Imine-assisted C–F bond activation using low-valent cobalt compounds supported by trimethylphosphine ligands and formation of novel organic fluorides†

Zhe Lian, Xiaofeng Xu, Hongjian Sun, Yue Chen, Tingting Zheng and Xiaoyan Li*

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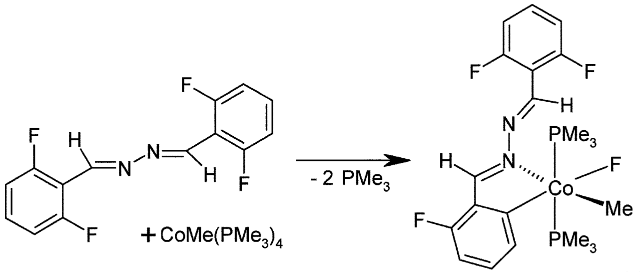
A cyclometalation reaction involving C–F bond activation at a cobalt(I) center with an aldazine-N atom as anchoring group affords *ortho*-chelated cobalt(III) complexes containing a [C–Co–F] fragment [CoFMe(PMe$_3$)$_2${(C$_6$H$_3$F-*ortho*)CH=N–R}] **5–8**. Under similar reaction conditions π-coordinated cobalt(0) complexes [Co(PMe$_3$)$_3$((C$_6$H$_3$F-*ortho*)CH=N–R)] **12–14** were formed when [Co(PMe$_3$)$_4$], instead of [CoMe(PMe$_3$)$_4$], was applied. C–F bond activation did not occur. Carbonylation of complexes **6–8** delivered novel organic fluorides **15–17**. A proposed formation mechanism of the novel organic fluorides with demetallation and carbonylation of complexes **6–8** by CO is discussed with experimental support. As important intermediates, an acetyl cobalt complex, [CoFMeC=O(PMe$_3$)$_2${(C$_6$H$_3$F-*ortho*)CH=N–R}] **20**, and a 19-electron cobalt(0) complex, Co(CO)$_3$(PMe$_3$)$_2$ **21**, were structurally characterized. The crystal and molecular structures of complexes **5**, **6**, **8**, **12**, **20** and **21** were determined by X-ray diffraction.

1. Introduction

The activation of carbon–fluorine bonds is of great importance in organometallic chemistry and catalyst development because this type of reaction contributes to the fundamental understanding of the reactivity of stable bonds and the selective replacement of fluorine atoms.[1–4] There have been some reports on C–F bond activation by first-row transition metals.[5] We reported a cyclometalation reaction involving carbon–fluorine bond activation at a cobalt(I) center with an azine donor as anchoring group which, for the first time, afforded an *ortho*-chelated cobalt(III) complex containing a [C–Co–F] fragment (eqn (1)).[6]



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Herein we report on progress in the research of cyclometalation reactions involving C–F bond activation at electron-rich low valent cobalt centers with imine as pre-chelate ligands. The novel cobalt complexes **5–8** containing the [C–Co–F] fragment formed by oxidative addition of an aromatic C–F bond to cobalt(I) centers were isolated and characterized. π-Coordinated imine cobalt(0) complexes **12–14** were obtained by reactions of Co(PMe$_3$)$_4$ with the fluorinated aromatic imines **1–4**. Carbonylation of complexes **6–8** afforded novel organic fluorides **15–17** with demetallation. A mechanism is proposed on the basis of the experimental results.

2. Experimental

2.1 General procedures and materials

Standard vacuum techniques were used in manipulations of volatile and air-sensitive materials. Literature methods were used in the preparation of methyltetrakis(trimethylphosphine)cobalt(I) and tetrakis(trimethylphosphine)cobalt(0).[7] Schiff bases were obtained by condensation of 2,6-difluorobenzaldehyde with amines. Other chemicals were used as purchased. Infrared spectra (4000–400 cm^{-1}), as obtained from Nujol mulls between KBr disks, were recorded on a Nicolet 5700. ^{1}H and ^{31}P NMR (300 and 121 MHz respectively) spectra were recorded on a Bruker Avance 300 spectrometer. ^{31}P NMR resonances were obtained with broadband proton decoupling. Melting points were measured in capillaries sealed under argon and are uncorrected. X-Ray crystallography was performed with a Bruker Smart 1000 diffractometer. MS were obtained from Agilent 6510 Accurate-Mass Q-TOF LC/MS system

2.2 Syntheses

Complex 5. A solution of 1.07 g (2.83 mmol) of [CoMe(PMe$_3$)$_4$] in 30 mL of pentane was combined with a solution of **1** 0.59 g (2.83 mmol) in 20 mL of pentane at −80 °C. The reaction mixture was allowed to warm to ambient temperature and stirred for 18 h. During this period, the reaction mixture turned yellow–brown in color. After filtering, the solid residue was extracted with diethyl ether (40 mL). Crystallization from pentane and diethyl ether at 4 °C yielded red single crystals **5** suitable for X-ray structure analysis. Yield: 0.38 g (35.3%). Decomp. >135 °C. IR (Nujol): 1595 ν(C=N), 1581, 1567 ν(C=C), 940 ν(PMe$_3$) cm^{-1}.

School of Chemistry and Chemical Engineering, Shandong University, Shanda Nanlu 27, 250100, Jinan, People's Republic of China. E-mail: xli63@sdu.edu.cn; Fax: +86 531 88361350

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^{1}H NMR (300 MHz, C_6D_6, 296 K): δ 0.64 (m, 3H, CH_3), 0.80 (br, 18H, PCH_3), 3.46 (br, 3H, CH_3), 6.50–7.50 (m, 3H, Ar–H), 8.46 (s, 1H, CH=N). ^{31}P NMR (121 MHz, C_6D_6, 300 K): δ 28.9 s. Anal. Calc. for $C_{15}H_{28}CoF_2NP_2$: C 47.25, H 7.40, N 3.67%. Found: C 47.01, H 7.67, N 3.46%.

Complexes **6–8** were synthesized according to the method given above for **5**.

Complex 6. Yield: 38.6%. Decomp. >135 °C. IR (Nujol): 1592 ν(C=N), 1566 ν(C=C), 945 $\nu(PMe_3)$ cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 296 K): δ 0.64 (m, 3H, CH_3), 0.81 (br, 18H, PCH_3), 6.59–8.04 (m, 8H, Ar–H), 9.10 (s, 1H, CH=N). ^{31}P NMR (121 MHz, C_6D_6, 300 K): δ 31.0 s. Anal. Calc. for $C_{20}H_{30}CoF_2NP_2$: C 54.18, H 6.82, N 3.16%. Found: C 54.01, H 7.12, N 3.46%.

Complex 7. Yield: 46.1%. Decomp. >128 °C. IR (Nujol): 1597 ν(C=N), 1567 ν(C=C), 946 $\nu(PMe_3)$ cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 296 K): δ 0.64 (m, 3H, CH_3), 0.82 (m, 18H, PCH_3), 6.10–8.50 (m, 10H, Ar–H), 8.58 (s, 1H, CH=N). ^{31}P NMR (121 MHz, C_6D_6, 300 K): δ 30.5 s. Anal. Calc. for $C_{24}H_{32}CoF_2NP_2$: C 58.42, H 6.54, N 2.84%. Found: C 58.11, H 6.82, N 3.00%.

Complex 8. Yield: 30.4%. Decomp. >120 °C. IR (Nujol): 1603 ν(C=N), 1565 ν(C=C), 938 $\nu(PMe_3)$ cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 296 K): δ 0.64 (m, 3H, CH_3), 0.82 (m, 18H, PCH_3), 2.09 (3H, CH_3), 6.10–8.50 (m, 7H, Ar–H), 9.01 (s, 1H, CH=N). ^{31}P NMR (121 MHz, C_6D_6, 300 K): δ 30.9 s. Anal. Calc. for $C_{21}H_{32}CoF_2NP_2$: C 55.15, H 7.05, N 3.06%. Found: C 55.01, H 7.12, N 3.26%.

Complex 12. A solution of 1.00 g (2.75 mmol) of $[Co(PMe_3)_4]$ in 30 mL of pentane was combined with a solution of **2** 0.60 g (2.75 mmol) in 20 mL of pentane at −80 °C. The reaction mixture was allowed to warm to ambient temperature and stirred for 18 h. During this period, the reaction mixture turned yellow–brown in color. After filtering, the solid residue was extracted with diethyl ether (40 mL). Crystallization from pentane at 4 °C yielded red–brown single crystals **12** suitable for X-ray structure analysis. Yield: 0.48 g (30.4%). Decomp. >130 °C. IR (Nujol): 1624 ν(C=N), 1581 ν(C=C), 945 $\nu(PMe_3)$ cm^{-1}. Anal. Calc. for $C_{22}H_{36}CoF_2NP_3$: C 52.39, H 7.19, N 2.78%. Found: C 52.03, H 7.12, N 3.05%.

Complexes **13** and **14** were synthesized according to the method given above for **12**.

Complex 13. Yield: 37.5%. Decomp. > 153 °C. IR (Nujol): 1625 (C=N), 1557 (C=C), 946 (PMe_3) cm^{-1}. Anal. Calc. for $C_{26}H_{38}CoF_2NP_3$: C 56.32, H 6.91, N 2.53%. Found: C 56.01, H 7.03, N 2.56%.

Complex 14. Yield: 31.3%. Decomp. > 120 °C. IR (Nujol): 1622 (C=N), 1570 (C=C), 945 (PMe_3) cm^{-1}. Anal. Calc. for $C_{23}H_{38}CoF_2NP_3$: C 53.29, H 7.39, N 2.70%. Found: C 53.01, H 7.33, N 2.66%.

Complex 15. A solution of 1.00 g (2.26 mmol) **6** in 50 mL of pentane was stirred under 1 atm of CO for 24 h. The solution was filtered, freezing at 4 °C afforded 0.07 g of orange crystals of $Co(CO)_3(PMe_3)_2$. The solution was washed with 100 mL of saturated solution of NH_4Cl and dried over anhydrous magnesium in air. Column chromatographic separation using petroleum ether–ethyl acetate as eluent leads to analytically pure **15**. Yield: 59%. IR (Nujol): 1699 ν(C=O), 1624 ν(C=N), 1557 ν(C=C) cm^{-1}, ^{1}H NMR (300 MHz, C_6D_6, 296 K): δ 2.71 (s, 3H, CH_3), 6.9–7.4 (m, 8H, Ar–H), 8.83 (s, 1H, CH=N). Anal. Calc. for $C_{15}H_{12}FNO$: C 74.68, H 5.01, N 5.81%. Found: C 74.49, H 5.03, N 5.55%.

Complexes **16** and **17** were synthesized according to the method given above for **15**.

Complex 16. Yield: 62.4%. IR (Nujol): 1699 ν(C=O), 1624 ν(C=N), 1557 ν(C=C) cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 296 K): δ 2.86 (s, 3H, CH_3), 6.99–8.32 (m, 10H, Ar–H), 8.97 (s, 1H, CH=N). Anal. Calc. for $C_{19}H_{14}FNO$: C 78.34, H 4.84, N 4.81%. Found: C 78.48, H 5.01, N 4.73%.

Complex 17. Yield: 72.1%. IR (Nujol): 1699 ν(C=O), 1624 ν(C=N), 1557 ν(C=C) cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 296 K): δ 2.37 (s, 3H, Ar–CH_3), 2.70 (s, 3H, –$COCH_3$), 6.99–8.32 (m, 7H, Ar–H), 8.97 (s, 1H, CH=N). Anal. Calc. for $C_{16}H_{14}FNO$: C 75.28, H 5.53, N 5.49%. Found: C 75.47, H 5.33, N 5.56%.

Complexes 21 and 20. A solution of 1.52 g (3.32 mmol) of complex **8** in pentane was stirred under 1 atm of CO for 3 h. Complex **21** as yellow crystals was obtained from the yellow filtrate at −20 °C. Yield: 0.32 g (65%). IR (Nujol): 2095, 1969, 1924 ν(CO), 947 $\nu(PMe_3)$ cm^{-1}. Anal. Calc. for $C_9H_{18}CoO_3P_2$: C 45.77, H 7.68. Found: C 45.47, H 7.73%. At the same time a few fine red crystals of intermediate **20** were separated from the mother-liquor. The molecular structure of **20** was confirmed through X-ray diffraction.

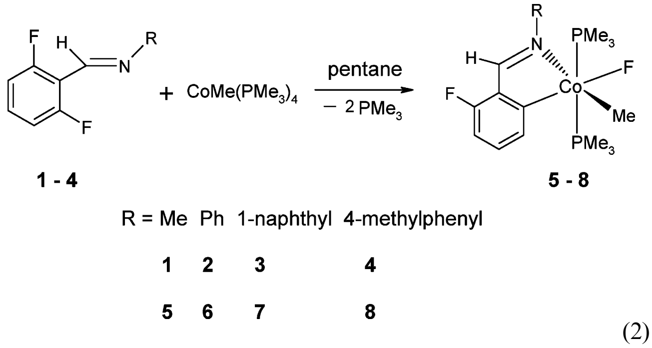
2.3 X-Ray structure determinations

Intensity data were collected on a Bruker SMART diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Crystallographic data for complexes **5**, **6**, **8**, **12**, **20** and **21** are summarized in Table 1. The structures were solved by direct methods and refined with full matrix least-squares on all F^2 (SHELXL-97) with non-hydrogen atoms anisotropic.

3. Results and discussion

3.1. Reactions of $[CoMe(PMe_3)_4]$ with fluorinated benzalimines

Reactions of $[CoMe(PMe_3)_4]$ with *ortho*-fluorinated substrates (**1–4**) containing an imine donor as anchoring group proceed by oxidative addition of the C–F bond to give rise to the *ortho*-metalated diorganocobalt(III) fluorides **5–8** (eqn (2)). Initial coordination of the N-donor appears to be the key step. With the HC=N-moiety as an anchoring group the oxidative addition reactions of the C–F bond at cobalt centers are favored by the chelate effect. Stable diorganocobalt(III) complexes **5–8** with [C–Co–F] fragments were isolated and characterized.



(2)

Table 1 Crystallographic data for complexes **5**, **6**, **8**, **12**, **20** and **21**

	5	**6**	**8**[a]	**12**	**20**[b]	**21**
Formula	$C_{15}H_{28}CoF_2NP_2$	$C_{20}H_{30}Co\ F_2NP_2$	$C_{47}H_{64}CoF_4N_3P_2$	$C_{22}H_{36}CoF_2NP_3$	$C_{22}H_{34}CoF_2NO_2P_2$	$C_9H_{18}CoO_3P_2$
Size/mm^3	0.17 × 0.16 × 0.12	0.30 × 0.28 × 0.25	0.15 × 0.15 × 0.10	0.23 × 0.15 × 0.14	0.35 × 0.32 × 0.28	0.15 × 0.15 × 0.10
M_r/g mol^{-1}	381.25	443.32	867.88	504.36	503.39	295.12
Crystal system	Orthorhombic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$Cmc2_1$	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$Pnma$
a/Å	13.136(12)	8.7532(18)	12.7602(13)	8.5130(17)	8.9511(6)	9.9363(7)
b/Å	12.813(17)	13.961(3)	22.376(2)	16.009(3)	31.208(2)	10.6261(8)
c/Å	11.417(10)	18.876(4)	17.1926(18)	18.999(4)	9.0569 (2)	13.7536(9)
α/°	90	87.60(3)	90	90	90	90
β/°	90	89.85(3)	102.235(7)	94.35(3)	95.8310(10)	90
γ/°	90	75.58(3)	90	90	90	90
V/Å^3	1921.6	2232.0(8)	4797.3(8)	2581.8(9)	2516.9(3)	1452.16(18)
Z	4	4	4	4	4	4
D_c/g cm^{-3}	1.318	1.319	1.202	1.298	1.328	1.350
μ/mm^{-1}	1.070	0.932	0.473	0.870	0.841	1.389
Rflns collected	10489	36864	22121	6781	12455	8191
Indep. rflns	2273	10236	8448	4795	4428	1756
Parameters	120	483	514	272	324	83
R_{int}	0.0440	0.0205	0.0329	0.0729	0.0374	0.0353
θ_{max}/°	27.53	27.54	25.05	27.14	25.00	27.68
R_1 ($I > 2\sigma(I)$)	0.0232 0	0352 0	0474 0	0699	0.0555	0.0307
wR_2 (all data)	0.0584	0.0991	0.1416	0.2035	0.1591	0.0796
GOF	0.985	1.020	1.047	0.984	1.019	1.024

[a] Diamine–pentane solvate. [b] Water solvate.

Complexes **5–8** were isolated from the pentane or diethyl ether solutions as red crystals in yields of 30–40%. In the infrared spectra of complexes **5–8**, the characteristic ν(C═N) bands are found in the region of 1592–1603 cm^{-1}. The imine-H proton resonances of **5–8** are recorded at 8.46–9.70 ppm, while Co-methyl protons resonate between 0.30–0.37 ppm. All spectroscopic data are compatible with an octahedral configuration around the cobalt atom in solution, consisting of a P–Co–P axis and equatorial coordination of C, C, F and N donor atoms. The crystal structures of complexes **5**, **6** and **8** were elucidated by X-ray diffraction analysis.

The molecular structures of complexes **5**, **6** and **8** (Fig. 1, 2 and 3) confirm the octahedral coordination geometry of cobalt. A five-membered metallacycle is formed through the coordination of the N atom of the imine group and the *ortho*-chelated C atom. The sum of internal bond angles (540°) of this chelate ring indicates ideal planarity. Typically, the F atom is *trans*-oriented to the phenyl-C atom, which is well understood in terms of mutual *trans*-influence. The bite angle of the chelating ligand in complex **6** (C26–Co1–N2 83.29(8)°) is close to those in complexes **5** (C1–Co1–N2 83.17(11)°) and **8** (C1–Co1–N1 83.36(12)°), but significantly larger than that found in a related compound,[8] The two axial trimethylphosphine ligands are slightly displaced (P2–Co1–P1 173.91(3)°) towards the Co–methyl group for steric reasons. The C═N bond lengths (N2–C7 1.284(3) Å, **5**; N2–C23 1.294(3) Å, **6** and N1–C7 1.290(4) Å, **8**) are comparable with that (1.293(8) Å) in the *ortho*-metalated cobalt(III) fluoride,[6] but a bit larger than in the uncoordinated imine molecules.

The Co–F bond lengths in complex **5** (Co1–F200 1.9285(14) Å) and in complex **6** (Co1–F3 1.926(1) Å) are shorter than in complex **8** (Co1–F1 1.9584(17) Å). Co–C$_{phenyl}$ bond lengths in complex **5** (Co1–C1 1.906(3) Å), **6** (Co1–C26 1.910(2) Å) and **8** (Co1–C1 1.899(3) Å) are remarkably shorter than Co–C$_{methyl}$ bond lengths in these three complexes (Co1–C100 2.016(3) Å, **5**; Co1–C3 2.004(2) Å, **6** and Co1–C14 2.004(3) Å, **8**) because of the *trans*-influence of the fluorine atoms with strong electron-withdrawing ability. There are two independent molecules in the asymmetric unit and only one of them is shown in Fig. 2.

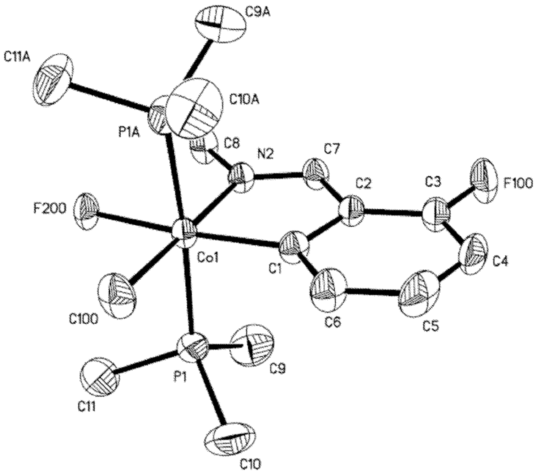


Fig. 1 Molecular structure of **5** with 30% probability ellipsoids. A-labelled atoms are related to the corresponding atoms by the symmetry operation (1 − *x*, +*y*, +*z*). Selected bond distances (Å) and angles (°): N2–Co1 1.966(2), P1–Co1 2.2068(5), F200–Co1 1.9285(14), Co1–P1A 2.2068(5), C1–Co1 1.906(3), C100–Co1 2.016(3), C7–N2 1.284(3), C1–C2 1.418(3); C1–C2–C7 114.7(2), P1–Co1–P1 173.51(4), F200–Co1–C100 89.77(12), C1–Co1–N2 83.17(11), C7–N2–Co1 115.62(18), C2–C1–Co1 112.07(19), N2–C7–C2, 114.5(2), N2–Co1–C100 178.91(13).

CoMe(PMe$_3$)$_4$ did not react with fluoroaromatic imines (**9**, **10** and **11**) that contain bulky groups at the imine–N atom (eqn (3)).

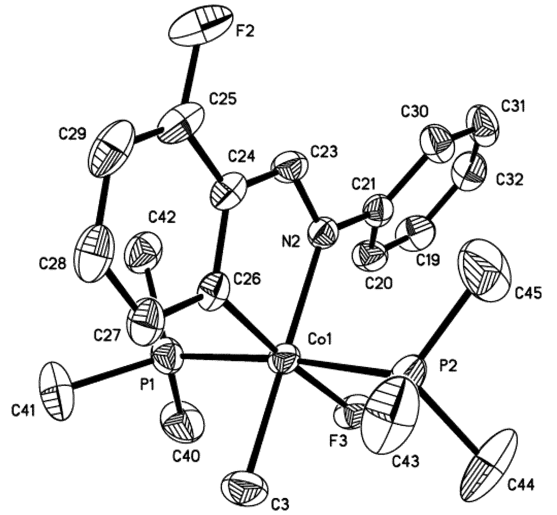


Fig. 2 Molecular structure of **6** with 30% probability ellipsoids, selected bond lengths (Å) and angles (°): C26–Co1 1.910(2), Co1–F3 1.926(1), C3–Co1 2.004(2), Co1–N2 2.040(2), Co1–P1 2.214(1), Co1–P2 2.212(1), N2–C23 1.294(3), C24–C26 1.414(3); C26–Co1–F3 175.29(1), C26–Co1–C3 96.88(10), F3–Co1–C3 87.72(9), C23–N2–Co1 112.06(13), N2–C23–C24 116.90(18), C26–Co1–N2 83.29(8), F3–Co1–N2 92.11(6), P1–Co1–P2 173.91(3), C26–C24–C23 115.12(17), C24–C26–Co1 112.57(14).

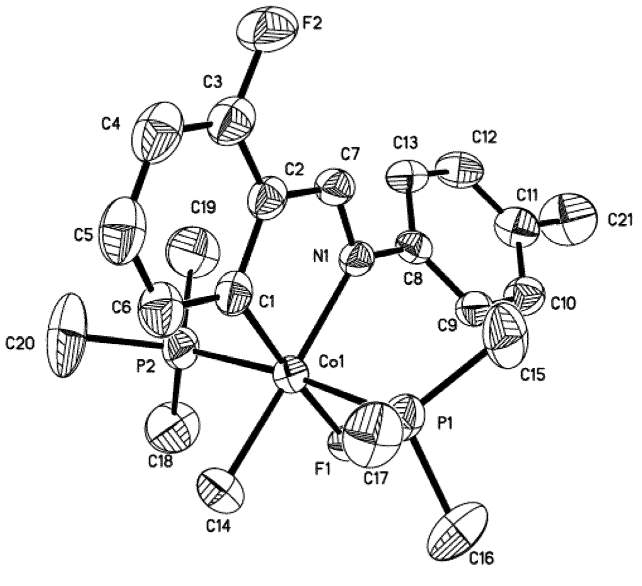
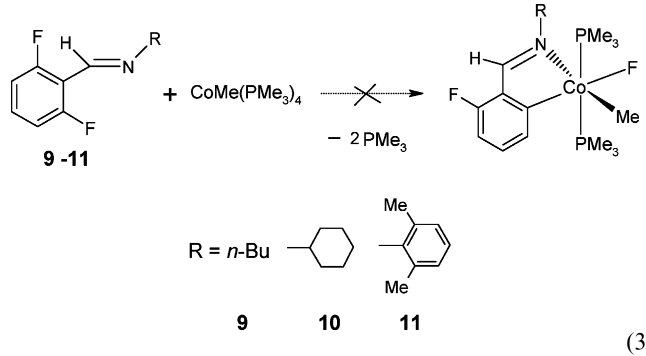


Fig. 3 Molecular structure of **8** with 30% probability ellipsoids, only one of the three components in the crystal cell is shown. Selected bond lengths (Å) and angles (°): Co1–C1 1.899(3), Co1–F1 1.9584(17), Co1–C14 2.004(3), Co1–N1 2.047(2), Co1–P2 2.2157(10), Co1–P1 2.2234(10), N1–C7 1.290(4), C2–C7 1.429(4); N1–Co1–P2 92.43(7), N1–Co1–P1 93.92(7), P2–Co1–P1 173.60(4), F1–Co1–N1 92.43(8), C1–Co1–C14 94.98(16), C1–Co1–N1 83.36(12), C7–N1–Co1 111.5(2), C2–C1–Co1 112.6(2), C1–C2–C7 115.2(3), N1–C7–C2 117.3(3).

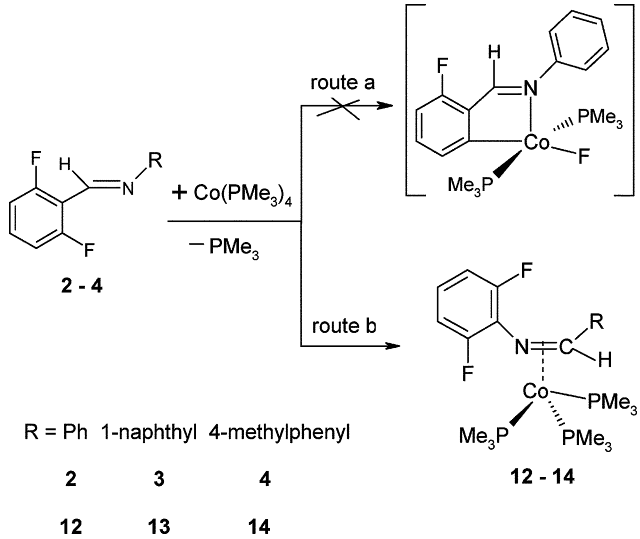
It is proposed that the spatial hindrance of the bulky groups makes the coordination of nitrogen atom to cobalt centre difficult. This coordination is a necessary pre-condition for the activation and cleavage of the C–F bond.



(3)

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

When $Co(PMe_3)_4$ instead of $CoMe(PMe_3)_4$ was used under similar reaction conditions, no C–F activation was observed *via* route **a** of Scheme 1. Unexpectedly the π-coordinated cobalt(0) complexes **12–14** were obtained (route **b**, Scheme 1).



Scheme 1 Preparation of π-coordinated cobalt(0) complexes **12–14**.

The reaction of *N*-phenyl-2,6-difluorobenzalimine **2** with $Co(PMe_3)_4$ afforded complex **12** as brown–red crystals (from pentane solution at 0 °C). Complex **12** is paramagnetic and was characterized by single-crystal X-ray diffraction.

Complex **12** has a tetrahedral coordination geometry with a π-coordinated imine (C7–N1) group and three σ-coordinated trimethylphosphine ligands with normal Co–P distances (Fig. 4) which makes complex **12** a formal cobalt(0) complex. The Co1–N1 distance (1.919(4) Å) is a bit shorter than Co1–C7 distance (2.015(4) Å) as expected for the smaller covalent radius of the nitrogen atom. Owing to the π-coordination of C═N, the C═N bond length (N1–C7 1.396(5) Å) is remarkably longer than those in the complexes **5**, **6** and **8** (average: 1.289 Å) and is between a C–N single bond and C═N double bond, while σ-N coordination of the C═N group is indicated in complexes **5**, **6** and **8**.

Compared with the reaction of $Co(PMe_3)_4$ and *N*-phenyl-2-chlorobenzalimine, in which C–Cl bond activation occurred with the formation of a five-membered chelate ring,[9] no C–F cleavage was observed (Scheme 1). Because the C–F bond energy is larger than that of C–Cl bond, the coordination of nitrogen

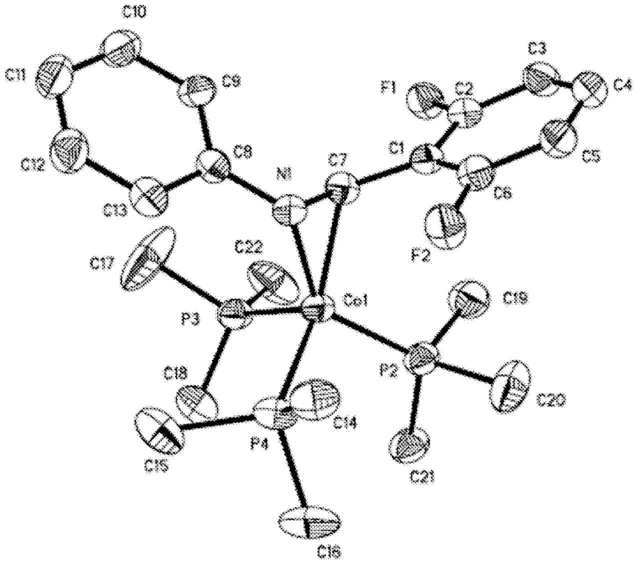


Fig. 4 Molecular structure of **12** with 30% probability ellipsoids, Selected bond lengths (Å) and angles (°): N1–Co1 1.919(4), Co1–C7 2.015(4), Co1–P2 2.1933(14), Co1–P3 2.2338(16), Co1–P4 2.2093(14), N1–C7 1.396(5); N1–Co1–C7 41.47(16), N1–Co1–P2 138.04(11), C7–Co1–P2 102.92(12), N1–Co1–P3 107.47(13), C7–Co1–P3 100.39(14), P2–Co1–P3 99.28(6), N1–Co1–P4 102.69(12), C7–Co1–P4 142.35(13), P2–Co1–P4 102.16(6), P3–Co1–P4 102.75(6).

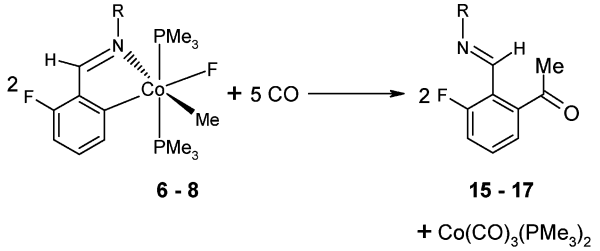
atom and the formation of the chelate ring can not compensate the energy, which is necessary for the C–F bond cleavage. In addition, the π-coordination of C═N to cobalt(0) centre makes a great contribution to the backbonding which is beneficial for the stability of complexes **12–14**. The π-coordinated cobalt(0) complexes **12–14** are likely to be kinetic products, compared with the expected cyclometalated products that arise from C–F bond activation.

Under similar conditions complex **13** and **14** were isolated through the reaction of **3** and **4** with $Co(PMe_3)_4$. In the IR spectra the ν(C═N) vibrations for complexes **13** (1625 cm^{-1}) and **14** (1622 cm^{-1}) are comparable with that of complex **12** (1624 cm^{-1}).

3.3. Formation of novel organic fluorides with demetallation and carbonylation of complexes 6–8 by CO

The carbonylation of aryl chlorides and bromides is of particular interest. In these carbonylations carbon monoxide is widely used as a cheap and readily available reagent for C–C coupling reaction.[10]

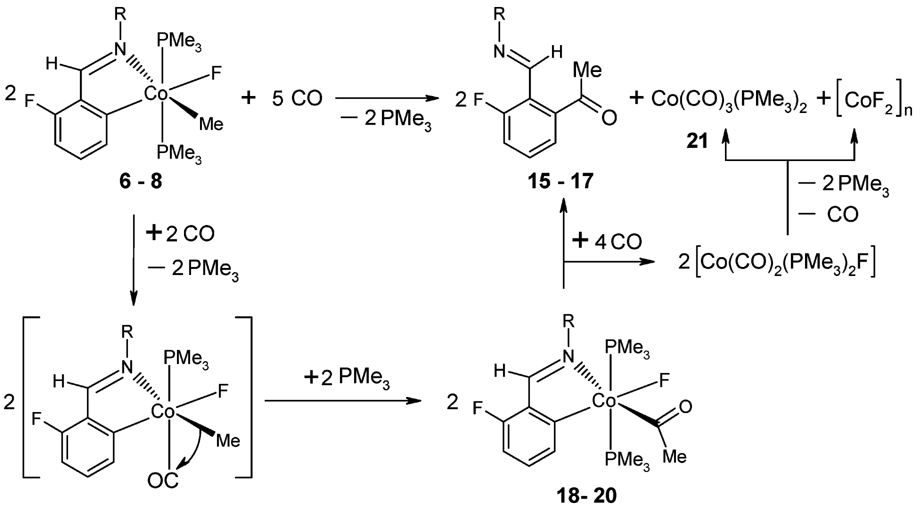
Pentane solutions of complexes **6–8** were stirred under 1 bar of CO for 24 h (eqn (4)). After work-up, column chromatographic separation using petroleum ether–ethyl acetate as eluent led to organic fluorides **15–17**. Compounds **15–17** were characterized by IR, NMR and MS. $Co(CO)_3(PMe_3)_2$ was confirmed by single-crystal X-ray diffraction.



6 - 8 **15 - 17** (4)

R =	Ph	1-naphthyl	4-methylphenyl
	6	7	8
	15	16	17

A proposed mechanism is described in Scheme 2. Substitution of one trimethylphosphine ligand by a carbonyl ligand is likely to be the first step. Subsequent insertion of the carbonyl ligand into the Co–methyl bond gives an acetyl cobalt complex as an important intermediate. With complex **8** the intermediate **20**, an acetyl cobalt complex, was isolated and structurally characterized (Fig. 5). The novel organic fluorides **15–17** form through reductive elimination with C, C-coupling. The unstable cobalt(I) complex, $[Co(CO)_2(PMe_3)_2F]$, disproportionates to insoluble cobalt difluoride and the soluble cobalt(0) complex $Co(CO)_3(PMe_3)_2$ (**21**). Complex **21** was structurally characterized by X-ray single-crystal diffraction (Fig. 6). The characterization of $[CoF_2]_n$ was not successful.



Scheme 2 Proposed formation mechanism for organic fluorides **15–17**.

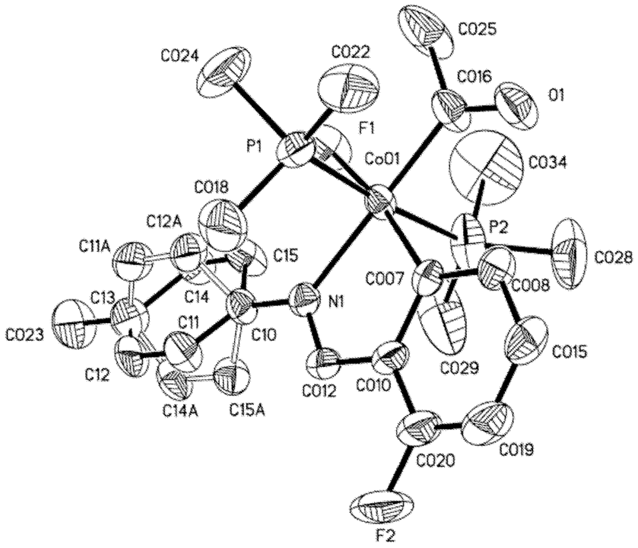


Fig. 5 Molecular structure of **20** with 30% probability ellipsoids, the water molecule in the crystal cell is omitted for the clarity. Selected bond lengths (Å) and angles (°): Co01–F1 1.928(3), Co01–C007 1.930(4), Co01–N1 2.092(3), Co01–P1 2.2115(15), Co01–P2 2.2162(17), Co01–C016 1.904(5), C012–N1 1.275(5), C010–C012 1.435(6), C10–N1 1.438(5), C016–O1 1.194(5), C016–C025 1.541(7); N1–Co01–C007 82.5(7), N1–C012–C010 117.5(4), P1–Co1–P2 173.49(6), F1–Co01–C007 170.78(15), N1–Co01–C016 178.56(18), C025–C016–O1 115.2(5), Co01–C016–O1 127.7(4), Co01–C016–C025 117.2(4).

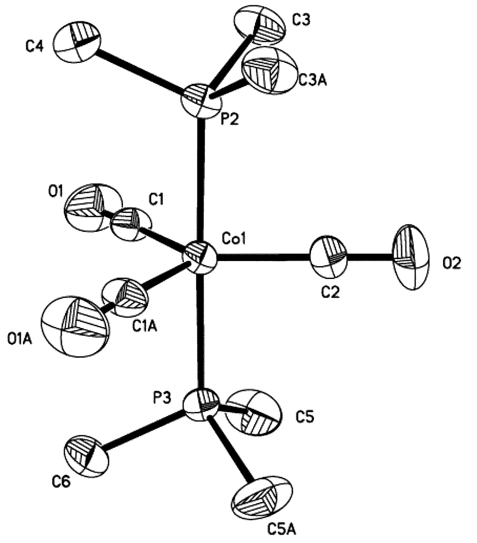


Fig. 6 Molecular structure of **21** with 30% probability ellipsoids. A-labelled atoms are related to the corresponding atoms by the symmetry operation (+*x*, 1/2 − *y*, +*z*). Selected bond lengths (Å) and angles (°): C1–O1 1.114(3), C1–Co1 1.843(3), Co1–C1A 1.843(3), Co1–P3 2.1825(9), Co1–P2 2.1908(9), C2–Co1 1.762(4), O2–C2 1.129(4); C1–Co1–C1A 115.69(16), C2–Co1–C1 122.15(8), C2–Co1–C1A 122.15(8), P3–Co1–P2 178.97(4), O1–C1–Co1 178.5(2), O2–C2–Co1 180.0(4).

Complex **20** has six-coordinated cobalt in octahedral geometry with two phosphorus atoms, one imine-nitrogen atom, one fluorine atom and two carbon atoms. This cobalt(III) intermediate with a *cis*-orientated aryl-carbon atom and acetyl-carbon atom is not stable and easily transforms to the cobalt(I) complex with reductive elimination to afford novel organic fluorides **15–17**.

The crystal of complex **21** belongs to the *Pnma* space group in the orthorhombic crystal system with D_{3h} symmetry for the molecular structure. $Co(CO)_3(PMe_3)_2$ has a trigonal bipyramidal configuration with two axial trimethylphosphine ligands, while three carbonyl ligands are oriented in the equatorial plane. From the axial view the two trimethylphosphine ligands are in eclipsed conformation, while three carbonyl ligands are located in staggered positions with respect to the two axial phosphine ligands. The bond angle of P–Co–P is 178.97(4)°. The Co–C and carbonyl $C\equiv O$ bond lengths are in the normal region.[11]

Complex **21** is a neutral complex with cobalt in zero oxidation state.[12–14] To our knowledge, this is one of a small number of five-coordinated 19-electron cobalt(0) complexes without support of a chelate ligand or other auxiliary reagent.[12,13] Zhuang reported a 19-electron cobalt(0) complex, $Co(CO)_2(PPh_3)_2(CO\text{–}BEt_3)$, which is stabilized by terminal linking of the carbonyl ligand to BEt_3.[11] Tyler presented a formal 19-electron cobalt(0) complex, $Co(CO)_3L_2$ (L_2 = 2,3-bis(diphenylphosphino)maleic anhydride), which was referred to as an (18 + δ) cobalt(0) complex and was applied as a catalyst in cyclooligomerization of acetylenes.[13] The IR bands at 2095, 1969 and 1924 cm^{-1} of complex **21** are assigned to the $C\equiv O$ stretches, by comparison to those of $Co(CO)_3L_2$ complexes.[15]

4. Conclusion

A cyclometalation reaction involving C–F bond activation at a cobalt(I) center with aldazine–N atom as an anchoring group affords *ortho*-chelated cobalt(III) complexes containing a [C–Co–F] fragment $[CoFMe(PMe_3)_2\{(C_6H_3F\text{-}ortho)CH{=}N\text{–}R\}]$ **5–8**. Under similar reaction conditions π-coordinated cobalt(0) complexes $[Co(PMe_3)_3((C_6H_3F\text{-}ortho)CH{=}N\text{–}R)]$ **12–14** were formed when $[Co(PMe_3)_4]$, instead of $[CoMe(PMe_3)_4]$, was applied. No C–F bond activation was then observed. Carbonylation of complexes **6–8** delivered novel organic fluorides **15–17** with demetallation. As important intermediates, an acetyl cobalt complex, $[CoFMeC{=}O(PMe_3)_2\{(C_6H_3F\text{-}ortho)CH{=}N\text{–}R\}]$ **20**, and a cobalt(0) complex, $Co(CO)_3(PMe_3)_2$ **19**, were structurally characterized by X-ray diffraction. The crystal and molecular structures of complexes **5**, **6**, **8**, **12**, **20** and **21** were determined by X-ray diffraction.

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