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Preparation of organocobalt complexes through C – F/C – H bond activation of polyfluoroaryl imines

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ABSTRACT

In this paper, we reported the C – F and C – H bond activation of polyfluoroimine ligands induced by $CoMe(PMe_3)_4$. The reaction of pentafluorophenylmethylidene-2,6-di*iso*propylaniline **1** with $CoMe(PMe_3)_4$ afforded an *ortho*-chelated cobalt(I) complex $[Co(PMe_3)_3(C_6F_4\text{-}ortho\text{-}CH = N\text{-}C_6H_3(iso\text{-}Pr)_{2(ortho,\ ortho)})]$ (**5**) via C – F bond activation and subsequent elimination of methyl fluoride. Under similar reaction conditions, the reactions of polyfluoroaryl imines **2**–**4** with $CoMe(PMe_3)_4$ afforded the penta-coordinate cobalt(I) complexes **6**–**8** via C – H bond activation and subsequent elimination of methane $[Co(PMe_3)_3(C_6H_2F_{2(meta,\ meta)}\text{-}ortho\text{-}(CH = N\text{-}C_6H_4Cl_{para})]$ (**6**), $[Co(PMe_3)_3(C_6H_2F_{2(meta,\ para)}\text{-}ortho\text{-}(CH = N\text{-}C_6H_4Cl_{para})]$ (**7**), and $[Co(PMe_3)_3(C_6HF_{3(meta,\ meta,\ para)}\text{-}ortho\text{-}(CH = N\text{-}C_6H_4Cl_{para})]$ (**8**). Complexes **5**–**8** were characterized through IR, ^1H NMR, ^{31}P NMR, ^{19}F NMR and elemental analyses. The crystal and molecular structures of complexes **5**, **6** and **8** were determined by X-ray single crystal diffraction. The reactions of **8** with MeI and EtBr afforded organic fluorides **9**–**10**. A proposed formation mechanism of **9**–**10** with the oxidative addition of RX at the cobalt(I) center of **8** and reductive elimination via C,C-coupling was discussed.

Fluorinated aromatic compounds are important components in diverse fields of science and technology, including pharmaceuticals and agrochemicals [1]. However, there are no identified natural fluoroaromatic building blocks, which must be generated by synthesis [2]. A feasible and direct approach is to functionalize aryl fluoride via C – H or C – F bond activation by transition–metal complexes. There have been some reports on C – F and C – H bond activation of fluorinated compounds with Ru, Rh, Pd, Ni, and Fe complexes [3–13]. By contrast, few publications were disclosed on cobalt mediated C – F and C – H bond activation of polyfluoroorganic compounds. Holland provided the research result of C – F bond activation of fluorobenzene by low-coordinated cobalt complex [14]. Klein published the selective *ortho*-(C – H) and (C – F) bond activation of arylketones at cobalt centers [15].

In recent years, we focused our research in the field of C – F or C – H bond activation and functionalization of polyfluoroorganic compounds mediated by electron-rich cobalt complexes. After isolation and characterization of the first cobalt(III) complex containing a [C–Co–F] fragment through C – F bond activation of fluorinated imine with $CoMe(PMe_3)_4$ in 2006 [16], a series of organocobalt complexes were synthesized through C – F bond activation [17–21]. As a continuation of our research, in this paper, we present the recent results of our study on C – F or C – H bond activation of fluorinated imines (**1**–**4**) by $CoMe(PMe_3)_4$. Four organocobalt complexes (**5**–**8**) were prepared and characterized. The reactivity of complex **8** with MeI and EtBr was also investigated.

The reactions of pentafluorophenylmethylidene-2,6-di*iso*propylaniline **1** [18] with $CoMe(PMe_3)_4$ afforded a penta-coordinate cobalt(I) complex **5** via C – F bond activation and subsequent elimination of methyl fluoride (Scheme 1) [22].

Cobalt(I) complex **5** was isolated as dark brown crystals in the yield of 66% by crystallization from pentane at 4 °C. Complex **5** in the solid state is stable for several hours at room temperature. In the infrared spectrum of complex **5**, the $\nu(C{=}N)$ band was recorded at 1621 cm^{-1}. Compared with the C=N band (1648 cm^{-1}) of compound **1**, 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 center. In the ^1H NMR spectrum, an imine-H proton was recorded at 8.88 ppm as a singlet while the 27 protons of the three PMe_3 ligands were found at 0.84 ppm as a doublet (9H, $^2J_{PH} = 9$ Hz) and at 1.13 ppm as a singlet (18H) in the integral ratio of 1: 2. In the ^{31}P NMR spectrum, three broad singlets at − 1.26, − 15.85 and − 16.07 ppm with the integral ratio of 1:1:1 suggest that the three phosphorus atoms have different chemical environments.

The spectroscopic information indicates that complex **5** is a penta-coordinate compound. This was confirmed by X-ray diffraction (Fig. 1) [23]. Complex **5** has a trigonal bipyramid geometry (TBP) with P2, P3 and N1 atoms in the equatorial plane. The three bond angles in this

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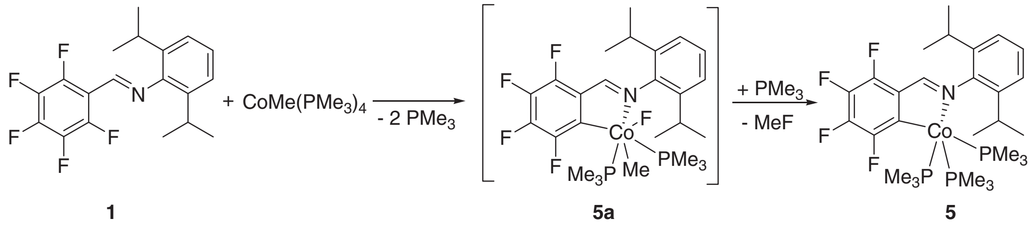
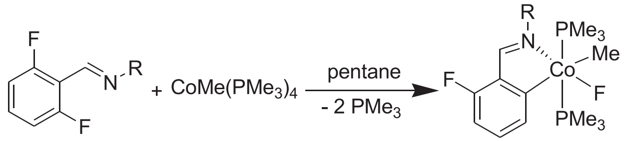


Scheme 1. Reaction of **1** with $CoMe(PMe_3)_4$.

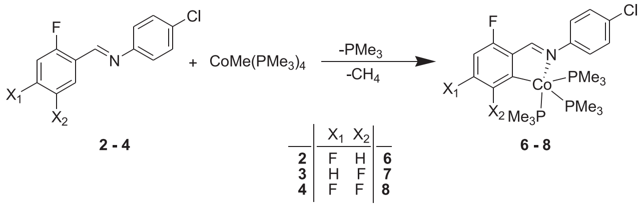
plane are N1–Co1–P2 118.34(7)°, N1–Co1–P3 123.23(7)° and P3–Co1–P2 116.45(4)° with the sum of 358.2°. P1 and C6 atoms are located in the axial positions with a bond angle of C6–Co1–P1 177.58(9)°. The axial bond distance Co1–P1 (2.2348(9) Å) is remarkably longer than the equatorial bond distance Co1–P2 (2.2200(9) Å) or Co1–P3 (2.2138(10) Å) due to the TBP geometry [24].



(1)

According to our early report on the C – F bond activation of 2,6-difluorinated imines with $CoMe(PMe_3)_4$ (Eq. (1)) [17], oxidative addition of the *ortho*-(C – F) bond at the cobalt(I) center is the first step via cyclometalation with the imine as an anchoring group to form an intermediate cobalt(III) **5a** containing a [C–Co–F] fragment (Scheme 1). However, **5a** with four electron-withdrawing fluorine atoms on the phenyl ring is not stable as the product in Eq. (1) with one fluorine atom on the phenyl ring. This instability is probably caused by the weaker coordination ability of the imine-N atom in **5a**. In addition, the larger steric hindrance, the *iso*-propyl groups close to the C═N, is beneficial to the C,C-coupling reaction. Reductive elimination of **5a** afforded cobalt(I) complex **5** with the escape of MeF.

Under similar reaction conditions, the reactions of polyfluoroaryl imines **2**–**4** [18] with $CoMe(PMe_3)_4$ afforded the penta-coordinate cobalt(I) complexes **6**–**8** via C – H bond activation and subsequent elimination of methane (Eq. (2)) [22].



(2)

Complexes **6**, **7** and **8** were obtained as dark green crystals by crystallization from pentane at 4 °C in the yields of 53–80%. In the infrared spectra of complexes **6**–**8**, the characteristic ν(C═N) bands were recorded at 1590 (**6**), 1589 (**7**) and 1605 cm^{-1} (**8**). In the ^1H NMR spectra, the imine-H proton resonances are located at 9.13 (**6**), 9.43 (**7**) and 9.02 ppm (**8**) as a singlet. PMe_3 proton resonance was recorded as a doublet (9H) and a singlet (18H). In the ^{31}P NMR spectra, three singlets are registered with the integral ratio of 1:1:1. All of the spectroscopic information indicates that complexes **6**–**8** have the structure as shown in Eq. (2). This conjecture was further confirmed by X-ray single crystal analysis (Figs. 2–3) [23].

Complexes **6** and **8** have similar structures as complex **5**. Both of them have a trigonal bipyramid geometry with two P atoms and one N atom in the triangular plane. The third P and C atoms of the fluoroaromatic ring are located in the axial positions. In this case, C – H bond is easier to be activated, especially with the escape of methane. Complexes **6**–**8** are not stable in the air.

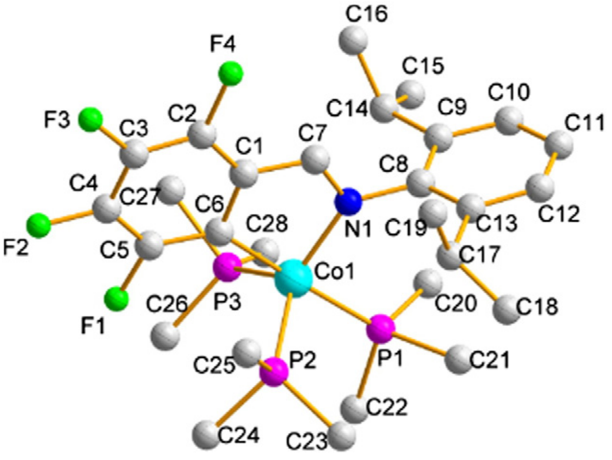


Fig. 1. Molecular structure of **5** (all the hydrogen atoms were omitted for clarity). Selected bond distances (Å) and angles (°): Co1–N1 1.958(2), Co1–C6 1.981(3), Co1–P3 2.214(1), Co1–P2 2.2200(9), Co1–P1 2.2348(9), N1–C7 1.319(3); N1–Co1–C6 81.0(1), N1–Co1–P3 123.23(7), C6–Co1–P3 88.60(9), N1–Co1–P2 118.34(7), C6–Co1–P2 86.58(8), P3–Co1–P2 116.45(4), N1–Co1–P1 96.79(7), C6–Co1–P1 177.58(9), P3–Co1–P1 93.36(4), P2–Co1–P1 93.80(3).

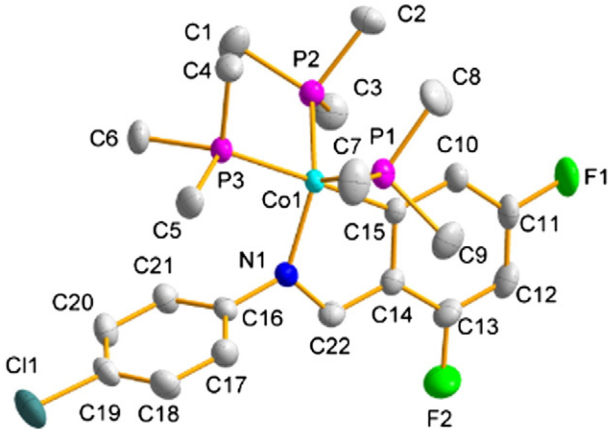


Fig. 2. Molecular structure of complex **6** (all the hydrogen atoms were omitted for clarity). Selected bond distances (Å) and angles (°): Co1–C15 1.942(2), Co1–N1 1.949(2), Co1–P2 2.1882(7), Co1–P1 2.1911(7), Co1–P3 2.2314(8), N1–C22 1.313(3); C15–Co1–N1 81.89(8), C15–Co1–P2 87.10(6), N1–Co1–P2 128.30(5), C15–Co1–P1 84.73(6), N1–Co1–P1 112.43(5), P2–Co1–P1 116.59(3), C15–Co1–P3 178.56(6), N1–Co1–P3 96.87(6), P2–Co1–P3 94.26(3), P1–Co1–P3 95.09(2).

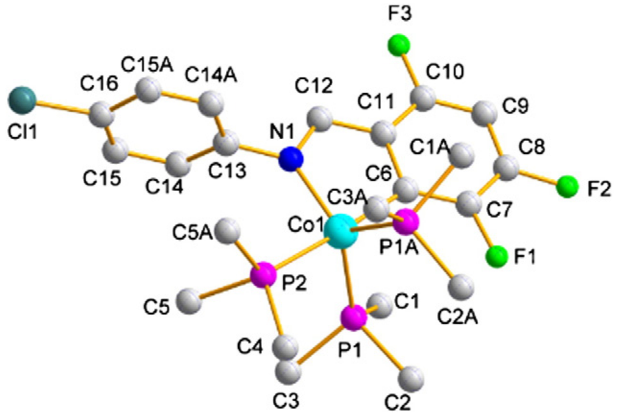
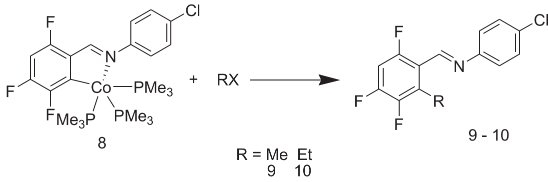


Fig. 3. Molecular structure of complex **8** (all the hydrogen atoms were omitted for clarity). Selected bond distances (Å) and angles (°): Co1–N1 1.959(2), Co1–C6 1.960(3), Co1–P1 2.2146(7), Co1–P1A 2.2146(7), Co1–P2 2.2462(9), N1–C12 1.317(4); N1–Co1–C6 81.4(1), N1–Co1–P1 121.33(2), C6–Co1–P1 87.99(5), N1–Co1–P1A 121.33(2), C6–Co1–P1A 87.99(5), P1–Co1–P1A 115.67(4), N1–Co1–P2 95.93(8), C6–Co1–P2 177.31(9), P1–Co1–P2 93.44(3), P1A–Co1–P2 93.44(3).

Among organic halides, MeI and EtBr are normally used as oxidants because of their good chemical activity. The pentane solution of complex **8** was reacted with MeI and EtBr (Eq. (3)). After work-up, column chromatographic separation using petroleum ether/triethylamine (200:1) as developing agent led to organic fluorides **9**–**10** in the yield of ca. 90%. Compounds **9** and **10** were characterized by ^{1}H, ^{19}F, and ^{13}C NMR spectra and mass spectrum. As byproducts, $CoCl(PMe_3)_3$ and $CoBr(PMe_3)_3$ were confirmed by IR spectrum [25].



(3)

Based upon these experimental results, a proposed mechanism for reaction (3) is described in Scheme 2. The first step should be the oxidative addition of RX at the cobalt(I) center of complex **8** to afford a hexa-coordinate cobalt(III) intermediate **8a**. The unstable **8a** delivered **8b** through reductive elimination with C,C-coupling. $CoX(PMe_3)_3$ was formed in the presence of trimethylphosphine in the solution to afford the novel fluorinated imine as the final products **9** and **10**.

In summary, we reported the C–F and C–H bond activation of polyfluoroimine ligands induced by $CoMe(PMe_3)_4$. Four organocobalt(I) complexes (**5**–**8**) were synthesized and characterized. The reactions of **8** with MeI and EtBr afforded organic fluorides **9**–**10** as C–C coupling products. The crystal and molecular structures of complexes **5**, **6** and **8** were determined by X-ray single crystal diffraction.

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Appendix A. Supplementary material

CCDC 927670 (**5**), 927669 (**6**) and 974818 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.inoche.2014.02.017.

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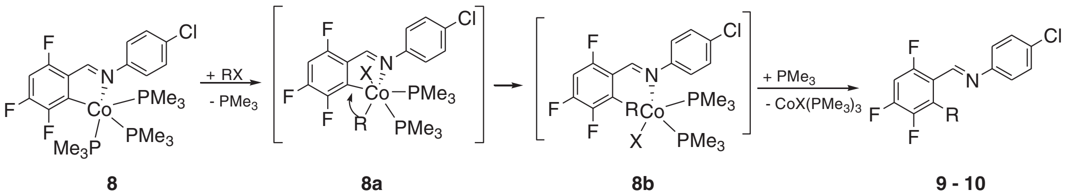
[21] F. Lu, H. Sun, X. Li, Chin. J. Chem. 31 (2013) 927–932.
[22] Synthesis of complex **5**: A solution of **1** (0.53 g, 1.50 mmol) in diethyl ether (30 mL) was added to a solution of $CoMe(PMe_3)_4$ (0.68 g, 1.80 mmol) in diethyl ether (20 mL) at −78 °C under N_2 atmosphere. The reaction mixture was warmed to ambient temperature and stirred for 12 h. During this period, the red reaction mixture turned dark brown in color. After filtering, crystallization from ether at 4 °C afforded brown single crystals of **5** (0.61 g, 66 %) suitable for X-ray analysis. Anal. calc. for $C_{28}H_{45}CoF_4NP_3$ (623.51 g mol^{-1}): C, 53.94; H, 7.27; N, 2.25%. Found: C, 53.52; H, 7.48; N, 2.46%. Dec. >127 °C. IR (Nujol mull): 1621 ν(C=N), 943 ν(PMe_3) cm^{-1}. NMR data: ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 8.88 (s, 1H, *CH* = N), 7.35–7.31 (m, 3H, Ar-*H*), 3.46–3.37 (m, 2H, Ar-*CH*-Me), 1.36 (d, *J* = 6.0 Hz, 6H, *CH*$_3$), 1.18 (d, *J* = 6.0 Hz, 6H, *CH*$_3$), 1.13 (s, 18H, P*CH*$_3$), 0.84 (d, *J* = 9.0 Hz, 9H, P*CH*$_3$), ^{31}P NMR (121 MHz, C_6D_6, 298 K): δ −1.3 (s, 1P, *P*Me$_3$), −15.8 (s, 1P, *P*Me$_3$), −16.1 (s, 1P, *P*Me$_3$), ^{19}F NMR (282 MHz, C_6D_6, 298 K), δ −112.0 (s, 1F), −115.9 (s, 1F), −150.9 (s, 1F), −166.4 (s, 1F). Complexes **6**–**8** were synthesized according to the similar method as that for complex **5**. Synthesis of **6**: Complex **6** as green crystals was obtained in the yield of 71%. Anal. calc. for $C_{22}H_{34}ClCoF_2NP_3$ (537.82 g mol^{-1}): C, 49.13; H, 6.37; N, 2.60%. Found: C, 49.22; H, 6.48; N, 2.54. Dec. >102 °C. IR (Nujol mull): 1590 ν(C=N), 938 ν(PMe_3) cm^{-1}. NMR data: ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 9.13 (s, 1H, *CH* = N), 7.82 (d, *J* = 9Hz, 1H, Ar-*H*), 7.04 (d, *J* = 6Hz, 2H, Ar-*H*), 6.82 (d, *J* = 9.0 Hz, 2H, Ar-*H*), 6.59 (t, *J* = 9.0 Hz, 1H, Ar-*H*), 0.79 (s, 27H, P*CH*$_3$), ^{31}P NMR (121 MHz, C_6D_6, 298 K): δ −0.9 (s, 1P, *P*Me$_3$), −15.8 (s, 2P, *P*Me$_3$), ^{19}F NMR (282 MHz, C_6D_6, 298 K), δ −115.3 (s, 1F), −116.8 (s, 1F). Synthesis of **7**: Complex **7** as green crystals was obtained in the yield of 53%. Dec. >98 °C. Anal. Calc. for $C_{22}H_{34}ClCoF_2NP_3$ (537.82 g mol^{-1}): C, 49.13; H,



Scheme 2. A proposed mechanism of demetallation of complex **8**.

6.37; N, 2.60%. Found: C, 49.02; H, 6.28; N, 2.74. IR (Nujol mull): 1589 ν(C═N), 945 ν(PMe_3) cm^{-1}. NMR data: ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 9.43 (s, 1H, C*H* = N), 7.13 (d, J = 6.0 Hz, 2H, Ar-*H*), 7.05 (s, 1H, Ar-*H*), 6.95 (d, J = 6.0 Hz, 2H, Ar-*H*), 6.73 (s, 1H, Ar-*H*), 1.07 (s, 18H, PCH_3), 0.86 (d, J = 6.0 Hz, 9 H, PCH_3), ^{31}P NMR (121 MHz, C_6D_6, 298 K): δ −1.6 (s, 1P, *P*Me$_3$), −15.5 (s, 2P, *P*Me$_3$), ^{19}F NMR (282 MHz, C_6D_6, 298 K), δ −90.5 (d, J = 14.1 Hz, 1F), −124.7 (d, J = 22.6 Hz, 1F). Synthesis of **8**: Complex **8** as green crystals was obtained in the yield of 80%. Anal. calc. for $C_{22}H_{33}ClCoF_3NP_3$ (555.78 g mol^{-1}): C, 47.54; H, 5.98; N, 2.52%. Found: C, 47.70; H, 6.07; N, 2.54. Dec. >115 °C. IR (Nujol mull): 1605 ν(C═N), 945 ν(PMe_3) cm^{-1}. NMR data: ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 9.02 (s, 1H, C*H* = N), 6.92 (d, J = 9.0 Hz, 2H, Ar-*H*), 6.70 (d, J = 9.0 Hz, 2H, Ar-*H*), 6.55–6.47 (m, 1H, Ar-*H*), 0.82 (s, 18H, PCH_3), 0.60 (d, J = 6.0 Hz, 9H, PCH_3), ^{31}P NMR (121 MHz, C_6D_6, 298 K): δ −1.0 (s, 1P, *P*Me$_3$), −17.0 (s, 1P, *P*Me$_3$), −17.2 (s, 1P, *P*Me$_3$), ^{19}F NMR (282 MHz, C_6D_6, 298 K), δ −115.7 (m, 1F), −120.7 (d, J = 19.7 Hz, 1F), −140.5 (d, J = 28.2Hz, 1F). Synthesis of complex **9**: A solution of MeI (0.22 g, 1.50 mmol) in diethyl ether (10 mL) was added to a solution of **8** (0.55 g, 1.00 mmol) in diethyl ether (40 mL) at −78 °C under N_2 atmosphere. The reaction mixture was warmed to ambient temperature and stirred for 24 h. During this period, the dark green reaction mixture turned light red in color. After filtering, crystallization from diethyl ether at 4 °C afforded violet-blue crystals of $Co(PMe_3)_3I$ (0. 34 g, 82%) identified through IR spectra [25]. After isolation of $Co(PMe_3)_3I$, the solution was concentrated by rotary evaporation to provide the crude product. Further column separation provided final product (SiO_2, petroleum ether:triethylamine (200:1) as eluant). Isolated yield: 0.25 g (88 %). NMR data: ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 8.70 (s, 1H, C*H* = N), 7.36 (d, J = 9 Hz, 2H, Ar-*H*), 7.12 (d, J = 9 Hz, 2H, Ar-*H*), 6.90–6.82 (m, 1H, Ar-*H*), 2.66 (d, J = 3.0 Hz, 3H, CH_3), ^{19}F NMR (282 MHz, $CDCl_3$, 298 K), δ −119.2 (dd, J = 5.6, 14.1 Hz, 1F), −128.8 (dd, J = 5.6, 22.6 Hz, 1F), −144.7 (dd, J = 14.1, 22.6 Hz, 1F). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ 158.6 (dd, J = 247.5, 9.0 Hz), 154.4 (d, J = 6.0 Hz), 151.1 (dt, J = 15.0, 270.0 Hz), 150.4 (s), 146.0 (dd, J = 16.5, 240.0 Hz), 132.0 (s), 129.5 (d, J = 15.8 Hz), 129.3 (s), 122.0 (s), 118.9 (d, J = 9.0 Hz), 103.1–102.4 (m), 12.7 (s). HRMS (EI) m/z calculated for $C_{14}H_9F_3NCl$: 283.6802; found: 284.0456. Synthesis of complex **10**: A solution of C_2H_5Br (0.g, 1.50 mmol) in diethyl ether (10 mL) was added to a solution of **8** (0.55 g, 1.00 mmol) in diethyl ether (40 mL) at −78 °C under N_2 atmosphere. The reaction mixture was warmed to ambient temperature and stirred for 24 h. During this period, the dark green reaction mixture turned light red in color. After filtering, crystallization from diethyl ether at 4 °C afforded blue crystals of $Co(PMe_3)_3Br$ (0.30 g, 81%) identified by IR spectra [25]. After isolation of $Co(PMe_3)_3Br$, the solution of diethyl ether was concentrated by rotary evaporation to provide the crude product. Further column separation provided final products (SiO_2, petroleum ether:triethylamine (200:1) as eluant). Isolated yield: 0.27 g (91 %). NMR data: ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 8.67 (s, 1H, C*H* = N), 7.34 (d, J = 9.0 Hz, 2H, Ar-*H*), 7.11 (d, J = 9.0 Hz, 2H, Ar-*H*), 6.88–6.79 (m, 1H, Ar-*H*), 3.26–3.17 (m, 2H, CH_2), 1.25 (t, J = 9.0 Hz, 3H, CH_3), ^{19}F NMR (282 MHz, $CDCl_3$, 298 K), δ −118.4 (dd, J = 5.6, 19.7 Hz, 1F), −128.7 (dd, J = 5.6, 22.6 Hz, 1F), −147.1 (dd, J = 14.1, 22.6 Hz, 1F). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ 158.7 (ddd, J = 250.5, 10.5, 3.0 Hz), 154.8 (d, J = 6.0 Hz), 151.5 (dt, J = 15.0, 255.0 Hz), 150.4 (s), 145.9 (ddd, J = 3.8, 12.0, 240.0 Hz), 135.7 (d, J = 15.0 Hz), 132.0 (s), 129.3 (d, J = 15.8 Hz), 122.0 (s), 118.5–118.4 (m), 103.2–102.6 (m), 19.2 (s), 14.3 (s). HRMS (EI) m/z calculated for $C_{15}H_{11}F_3NCl$: 297.707

[23] Crystallographic data for **5**: $C_{28}H_{45}CoF_4NP_3$, 623.49 g mol^{-1}, monoclinic, space group Pbca, a = 18.239(4) Å, b = 18.423(4) Å, c = 18.885(4) Å, V = 6346(2) Å^3, T = 293 K, Z = 8, Dc = 1.305 mg cm^{-3}, μ = 0.733 mm^{-1}. A total of 35691 reflections were collected, 7185 unique (Rint = 0.0718), R1 = 0.0471 (for 7185 reflections), wR2 = 0.1048(all data). Crystallographic data for **6**: $C_{22}H_{34}ClCoF_2NP_3$, 537.79 g mol^{-1}, orthorhombic, space group $P2_1/n$, a = 11.388(2) Å, b = 10.070(2) Å, c = 22.960(5) Å, β = 103.10°, V = 2564.5(9) Å^3, T = 293 K, Z = 4, Dc = 1.393 mg cm^{-3}, μ = 0.985 mm^{-1}. A total of 14799 reflections were collected, 5801 unique (Rint = 0.0239), R1 = 0.0340 (for 5801 reflections), wR2 = 0.0848 (all data). Crystallographic data for **8**: $C_{22}H_{33}ClCoF_3NP_3$, 555.78 g mol^{-1}, orthorhombic, space group $P2_1/m$, a = 11.503(2) Å, b = 10.226(2) Å, c = 11.725(2) Å, β = 106.24(3)°, V = 1324.2(5) Å^3, T = 293 K, Z = 2, Dc = 1.394 mg cm^{-3}, μ = 0.961 mm^{-1}. A total of 7805 reflections were collected, 3154 unique (Rint = 0.0196), R1 = 0.0354 (for 3154 reflections), wR2 = 0.0933(all data).

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[25] H.-F. Klein, H.H. Karsch, Inorg. Chem. 14 (1975) 473–477.