-coordinated trimethylphosphine ligands. The C=N bond length [N(1)—C(7)=1.382(4) Å] is a bit shorter than that [N(1)—C(7)=1.403(6) Å] in the similar cobalt complex.[16] This difference might be caused through the electron-withdrawing effect of fluorine and chlorine atoms, which makes the π-coordination in complex **4** weaker.



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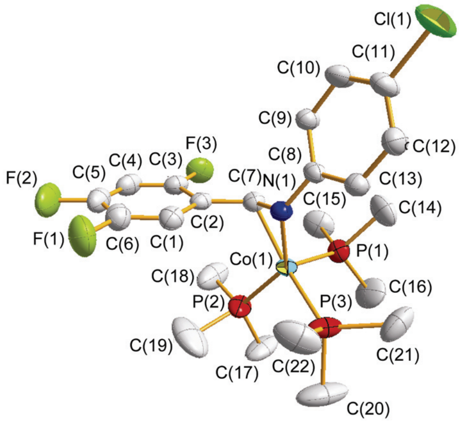
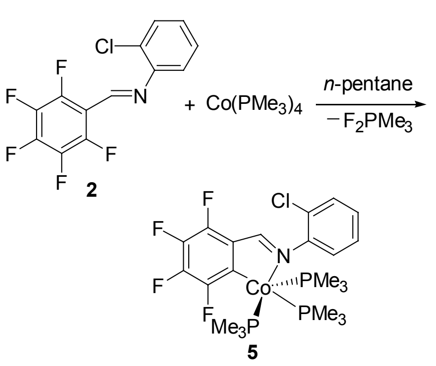


Figure 1 Molecular structure of complex **4**. (All the hydrogen atoms were omitted for clarity) Selected bond distances (Å) and angles (°): Co(1)—N(1) 1.905(2), Co(1)—C(7) 2.024(3), Co(1)—P(2) 2.1953(11), Co(1) — P(3) 2.2013(11), Co(1) — P(1) 2.2245(12), N(1)—C(7) 1.382(4); N(1)-Co(1)-C(7) 41.05(11), N(1)-Co(1)-P(2) 136.48(8), C(7)-Co(1)-P(2) 103.34(9), N(1)-Co(1)-P(3) 102.77(8), C(7)-Co(1)-P(3) 142.76(9), P(2)-Co(1)-P(3) 102.24(4), N(1)-Co(1)-P(1) 108.56(8), C(7)-Co(1)-P(1) 99.86(10), P(2)-Co(1)-P(1) 100.55(4), P(3)-Co(1)-P(1) 101.54(5).

Under similar reaction conditions, the reaction of perfluoroaryl imine **2** with Co(PMe$_3$)$_4$ resulted in the formation of *ortho*-metalated Co(I) complex **5** as a C—F bond activation product (Eq. 4).

Complex **5** was isolated as dark brown crystals in the yield of 50%. Complex **5** is not stable in the air and decomposes above 88 ℃ under nitrogen. Complex **5** was characterized by IR and NMR spectroscopy. In the infrared spectra of complex **5**, the characteristic ν(C=N) band was recorded at 1624 cm^{-1}. Compared with the (C=N) band (1647 cm^{-1}) of free ligand **2**, this substantial red shift upon coordination of the N-donor atom of the imine group indicates a weakening of the C=N double bond after coordination to the cobalt centre. In the ^{1}H NMR spectra, the CH proton of the imine group appears at δ 9.28 as a singlet while three PMe$_3$ protons resonate are recorded at δ 0.82 as a doublet (9H, $^2J_{\text{PH}}$= 6 Hz) and at δ 0.92 as a broad singlet (18H). In the ^{31}P NMR spectra, three broad singlets at δ −15.7, −16.0 and 1.1 with the integral ratio of 1 : 1 : 1 suggest that the three phosphorus atoms have different chemical environments. This is typical for the ^{31}P NMR spectra of the pentacoordinate cobalt(I) complexes.[22]



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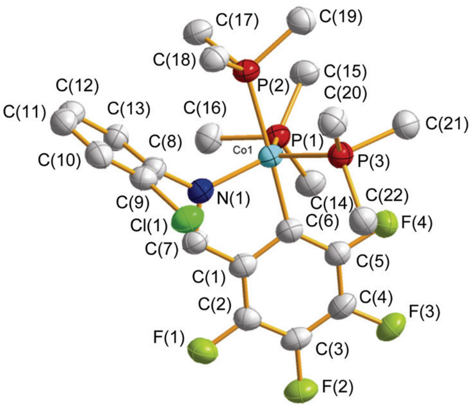
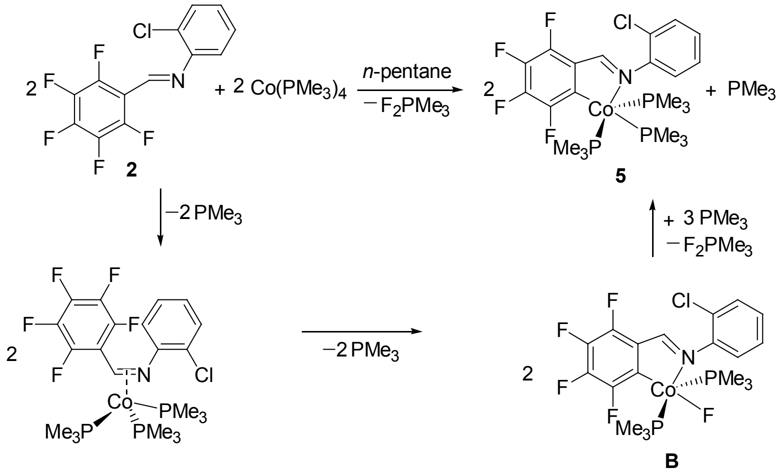


Figure 2 Molecular structure of complex **5** (all the hydrogen atoms were omitted for clarity). Selected bond distances (Å) and angles (°): Co(1)—C(6) 1.940(3), Co(1)—P(1) 2.1914(9), Co(1) — P(3) 2.1947(10), Co(1) — P(2) 2.2028(8), N(1) — Co(1) 1.923(3), N(1)—C(7) 1.305(4); N(1)-Co(1)-C(6) 80.87(13), N(1)-Co(1)-P(1) 109.04(9), C(6)-Co(1)-P(1) 84.94(10), N(1)-Co(1)-P(3) 124.54(9), C(6)-Co(1)-P(3) 90.35(10), P(1)-Co(1)-P(3) 124.66(4), N(1)-Co(1)-P(2) 97.76(8), C(6)-Co(1)-P(2) 177.21(11), P(1)-Co(1)-P(2) 93.25(3), P(3)-Co(1)-P(2) 92.43(4).

This result is verified by X-ray single crystal diffraction. The molecular structure of **5** is shown in Figure 2. Complex **5** has a trigonal bipyramid gemometry with P(1), P(3) and N(1) atoms in the equatorial plane. The three bond angles in this plane are N(1)-Co(1)-P(3)= 124.54(9)°, N(1)-Co(1)-P(1)=109.04(9)° and P(1)-Co(1)-P(3)=124.66(4)°. The P(2) and C(6) atoms are located in the axial positions with a bond angle of C(6)-Co(1)-P(2)=177.2(1)°. The distance of C(7)—N(1) (1.305(4) Å) is remarkably shorter than that of C=N (1.382(4) Å) in **4**, while π-coordination of the C=N group is indicated in complex **4**. However, this value is larger than those (average: 1.286 Å) in the *ortho*-metalated cobalt(III) fluoride.[16] The distance of Co(1) —P(2) [2.2028(8) Å] is longer than that of Co(1)—P(1) [2.1914(9) Å] and Co(1)—P(3) [2.1917(1) Å] due to the

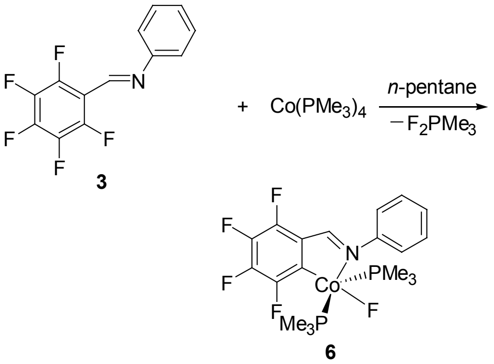
Scheme 1 Proposed formation mechanism of **5**



trans-influence of the phenyl-C(6) atom.

A possible formation mechanism of complex **5** is suggested in Scheme 1. The first step is the π-coordination of the imine group to the cobalt(0) center after dissociation of one phosphine ligand to give rise to intermediate **A**. With the chelate effect C—F bond is cleavaged by *ortho*-metalation to afford intermediate **B**, an organocobalt(II) fluoride via oxidative addition. The redox reaction of **B** with PMe_3 results in the formation of the end product **5** and difluorotrimethylphosphorane (F_2PMe_3). The formation of F_2PMe_3 in solution was verified via ^{31}P NMR and ^{19}F NMR.[15] Similar reaction mechanism was reported in our early work on the reaction of $Co(PMe_3)_4$ with perfluorinated toluene.[15]

In order to verify this mechanism, the following experiment was designed. To catch intermediate organocobalt(II) fluoride **B**, ligand **3** was introduced because **3** is more electron-rich than **2** due to the lack of one chlorine atom on the phenyl ring. Ligand **3** and $Co(PMe_3)_4$ were combined in pentane (Eq. 5). This mixture was stirred under ambient temperature for 24 h. After workup, an organocobalt(II) fluoride, complex **6**, was successfully isolated as dark brown crystal from the pentane solution in the yield of 41%. This is the first example of cobalt(II) complex containing a [C-Co-F] fragment. Complex **6** is paramagnetic and was characterized by X-ray single crystal diffraction.



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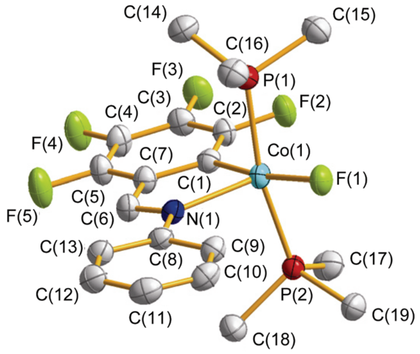


Figure 3 Molecular structure of **6**. (all the hydrogen atoms were omitted for clarity) Selected bond distances (Å) and angles (°): Co(1)—F(1) 1.9143(11), Co(1)—N(1) 2.1396(15), Co(1)—P(1) 2.2151(6), Co(1)—P(2) 2.2291(6), Co(1)—C(1) 1.9087(18), C(7)—N(1) 1.297(2); C(1)-Co(1)-F(1) 169.85(6), C(1)-Co(1)-N(1) 81.56(7), F(1)-Co(1)-N(1) 108.09(5), C(1)-Co(1)-P(1) 91.27(6), F(1)-Co(1)-P(1) 84.69(4), N(1)-Co(1)-P(1) 96.08(4), C(1)-Co(1)-P(2) 90.75(6), F(1)-Co(1)-P(2) 91.32(4), N(1)-Co(1)-P(2) 95.99(4), P(1)-Co(1)-P(2) 167.93(2).

The molecular structure of **6** is shown in Figure 3. The cobalt atom attains a penta-coordinate tetragonal pyramid with the imine-N(1) atom at the apical position. The distance of C(7)—N(1) (1.297(2) Å) in **6** is comparable with that in complex **5** (1.305(4) Å)). The Co—F bond length (Co(1)—F(1)=1.914(1) Å) in complex **6** is obviously shorter than those (1.926—1.941 Å) in the organocobalt(III) fluorides (with a [C-Co-F] fragment).[14,16] The Co—C bond lengths in both complex **6** [Co—C(1)=1.9087(18) Å] and complex **5** [Co(1)—C(6) =1.940(3) Å] are in the normal region.

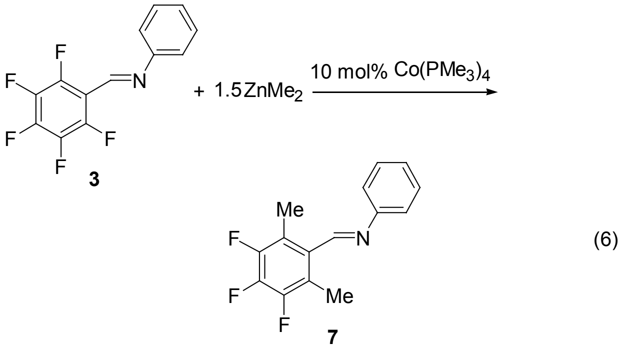
The completely different products of reactions 4 and 5 are entirely caused by the *ortho*-chlorine atom on the phenyl ring linked to the imine-N atom. In general, C—Cl bond is more easily activated than C—F bond, because the bond energy of the former is smaller than that of the latter. However, the C—F bonds of a perfluorophenyl ring are remarkably activated because the electron-withdrawing effect of the fluorine atoms. The similar selectivity on C—F bond activation with platinum was also reported by Crespo.[23] In addition, chelation is also beneficial to the formation of complex **6** and the imine group acts as an anchoring group for this *ortho*-metalation.

The reaction of $CoMe(PMe_3)_4$ with 2,6-difluorobenzophenone imine afforded the imine cobalt(I) complex via C—H bond activation, while the combination of $Co(PMe_3)_4$ with the same imine delivered another imine cobalt(I) complex via C—F bond activation.[17] The imine cobalt(I) and cobalt(III) chlorides were obtained through the reaction of *ortho*-chlorinated phenyl imine with electron-rich cobalt(I) complexes supported by trimethylphosphine ligands.[24]

Catalyitc alkylation of fluorinated benzalimine with zinc reagents by $Co(PMe_3)_4$

Kumada reported the first example of catalytic C—C bond cross-coupling of fluorobenzene with Grignard reagents by nickel catalysts.[25] Crespo and Martinez published that $[Me_2Pt(\mu\text{-}SMe_2)]_2$ could be used in the stoichiometric C—F activation.[23] Love disclosed the first example of Pt-catalyzed methylation and methoxylation of a variety of polyfluoroaryl imines through the mono-substitution reaction.[26] Nickel-catalyzed C,C-coupling reaction of aryl fluorides via C—F bond activation was studied by Chatani and his co-workers.[27] The nickel complexes $Ni(PMe_3)_4$ and $NiMe_2(PMe_3)_3$ supported by trimethyphosphine were also used to explore C,C-coupling reactions via C—F bond activation.[28]

Inspired by those results, we studied the catalytic C,C-coupling reaction of compound **3** and dimethyl zinc with $Co(PMe_3)_4$ as catalyst (Eq. 6). Bis-dimethylated product **7** was formed in excellent yields (Table 2).



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Comparing the results of Entry 1 to 10, it is concluded that DME is the best solvent and 30 ℃ is the best reaction temperature. From the results of Entry 11 to 13, it can be drawn that 8 h is enough for the reaction. Entry 14 is a control experiment.

To expand this catalytic system, other organozinc compounds (ZnBnCl, ZnPhBr and ZnCyCl) as alkylating reagents were also studied (Eq. 7). However, the reactivity of these three organozinc reagents is weaker than that of dimethylzinc. At the higher temperatures the C,C-coupling products could be obtained in different yields (Table 3).

Table 2 Optimization of conditions for catalytic dimethylation

Entry	Solvent	Reaction temp./℃	Reaction time/h	Compound **7** yield[a]/%
1	toluene	50	24	95
2	DMF	50	24	5
3	DMSO	50	24	95
4	dioxane	50	24	97
5	THF	50	24	95
6	DME	50	24	99
7	toluene	30	24	64
8	DMSO	30	24	70
9	dioxane	30	24	95
10	DME	30	24	99
11	DME	30	12	96
12	DME	30	8	95
13	DME	30	4	35
14[b]	DME	30	8	0

[a] Yield based on *in situ* ^{19}F NMR spectra and is the average of 2 times. [b] Blank experiment.

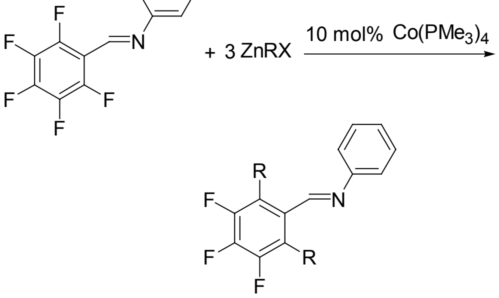

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Table 3 Co-catalyzed dimethylation with other organozinc reagents

Entry	Organozinc	Reaction time/h	Solvent	Reaction temp./℃	Yield[a]%
1	ZnBnCl	8	DME	30	3
2	ZnBnCl	8	DME	50	14
3	ZnBnCl	24	toluene	60	52
4	ZnBnCl	8	toluene	80	75
5	ZnBnCl	8	DMF	80	35
6	ZnBnCl	8	DMSO	80	33
7	ZnBnCl	8	dioxane	80	83
8	ZnPhBr	24	toluene	70	16
9	ZnCyCl	24	DME	50	22

[a] Yield based on *in situ* ^{19}F NMR spectra and is average of 2 times.

Conclusions

In conclusion, we have taken a step forward in selective C—F bond activation of polyfluorinated imines by cobalt(0) complex supported by trimethylphosphine ligands. For the first time, an *ortho*-chelated covalent cobalt(II) complex containing a [C—Co—F] fragment was isolated and structurally characterized by X-ray diffraction. The catalytic *ortho*-dialkylation of perfluoroaryl imine with organozinc reagents involving selective C—F bond activation via C,C-coupling reaction was studied with $Co(PMe_3)_4$ as catalyst under mild conditions. This work is of importance for cobalt-catalyzed C—F bond activation and functionalization of organic fluorides.

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(Cheng, F.)