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Selective C–F/C–H bond activation of fluoroarenes by cobalt complex supported with phosphine ligands†

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The reactions of pentafluoropyridine C_5NF_5, hexafluorobenzene C_6F_6, and perfluoronaphthalene $C_{10}F_8$ with cobalt(0) complex, $Co(PMe_3)_4$, were investigated. The Co(I) complexes $(4\text{-}C_5NF_4)Co(PMe_3)_3$ (**1**), $(C_6F_5)Co(PMe_3)_3$ (**2**), $(C_{10}F_7)Co(PMe_3)_3$ (**3**), $(4\text{-}C_5NF_4)Co(PMe_3)_4$ (**4**) and $(C_{10}F_7)Co(PMe_3)_4$ (**6**) were obtained by selective activation of the C–F bonds. The reactions of **1** and **2** with CO afforded dicarbonyl cobalt(I) complexes $(4\text{-}C_5NF_4)Co(CO)_2(PMe_3)_2$ (**7**), $(C_6F_5)Co(CO)_2(PMe_3)_2$ (**8**). Under similar reaction conditions, **2** as a C–H bond activation product was obtained from the reaction of pentafluorobenzene, C_6F_5H, with $Co(PMe_3)_4$. The byproducts, hydrodefluorination product 1,2,4,5-$C_6F_4H_2$ and F_2PMe_3 from the reaction of C_6F_5H and $Co(PMe_3)_4$ were also observed. The reaction mechanism of C_6F_5H with $Co(PMe_3)_4$ is proposed and partly-experimentally verified. The reaction of C_6F_5H with $Co(PMe_3)_4$ under 1 bar of CO at room temperature afforded hydrido dicarbonyl cobalt(II) complex $(C_6F_5)Co(H)(CO)_2(PMe_3)_2$ (**11**). Treatment of the mixtures of $C_6F_5H/Co(PMe_3)_4$ with hexachlorobenzene, C_6Cl_6, resulted in $(C_6F_5)CoCl(PMe_3)_3$ (**12**) *via* C–H bond cleavage with the hydrodechlorination product pentachlorobenzene, C_6Cl_5H, and 1,2,4,5-tetrachlorobenzene, $C_6Cl_4H_2$. The structures of complexes **1**, **2**, **6**, **7**, **8**, **11** and **12** were determined by X-ray diffraction.

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1. Introduction

More and more fluorinated organic compounds have been applied in agriculture, leather, pharmaceutical and materials as well as some other industrial branches because they have excellent stability and some special physical and chemical properties.[1–9] However, how to prepare efficiently polyfluorinated or partly-fluorinated organic compounds is still a challenge though some fluorinated methods have been developed. The selective C–F/C–H bond activation and functionalization of polyfluoro organic compounds with transition metal complexes have gradually become an effective way to obtain the desired fluorinated organic compounds.[10–15] Since the mid-1990s, the activation of the C–F bond by transition metal complexes has attracted more attention to explore effective synthesis of novel organic fluorides and to develop the synthetic methodology of organic fluorides *via* defluorination of polyfluorinated organic compounds.[16–24] Milstein reported the first example of catalytic C–F bond activation of pentafluorobenzene with a rhodium complex at room temperature.[25] Recently, substantial progress has been achieved in the field of C–F bond activation and functionalization by transition metal complexes as catalysts.[26–35] Braun disclosed that the Heck cross coupling of pentafluoropyridine was catalyzed by the C–F bond activation product of pentafluoropyridine with Pd(II) complex supported by phosphine ligands.[29] Love developed a method for the catalytic methylation of some polyfluoroaryl imines in high yields and high selectivity utilizing platinum and nickel complexes.[30] Radius described the cross coupling reactions of perfluorotoluene and perfluorobiphenyl with *N*-heterocyclic carbene (NHC) nickel complexes as the catalyst and the catalytic hydrodefluorination with silanes as the hydrogen source.[31,32]

In comparison with the studies on C–F bond activation and functionalization by nickel[36] and iron[15] complexes, few studies on C–F bond activation and functionalization with cobalt complexes were published. Holland studied the C–F bond activation of fluorobenzene by low-coordinate cobalt complex.[33] We reported the first organo cobalt(III) fluoride containing a [C–Co–F] fragment through a cyclometalation reaction involving C–F bond cleavage at a cobalt(I) center using azine as an anchoring group.[37] A synergistic effect of low-valent cobalt complex and trimethylphosphine ligand on selective C–F bond activation of perfluorinated toluene was explored affording a mono-(C–F) bond cleavage product and the double-(C–F) bond cleavage product, a benzyne cobalt complex (eqn (1)).[38]

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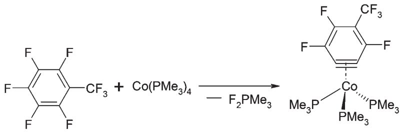


(1)

In this paper we report the recent results of our study on C–F bond activation and C–H bond activation of polyfluorinated aromatic compounds by tetrakis(trimethylphosphine)cobalt(0), $Co(PMe_3)_4$. The investigation was extended to C_5NF_5, C_6F_6, $C_{10}F_8$, and C_6F_5H. The reaction mechanism of C_6F_5H with $Co(PMe_3)_4$ *via* selective C–H bond activation is proposed and partly-experimentally verified.

2. Experimental section

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 $Co(PMe_3)_4$.[39] C_5NF_5, C_6F_6, C_6F_5H and $C_{10}F_8$ were obtained from ABCR. All other chemicals were used as purchased. Infrared spectra (4000–400 cm^{-1}), as obtained from Nujol mulls between KBr disks, were recorded on a Bruker ALPHA FT-IR Spectrometer. The *in situ* IR was carried out on a METTLER TOLEDO React IR IC 15. ^1H, ^{13}C, ^{31}P and ^{19}FNMR spectra (300, 75, 121 and 282 MHz, respectively) were recorded on a Bruker Avance 300 spectrometer. ^{13}C 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 argon and are uncorrected. GC-MS were recorded on a TRACE-DSQ.

Synthesis of complexes 1 and 4

A solution of C_5NF_5 (0.39 g, 2.30 mmol) in 30 mL of THF was combined with a solution of $Co(PMe_3)_4$ (0.83 g, 2.30 mmol) in THF (30 mL) at −80 °C. The reaction mixture was allowed to warm to ambient temperature and stirred for 30 h. During this period the pale yellow mixture turned brown-yellow in color. The volatiles were transferred under vacuum and the residue was extracted with pentane (40 mL) and diethyl ether (50 mL), respectively. Crystallization from pentane and diethyl ether at −4 °C afforded green single crystals of **1** (0.32 g, 32.0%) suitable for X-ray analysis. Analysis for **1**, $C_{14}H_{27}CoF_4NP_3$, 437.21 g mol^{-1}, [found (calcd)]: C, 38.87 (38.46); H, 6.20 (6.22); N, 2.90 (3.20). IR (Nujol, cm^{-1}): 1612, 1587 s, ν(C=C); 935 *vs.*, $\nu(PMe_3)$. Dec. 167 °C. The deep red single crystals of **4** (0.73 g, 62%) were obtained by concentration of the mother solution. Analysis for **4**, $C_{17}H_{36}CoF_4NP_4$, 513.11 g mol^{-1}, [found (calcd)]: C, 39.88 (39.78); H, 6.90 (7.07); N, 2.67 (2.73). IR (Nujol, cm^{-1}): 1631 s, 1613, 1579 s, ν(C=C); 937 *vs.*, ν (PMe_3). ^1H NMR (300 MHz, benzene-d_6, 300 K): δ 0.91 (br, PCH_3). ^{31}P NMR (121.4 MHz, pentane, 297 K): δ 31.6 (s, PCH_3). ^{19}F NMR (282 MHz, benzene-d_6, 300 K): δ −91.4 (s, 2F), −140.0 (s, 2F). Dec. 265 °C.

Synthesis of complex 2

A solution of C_6F_6 (0.72 g, 3.90 mmol) in 30 mL of THF was combined with a solution of $Co(PMe_3)_4$ (1.41 g, 3.90 mmol) in THF (30 mL) at −80 °C. The reaction mixture was warmed to ambient temperature and stirred for 30 h. During this period the pale yellow mixture turned brown-yellow in color. The volatiles were transferred under vacuum and the residue was extracted with pentane (40 mL) and diethyl ether (50 mL), respectively. Crystallization from pentane and diethyl ether at −4 °C afforded green single crystals of **2** (0.90 g, 51.0%). Analysis for **2**, $C_{15}H_{27}CoF_5P_3$, 454.21 g mol^{-1}, [found (calcd)]: C, 39.87 (39.66); H, 5.90 (5.99). IR (Nujol, cm^{-1}): 1624 s, 1598 s, ν(C=C); 947 *vs.*, $\nu(PMe_3)$. Dec. 220 °C.

Synthesis of complexes 3 and 6

At −78 °C, $Co(PMe_3)_4$ (0.90 g, 2.46 mmol) was added into a solution of $C_{10}F_8$ (0.67 g, 2.46 mmol) in 30 mL of pentane. After stirring for 18 h at room temperature the solution turned to red from brown. Crystallization from the filtrate at −30 °C afforded green crystals of **3** (0.47 g, 35.0%). Analysis for **3**, $C_{19}H_{27}CoF_7P_3$, 540.26 g mol^{-1}, [found (calcd)]: C, 42.02 (42.24); H, 5.30 (5.04). IR (Nujol, cm^{-1}): 1651 s, 1620 s, 1588 s, ν(C=C); 935 *vs.*, $\nu(PMe_3)$. m.p.: 85 °C. The deep red single crystals of **6** (0.82 g, 54.0%) were obtained by concentration of the mother solution. Analysis for **6**, $C_{22}H_{36}CoF_7P_4$, 616.34 g mol^{-1}, [found (calcd)]: C, 42.60 (42.87); H, 5.81 (5.89). IR (Nujol mull, cm^{-1}): 1660 s, 1572 s, ν(C=C), 936 *vs.*, $\nu(PMe_3)$. ^1H NMR (300 MHz, benzene-d_6, 297 K): δ 0.95 (br, 18H, PCH_3), 1.44 (br, 18H, PCH_3). ^{31}P NMR (121.4 MHz, benzene-d_6, 297 K): δ 31.0 (s, PCH_3). ^{19}F NMR (282 MHz, benzene-d_6, 300 K): δ −116.89 (dd, J_{F1F4} = 19 Hz, J_{F1F8} = 65 Hz, F_1, 1F), −134.61 (m, F_3, 1F), −144.93 (dt′, J_{F1F8} = 65 Hz, J_{F7F8} = 19 Hz, J_{F5F8} = 17 Hz, F_8, 1F), −146.39 (dt′, J_{F4F5} = 56 Hz, J_{F5F6} = J_{F5F8} = 15 Hz, F_5, 1F), −149.93 (dt′, J_{F4F5} = 56 Hz, J_{F3F4} = J_{F1F4} = 19 Hz, F_4, 1F), −154.05 (t′, J_{F7F8} = 22 Hz, J_{F6F7} = 19 Hz, F_7, 1F), −156.85 (m, F_6, 1F).[40] m.p.: 94 °C.

Synthesis of complex 7

A solution of **1** (0.42 g, 0.96 mmol) in 50 mL of pentane was stirred under 1 bar of CO at ambient temperature for 12 h, The color changed from red-brown to yellow. Upon filtration and cooling to 4 °C, complex **7** (0.30 g, 75%) was obtained as yellow cubic crystals. Analysis for **7**, $C_{13}H_{18}CoF_4NO_2P_2$ 417.15 g mol^{-1}, [found (calcd)]: C, 37.67 (37.43); H, 4.20 (4.35); N, 3.25 (3.36). IR (Nujol, cm^{-1}): 1969, 1900 ν(CO); 1587, 1543 ν(C=C); 946ν (PMe_3). ^1H NMR (300 MHz, C_6D_6, 297 K): δ 0.87 (t′, $^2J_{PH}$ + $^4J_{PH}$ = 8.7 Hz, PCH_3). ^{31}P NMR (121 MHz, benzene-d_6, 295 K): δ 28.5 (s, PCH_3). ^{19}F NMR (282 MHz, benzene-d_6, 300 K): δ −98.50 (m, 2F), −114.76 (m, 2F). m.p.: 135 °C.

Synthesis of complex 8

A solution of **2** (0.45 g, 1.0 mmol) in 50 mL of pentane was stirred under 1 bar of CO at ambient temperature for 12 h.

The red-brown solution slowly turned yellow. Upon filtration and cooling to 4 °C, complex **8** (0.28 g, 64%) was obtained as yellow cubic crystals. Analysis for **8**, $C_{14}H_{18}CoF_5O_2P_2$ 434.15 g mol^{-1}, [found (calcd)]: C, 38.66 (38.73); H, 4.32 (4.18). IR (Nujol mull, cm^{-1}): 1967, 1901 ν(CO); 1600, 1538 ν(C═C); 942ν(PMe$_3$). ^{1}H NMR (300 MHz, C_6D_6, 297 K): δ 0.93 (t′, $|^2J_{PH} + {}^4J_{PH}|$ = 8.4 Hz, PCH_3). ^{31}P NMR (121 MHz, C_6D_6, 295 K): δ 29.3 (s, PCH$_3$). ^{19}F NMR (282 MHz, benzene-d$_6$, 300 K): δ −107.0 (d, J_{F2F3} = 25.4 Hz, 2F), −159.9 (t, $J_{F3F4} = J_{F4F5}$ = 20.8 Hz, 1F), −162.05 (q, 2F). m.p.: 152 °C.

Reaction of C_6F_5H with $Co(PMe_3)_4$

A solution of C_6F_5H (0.37 g, 2.20 mmol) in 30 mL of pentane was combined with a solution of $Co(PMe_3)_4$ (0.80 g, 2.20 mmol) in pentane (30 mL) at −80 °C. This mixture was allowed to warm to ambient temperature and stirred for 18 h to form a red-brown, turbid mixture. After work-up, crystallization from pentane at −4 °C afforded red-brown single crystals of **2** (0.66 g, 66%). 1,2,4,5-$C_6F_4H_2$ was detected by ^{19}F NMR in a yield of 3%. Under the same reaction conditions, a solution of C_6F_5H (0.74 g, 4.40 mmol) in 60 mL of pentane was combined with a solution of $Co(PMe_3)_4$ (0.80 g, 2.20 mmol) in pentane (60 mL) at −80 °C. 1,2,4,5-$C_6F_4H_2$ was detected by ^{19}F NMR in the yield of 14%.

Experimental evidence of intermediate 9

(a) IR monitoring: a solution of C_6F_5H (0.37 g, 2.20 mmol) in 30 mL of pentane was combined with a solution of $Co(PMe_3)_4$ (0.80 g, 2.20 mmol) in pentane (30 mL) at −80 °C. This mixture was allowed to warm to ambient temperature and stirred for 10 h to form a red-brown, turbid mixture. 5 mL of the reaction mother solution was sampled. The volatiles of this solution were removed *via* vacuum. The solid residue was used for the FTIR analysis. A vibration at 1906 cm^{-1} was found to be the signal of the Co–H bond of intermediate **9**. *(b) In situ ^{1}H NMR*: the sample of C_6F_5H (0.011 g, 0.074 mmol) was added in a solution of 0.6 mL of C_6D_6 with $Co(PMe_3)_4$ (0.027 g, 0.074 mmol) in a NMR tube at −80 °C. This mixture was allowed to warm to ambient temperature and stirred for 10 h to form a red-brown, turbid mixture. The *in situ* ^{1}H NMR in C_6D_6 indicates clearly the presence of the Co–H group of intermediate **9** with the hydrido resonance at −17.3 ppm as a quintet with the coupling constant of J_{PH} = 34 Hz.

Synthesis of complex 11

A solution of C_6F_5H (0.65 g, 3.86 mmol) and $Co(PMe_3)_4$ (1.40 g, 3.86 mmol) in 50 mL of pentane was stirred for 12 h, then stirred under 1 bar of CO for 12 h. The red-brown solution slowly turned yellow. Upon filtration and cooling to 4 °C, complex **11** (1.0 g, 59.6%) was obtained as yellow cubic crystals. Analysis for **11**, $C_{14}H_{19}CoF_5O_2P_2$ 435.16 g mol^{-1}, [found (calcd)]: C, 38.56 (38.64); H, 4.22 (4.40). IR (Nujol, cm^{-1}): 2002, 1968 ν(CO); 1902, ν(Co–H); 1616, 1597 ν(C═C); 942 ν(PMe$_3$). m.p.: 97 °C.

Reaction of C_6F_5H with $Co(PMe_3)_4$ and C_6Cl_6

A solution of C_6F_5H (0.50 g, 2.97 mmol) and $Co(PMe_3)_4$ (1.08 g, 2.97 mmol) in 50 mL of THF was stirred for 12 h, then C_6Cl_6 (0.85 g, 2.97 mmol) was added with stirring at −80 °C. This reaction mixture was allowed to warm to room temperature and stirred for 12 h. The solution color changed from red-brown to green. The volatiles were transferred under vacuum and the residue was extracted with pentane (30 mL) and diethyl ether (30 mL). Complex **12** (1.04 g, 71%) as green crystals was obtained from pentane/diethyl ether at −4 °C. Analysis for **12**, $C_{15}H_{27}CoClF_5P_3$ 489.66 g mol^{-1}, [found (calcd)]: C, 36.51 (36.79); H, 5.38 (5.56). IR (Nujol, cm^{-1}): 1627 s, 1601 s ν(C═C); 948 ν (PMe$_3$). m.p.: 157 °C. The mother solution was quenched with dilute HCl (1 M) and extracted by diethyl ether. The organic phase was dried over magnesium sulfate. After filtration, C_6Cl_5H and 1,2,4,5-$C_6Cl_4H_2$ were separated by column chromatography (silica) using petroleum ether (60–90 °C) in the yield of 58% and 12% respectively.

Crystallographic data of complex 1

$C_{14}H_{27}CoF_4NP_3$, 437.21 g mol^{-1}, 0.30 × 0.28 × 0.21 mm, monoclinic, $P2(1)/n$, a = 8.5810(10), b = 16.6960(13), c = 14.853(2) Å; β = 99.750(12)°. V = 2097.2(4) A^3, T = 140(2) K, Z = 4, D_{calc} = 1.385 Mg m^{-3}, μ = 1.076 mm^{-1}, data coll. range 1.85 < 2θ < 29.17°, $-11 \le h \le 11$, $-22 \le k \le 22$, $-20 \le l \le 20$, no. unique data = 5626 (R(int) = 0.0294), parameters = 217, GOF on F^2 = 1.077, R_1 ($I > 2\sigma(I)$) = 0.0532, wR_2 = 0.1485 (all data).

Crystallographic data of complex 2

$C_{15}H_{27}CoF_5P_3$, 454.21 g mol^{-1}, 0.25 × 0.22 × 0.19 mm, monoclinic, $P2(1)/n$, a = 13.243(3), b = 11.838(2), c = 13.762(3) Å; β = 92.98(3)°. V = 2154.6(7) A^3, T = 150(2) K, Z = 4, D_{calc} = 1.400 Mg m^{-3}, μ = 1.056 mm^{-1}, data coll. range 2.31 < 2θ < 25.00°, $-15 \le h \le 7$, $-12 \le k \le 14$, $-16 \le l \le 16$, no. unique data = 3582 (R(int) = 0.0173), parameters = 235, GOF on F^2 = 1.044, R_1 ($I > 2\sigma(I)$) = 0.0370, wR_2 = 0.1001 (all data).

Crystallographic data of complex 6

$C_{22}H_{36}CoF_7P_4$, 616.32 g mol^{-1}, 0.15 × 0.12 × 0.10 mm, orthorhombic, $Pbca$, a = 16.1878(19), b = 18.288(2), c = 18.646(2) Å; V = 5519.9(11) A^3, T = 273(2) K, Z = 8, D_{calc} = 1.483 Mg m^{-3}, μ = 0.911 mm^{-1}, data coll. range 2.00 < 2θ < 25.05°, $-19 \le h \le 13$, $-21 \le k \le 21$, $-22 \le l \le 22$, no. unique data = 4886 (R(int) = 0.0521), parameters = 307, GOF on F^2 = 1.009, R_1 ($I > 2\sigma(I)$) = 0.0384, wR_2 = 0.1047 (all data).

Crystallographic data of complex 7

$C_{13}H_{18}CoF_4NO_2P_2$, 417.15 g mol^{-1}, 0.31 × 0.25 × 0.21 mm, monoclinic, $P2(1)/c$, a = 12.367(3), b = 11.760(2), c = 12.486(3) Å; β = 93.84(3)°. V = 1811.8(6) A^3, T = 293(2) K, Z = 4, D_{calc} = 1.529 Mg m^{-3}, μ = 1.166 mm^{-1}, data coll. range 2.38 < 2θ < 25.00°, $-14 \le h \le 12$, $-13 \le k \le 10$, $-14 \le l \le 14$, no. unique data = 2770 (R(int) = 0.0106), parameters = 214, GOF on F^2 = 1.065, R_1 ($I > 2\sigma(I)$) = 0.0225, wR_2 = 0.0607 (all data).

Crystallographic data of complex 8

$C_{14}H_{18}CoF_5O_2P_2$, 434.15 g mol^{-1}, 0.30 × 0.22 × 0.20 mm, monoclinic, $P2(1)/c$, a = 12.4005(11), b = 12.1015(10), c = 13.0277(11) Å; β = 91.942(2)°. V = 1953.9(3) A^3, T = 273(2) K, Z = 4, D_{calc} = 1.476 Mg m^{-3}, μ = 1.090 mm^{-1}, data coll. range 1.64 < 2θ < 27.46°, $-16 \le h \le 8$, $-15 \le k \le 15$, $-14 \le l \le 16$, no. unique data = 4411 (R(int) = 0.0328), parameters = 227, GOF on F^2 = 1.013, R_1 ($I > 2\sigma(I)$) = 0.0405, wR_2 = 0.1111 (all data).

Crystallographic data of complex 11

$C_{14}H_{19}CoF_5O_2P_2$, 435.16 g mol^{-1}, 0.22 × 0.21 × 0.19 mm, orthorhombic, $Pbcn$, a = 12.409(10), b = 13.286(11), c = 11.917(10) Å. V = 1965(3) A^3, T = 293(2) K, Z = 4, D_{calc} = 1.471 Mg m^{-3}, μ = 1.084 mm^{-1}, data coll. range 2.25 < 2θ < 25.00°, $-14 \le h \le 14$, $-15 \le k \le 7$, $-14 \le l \le 14$, no. unique data = 1719 (R(int) = 0.1412), parameters = 159, GOF on F^2 = 1.085, R_1 ($I > 2\sigma(I)$) = 0.0539, wR_2 = 0.1639 (all data).

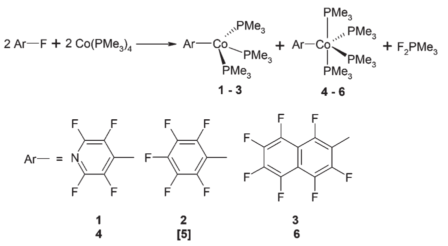
Crystallographic data of complex 12

$C_{15}H_{27}ClCoF_5P_3$, 489.66 g mol^{-1}, 0.30 × 0.28 × 0.25 mm, monoclinic, $C2/c$, a = 15.067(4), b = 9.121(2), c = 32.289(8) Å; β = 94.067(4)°. V = 4426.3(19) A^3, T = 293(2) K, Z = 8, D_{calc} = 1.470 Mg m^{-3}, μ = 1.150 mm^{-1}, data coll. range 1.26 < 2θ < 26.00°, $-16 \le h \le 18$, $-5 \le k \le 11$, $-39 \le l \le 36$, no. unique data = 4356 (R(int) = 0.0924), parameters = 235, GOF on F^2 = 1.018, R_1 ($I > 2\sigma(I)$) = 0.0424, wR_2 = 0.1204 (all data).

Crystallographic data for complexes **1**, **2**, **6**, **7**, **8**, **11** and **12** have been deposited in the Cambridge Crystallographic Data Centre as supplementary publications with the CCDC-871947 (**1**), 846414 (**2**), 718812 (**6**), 871948 (**7**), 871949 (**8**), 871950 (**11**) and 871951 (**12**).

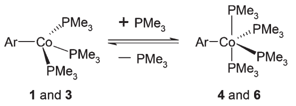
3. Results and discussion

3.1 Selective C–F bond activation of perfluorinated arenes



(2)

The reactions of C_5NF_5, C_6F_6 and $C_{10}F_8$ with $Co(PMe_3)_4$ in THF or pentane gave rise to the corresponding tetra-coordinate cobalt(I) complexes **1–3** and penta-coordinate cobalt(I) complexes **4–6** (eqn (2)). Complexes **1** and **4** are the C–F cleavage products at 4-position of C_5NF_5 while complexes **3** and **6** are the C–F cleavage products at the β-position of $C_{10}F_8$. The formation of F_2PMe_3 in solution was verified *via* ^{19}F NMR and ^{31}P NMR.[41] It was found that the green solution of complexes **1** and **3** turned red with the addition of excess of PMe_3 (eqn (3)). When the amount of PMe_3 of the solution was reduced under vacuum conditions, the red solutions of complexes **4** and **6** turned to green. This implies an equilibrium between the tetra-coordinate cobalt(I) complexes **1**/**3** and the penta-coordinate cobalt(I) complexes **4**/**6**. The stable penta-coordinate cobalt(I) complexes **4** and **6** as red crystals were isolated and characterized. It was found that the tetra-coordinate cobalt(I) complex **2** was more stable in comparison with complexes **1** and **3**. Complex **2** could not transform into penta-coordinate cobalt(I) complex **5** in the presence of PMe_3. It is considered that the electrophilicity of the cobalt center in complex **2** is weaker than that of complexes **1** and **3**. From the viewpoint of electrostatic theory, complex **2** is more stable than complexes **1** and **3**. Therefore, complex **2** does not tend to combine another phosphine ligand to form a penta-coordinate complex **5**.



(3)

The molecular structures of complexes **1** and **2** are shown in Fig. 1 and 2. The cobalt atoms of both complexes are located at the center of a distorted tetrahedron. The Co–C bond distance in complex **2** is 2.041(3) Å (Co1–C10), a bit longer than that (Co1–C10 = 2.032(2) Å) in complex **1**. This could be due to the stronger electron-withdrawing power of the nitrogen atom of the pyridinyl group. All of the Co–P bond distances are in the expected range for Co–P bonds.

In our earlier work[38] a tris(trimethylphosphine)(4-trifluoromethyltetrafluorophenyl)cobalt(I) complex was isolated and structurally characterized as an intermediate of the reaction of octafluorotoluene with $Co(PMe_3)_4$. These three cobalt(I) complexes belong to the same kind of cobalt(I) complexes with one perfluorinated aromatic ligand and three neutral phosphines as supporting ligands. Most of the bond parameters and structural characteristics of them are comparable.

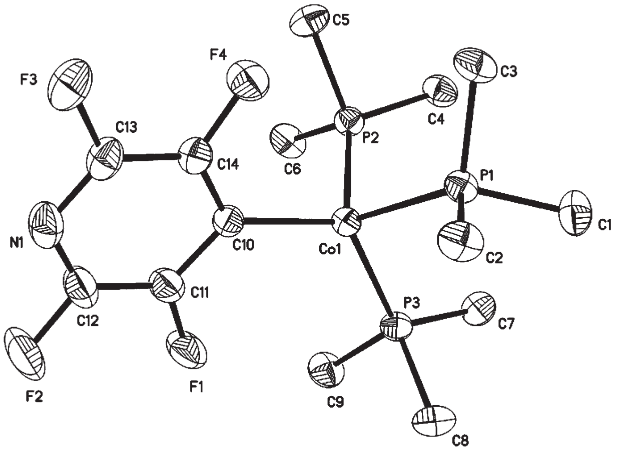


Fig. 1 Molecular structure of **1** (all the hydrogen atoms were omitted for clarity). Selected bond distances (Å) and angles [°]: Co1–C10 2.032(2), Co1–P2 2.2276(7), Co1–P3 2.2385(8); Co1–P1 2.2412(7), C10–Co1–P2 109.34(7), C10–Co1–P3 125.30(7), P2–Co1–P3 102.33(3), C10–Co1–P1 112.16(7), P2–Co1–P1 102.39(3), P3–Co1–P1 102.72(3).

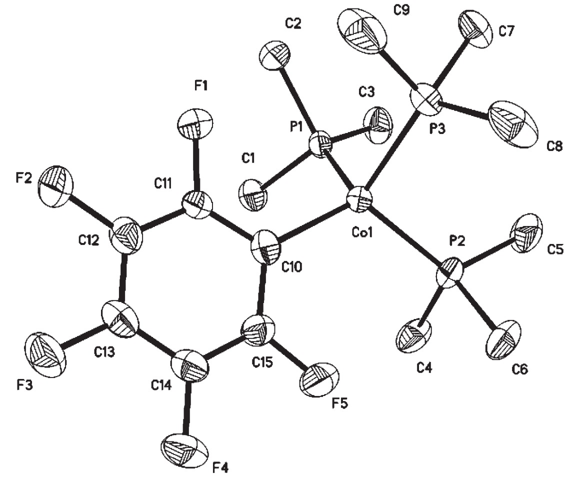


Fig. 2 Molecular structure of **2** (all the hydrogen atoms were omitted for clarity). Selected bond distances (Å) and angles [°]: C10–Co1 2.041(3), Co1–P3 2.2304(9), Co1–P1 2.2355(9), Co1–P2 2.2281(9); C10–Co1–P1 110.86(9), P3–Co1–P1 100.87(4), C10–Co1–P2 120.16(10), P3–Co1–P2 103.74(4), P1–Co1–P2 101.78(4).

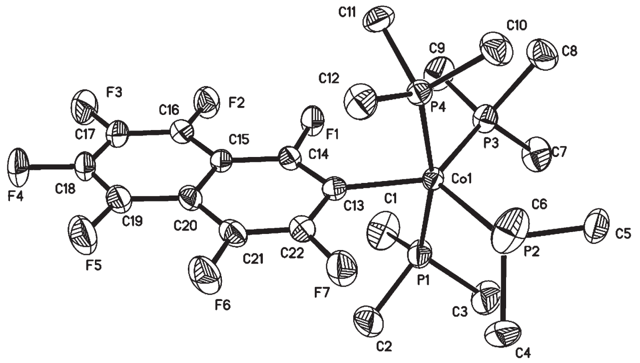


Fig. 3 Molecular structure of **6** (all the hydrogen atoms were omitted for clarity). Selected bond distances (Å) and angles [°]: Co1–C13 2.008(3), Co1–P4 2.1850(9), Co1–P1 2.1879(10), Co1–P3 2.1954(10), Co1–P2 2.2020(10); C13–Co1–P4 82.61(9), C13–Co1–P1 83.87(9), P4–Co1–P1 165.43(4), C13–Co1–P3 129.35(9), C13–Co1–P2 118.84(9), P3–Co1–P2 111.78(4).

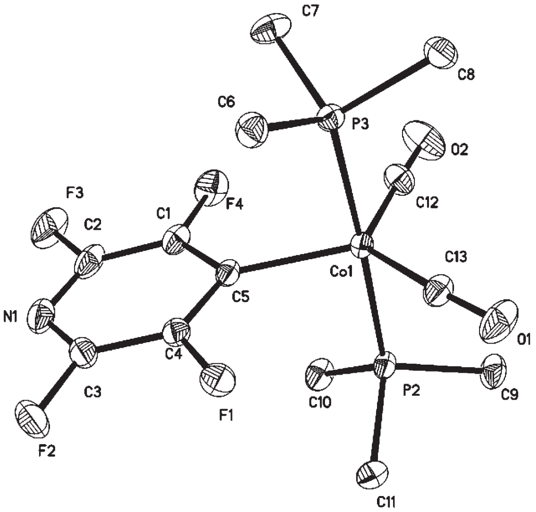
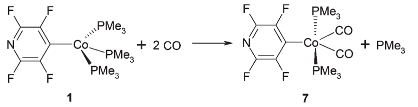


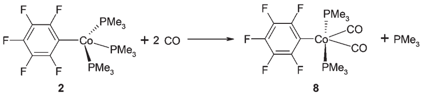
Fig. 4 Molecular structure of **7** (all the hydrogen atoms were omitted for clarity). Selected bond distances (Å) and angles [°]: Co1–C13 1.7499(16), Co1–C12 1.7585(19), Co1–C5 1.9984(15), Co1–P3 2.1869(5), Co1–P2 2.1877(5); C13–Co1–C12 123.26(8), C13–Co1–C5 122.11(7), C12–Co1–C5 114.61(8), C13–Co1–P3 90.43(5), C12–Co1–P3 91.62(6), C5–Co1–P3 89.08(5), C13–Co1–P2 88.79(6), C12–Co1–P2 91.61(6), C5–Co1–P2 88.50(5), P3–Co1–P2 176.563(18).

The molecular structure of penta-coordinate cobalt(I) complex **6** (Fig. 3) has a distorted trigonal-bipyramidal coordination geometry. Two axial trimethylphosphine ligands with an angle of P1–Co1–P4 (165.43(4)°) tilt toward the perfluorinated naphthyl ligand due to the repulsion between the two equatorial trimethylphosphine ligands. The central cobalt atom deviate is 0.0157 Å from the equatorial plane. The Co1–C13 distance (2.008(3) Å) is shorter than those in complexes **1** and **2**.

Both complex **1** and complex **2** reacted with CO under atmospheric pressure at room temperature in a pentane solution to give rise to the ligand substituted products, carbonyl complexes **7** and **8** (eqn (4) and (5)). Complexes **7** and **8** were isolated as yellow crystals. The experiments showed that the final product was penta-coordinate dicarbonyl diphosphine cobalt(I) complex **7**, regardless of which complex (tetra-coordinate complex **1** or penta-coordinate complex **4**) was used as the reactant. The characteristic carbonyl vibrations in the IR spectra are at 1900/1969 cm^{-1} for **7** and 1901/1967 cm^{-1} for **8**. One singlet at 30.0 ppm (**7**) and 30.3 ppm (**8**) in the ^{31}P NMR spectra implies two equivalent trimethylphosphine ligands.



(4)



(5)

The molecular structures of complexes **7** and **8** reveal that both cobalt atoms are situated at the center of a trigonal-bipyramidal geometry (Fig. 4 and 5). They belong to the C_{2v} space group. Two trimethylphosphine ligands are located at the axial positions with the bond angles of 176.56(18)° (**7**) and 176.29(4)° (**8**). In the equatorial plane are two carbonyl ligands and one perfluorinated aromatic ligand. The fluorinated 4-pyridinyl ring of **7** and the pentafluorophenyl ring of **8** are in the equatorial planes. The four Co–CO bond distances of the two complexes are in the range of normal Co–CO (terminal) bond distances.[42] The Co–C$_{\text{phenyl}}$ bond distances (Co1–C5 = 1.9984(15) Å (**7**); Co1–C1 = 2.013(3) Å (**8**)) are as expected for organo cobalt complexes. The bond angles between two carbonyl ligands are 123.26(8)° (**7**) and 122.80(19)° (**8**). Similar dicarbonyl cobalt complexes were reported with similar structural characteristics.[26,28]

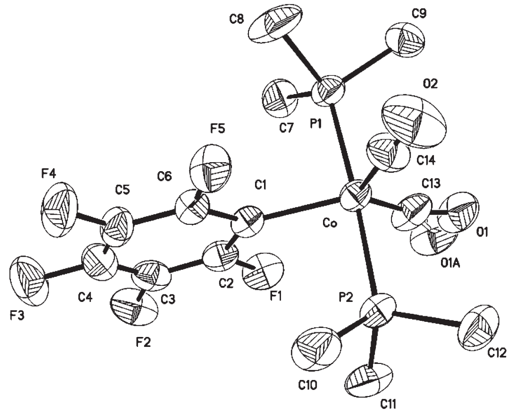
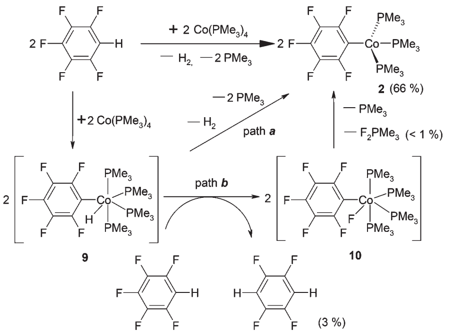


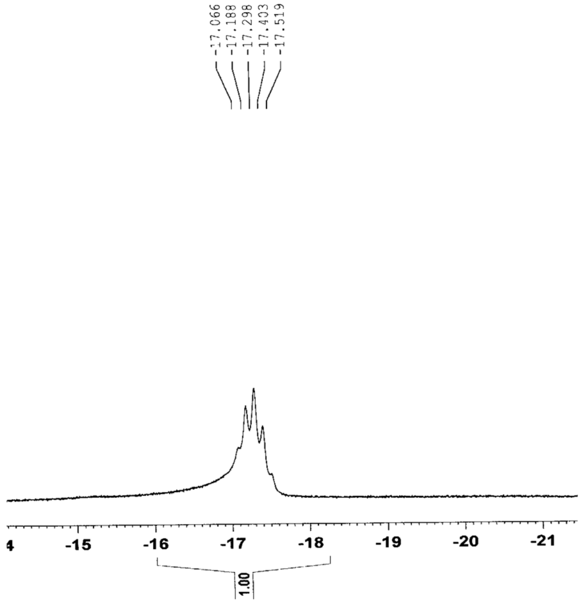
Fig. 5 Molecular structure of **8** (all the hydrogen atoms were omitted for clarity). Selected bond distances (Å) and angles [°]: C1–Co 2.013(3), C13–Co 1.743(4), C14–Co 1.741(4), Co–P1 2.1856(8), Co–P2 2.1891(8); C13–Co–C14 122.80(19), C14–Co–C1, 116.24(14), C13–Co–P1 89.93(11), C14–Co–P1 91.99(11), C13–Co–P2 90.68(11), C14–Co–P2 90.76(11), C1–Co–P2 88.40(8), P1–Co–P2 176.29(4), C1–Co–P1 88.15(8).



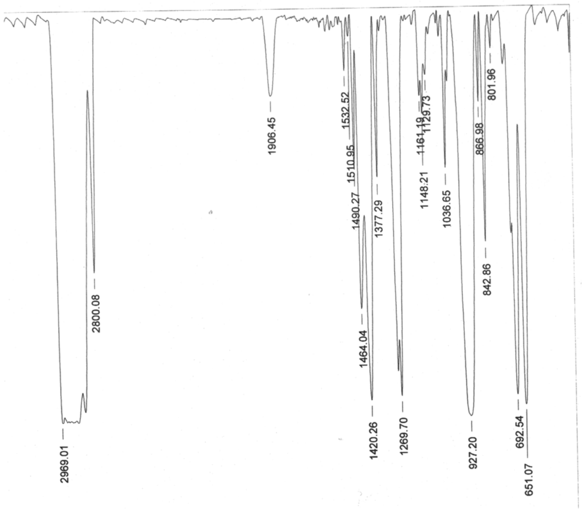
Scheme 1 Proposed mechanism of reaction of C_6F_5H with $Co(PMe_3)_4$.

3.2 C–H bond activation of C_6F_5H

The C–F/C–H bond activation are competitive reactions between polyfluoroarenes and transition metal complexes. The reaction of $Co(PMe_3)_4$ with C_6F_5H in pentane was carried out to study which bond activation is preferred. Complex **2** as a main product was isolated from the mother solution of the reaction of C_6F_5H with $Co(PMe_3)_4$ in a yield of 66% (Scheme 1). 1,2,4,5-$C_6F_4H_2$ and F_2PMe_3 as byproducts were verified *via in situ* ^{19}F NMR and GC-MS (1,2,4,5-$C_6F_4H_2$) and *via in situ* ^{19}F NMR and ^{31}P NMR (for F_2PMe_3).[41] But the yields of two byproducts were low (1,2,4,5-$C_6F_4H_2$: 3%; F_2PMe_3; <1%). According to the experimental results and our early work on C–F bond activation,[15,38] the reaction sequence is proposed in Scheme 1. The first step is the formation of the hydrido cobalt(II) intermediate **9** through C–H bond activation *via* oxidative addition. Intermediate **9** is not stable. There are two possible paths, through which **9** can transform into end product **2**. Path ***a*** is one-electron reductive elimination of **9** to afford **2** with the escape of H_2. A try to isolate intermediate **9** failed. **9** was verified through *in situ* IR and *in situ* ^1H NMR spectra (Fig. 6). A vibration at 1906 cm^{-1} in the *in situ* IR spectrum was found to be the possible signal of the Co–H bond of **9**. The *in situ* ^1H NMR in C_6D_6 also indicates clearly the presence of a Co–H group with the hydrido resonance at −17.3 ppm as a quintet with the coupling constant of J_{P-H} = 34 Hz. In order to understand the existence of 1,2,4,5-$C_6F_4H_2$ and F_2PMe_3, path ***b*** as described in Scheme 1 was proposed. In path ***b***, **9** reacts with another molecule of C_6F_5H to give rise to the hydrodefluorination product 1,2,4,5-$C_6F_4H_2$ and intermediate **10** through ligand exchange *via* C–F bond activation at the 3-position of C_6F_5H. Intermediate **10** is an unstable organo cobalt(II) fluoride and transforms into complex **2** with the formation of F_2PMe_3 in the presence of trimethylphosphine. Because of the



(a) ^1H NMR



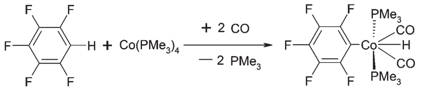
(b) IR

Fig. 6 The bands of the Co–H of intermediate **9** in *in situ* ^1H NMR (a) and IR (b).

strong bond energy of the C–F bond, we consider that the ligand exchange reaction *via* C–F bond activation in path ***b*** is not thermodynamically preferred. Therefore, the yield of 1,2,4,5-$C_6F_4H_2$ is very low. Even if the molar ratio of C_6F_5H to $Co(PMe_3)_4$ was increased from 1 : 1 to 2 : 1, the yield of 1,2,4,5-$C_6F_4H_2$ was changed only from 3 to 14%. We considered that **2** was formed mainly through path ***a*** in this reaction.

3.3 Further experimental study for the mechanism in Scheme 1

In order to verify the reaction mechanism proposed in Scheme 1, the following two experiments were designed. In the process of isolating and confirming the hydrido intermediate **9**, carbon monoxide was introduced as a supporting ligand to catch the stability of **9** (eqn (6)). C_6F_5H and $Co(PMe_3)_4$ were combined in pentane. This mixture was stirred under 1 bar of CO for 12 h. After work-up, the hydrido dicarbonyl cobalt(II) complex **11** was isolated as yellow crystals from the pentane solution. In the IR spectra of complex **11** two strong absorption bands at 1968 and 2002 cm^{-1} correspond to the two terminal carbonyl ligands while the vibration of Co–H bond is located at 1902 cm^{-1}.



11

(6)

The molecular structure of complex **11** confirms a strongly distorted hexa-coordinate octahedron (Fig. 7). Two trimethylphosphine ligands are in the axial positions almost on a straight line with an angle of P1–Co1–P1A = 179.79(11)°. The distance Co1–H1 (1.62(9) Å) is in the normal range.[43] Two carbonyl ligands tilt toward the direction of the hydrido ligand because of the large pentafluorophenyl group and the small hydrido ligand. Therefore, the bond angle C1–Co1–C2 is 108.2(4)° while the bond angle H1–Co1–C1 is 104(3)°. The bond distances Co1–C1 (1.828(16) Å) is significantly shorter than Co1–C2 (2.023(8) Å) due to the π-backbonding between the cobalt atom and the carbonyl ligands. This also explains the multiple bond character of the Co–CO linkage. The similar differences can also be found in the aforementioned dicarbonyl organo cobalt(I) complexes **7** and **8** (Fig. 4 and 5).

In order to further understand the ligand exchange reaction in Scheme 1 and to indirectly verify the existence of intermediate **10**, C_6Cl_6 was added into the mixture of C_6F_5H and $Co(PMe_3)_4$. As expected, from the reaction solution tris(trimethylphosphine)pentafluorophenylcobalt(II) chloride (**12**) was obtained in a yield of 71% (eqn (7)). C_6Cl_5H as the second product was also isolated in a yield of 58%. Complex **12** attains a trigonal-bipyramidal coordination geometry with two axial trimethylphosphine ligands (P1–Co1–P3 = 168.67(4)°) (Fig. 8). Owing to the repulsion of the in-plane orientation of F and Cl atoms, the bond angle (C6–Co1–Cl1 = 141.09(11)°) is much larger than the other two bond angles (C6–Co1–P2 = 112.75(11)° and Cl1–Co1–P2 = 106.16(4)°) in the equatorial plane. Both axial trimethylphosphine ligands are in an eclipsed conformation in the axial positions while the three equatorial ligands are orientated in a staggered conformation with the two axial ligands between them. The equatorial bond Co1–P2 (2.3011(10) Å) is considerably larger than both axial P–Co bonds (P3–Co1 = 2.2179(10) Å and P1–Co1 = 2.2211(9) Å). In addition, 1,2,4,5-$C_6Cl_4H_2$ was detected as a further hydrodechlorination product of C_6Cl_5H in a yield of 12%.

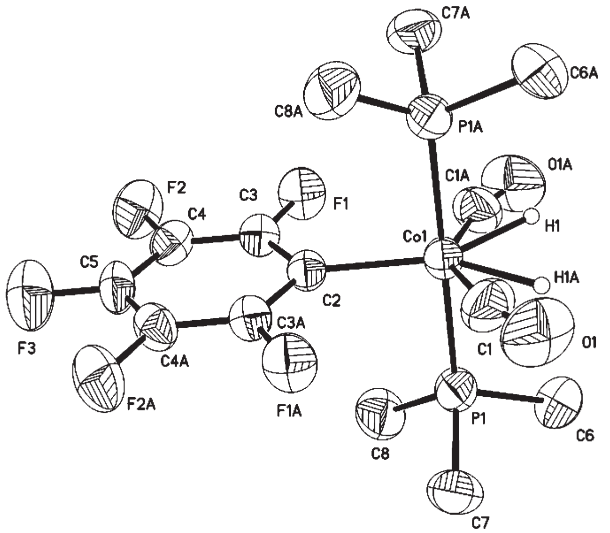


Fig. 7 Molecular structure of **11** (the hydrogen atoms ware omitted for clarity). Selected distances [Å] and angles [°]: Co1–C1 1.828(16), Co(1)–C(2) 2.023(8), Co1–P1 2.222(2), Co1–H1 1.62(9); O(1)–C(1) 1.060(13), C(1)–Co(1)–C(2) 108.2(4), C(1)–Co(1)–P(1) 91.5(3), C(2)–Co(1)–P(1), 89.89(6), P1–Co1–P1A 179.79(11), C(2)–Co(1)–H(1) 147(3), P(1)–Co(1)–H(1) 95(3), C(1)–Co(1)–H(1) 104(3), C(1)A–Co(1)–H(1) 40(3), C(1)A1–Co(1)–C(1) 143.7(9).

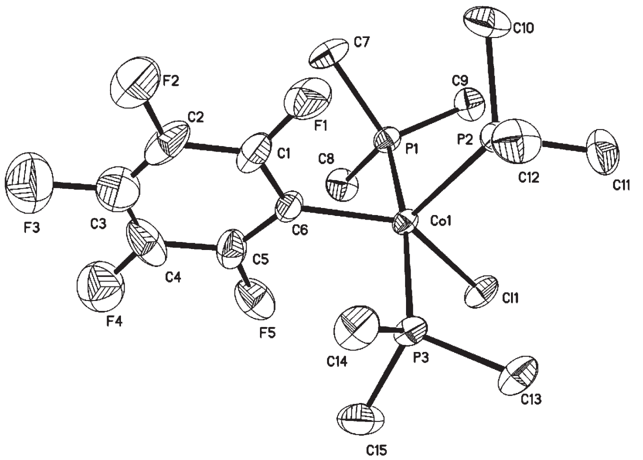
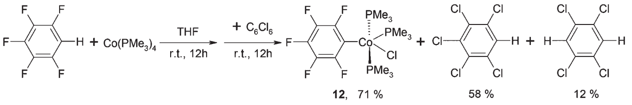


Fig. 8 Molecular structure of **12** (the hydrogen atoms ware omitted for clarity). Selected distances [Å] and angles [°]: Co1–C6 1.983(3), Co1–P3 2.2179(10), Co1–P1 2.2211(9), Co1–P2 2.3011(10), Co1–Cl1 2.3146(9); C6–Co1–P3 88.16(10), C6–Co1–P1 88.60(10), P3–Co1–P1 168.67(4), C6–Co1–P2 112.75(11), P3–Co1–P2 95.47(4), P1–Co1–P2 95.79(4), C6–Co1–Cl1 141.09(11), P3–Co1–Cl1 88.08(4), P1–Co1–Cl1 87.63(3), P2–Co1–Cl1 106.16(4).



(7)

It should be noted that neither 1,2,4,5-$C_6F_4H_2$ nor F_2PMe_3 was found in the reaction of eqn (7) with the participation of C_6Cl_6. It is obvious that the ligand exchange reaction *via* C–Cl bond activation is thermodynamically preferred because the C–Cl bond in C_6Cl_6 is weaker than the C–F bond in C_6F_5H.

4. Conclusion

In summary, the reactions of pentafluoropyridine C_5NF_5, hexafluorobenzene C_6F_6, and perfluoronaphthalene $C_{10}F_8$ with cobalt(0) complex, $Co(PMe_3)_4$, were investigated. The Co(I) complexes $(4\text{-}C_5NF_4)Co(PMe_3)_3$ (**1**), $(C_6F_5)Co(PMe_3)_3$ (**2**), $(C_{10}F_7)Co(PMe_3)_3$ (**3**), $(4\text{-}C_5NF_4)Co(PMe_3)_4$ (**4**) and $(C_{10}F_7)Co(PMe_3)_4$ (**6**) were obtained by the selective activation of the C–F bonds. The reactions of **1** and **2** with CO afforded dicarbonyl cobalt(I) complexes $(4\text{-}C_5NF_4)Co(CO)_2(PMe_3)_2$ (**7**), $(C_6F_5)Co(CO)_2(PMe_3)_2$ (**8**). Under similar reaction conditions, **2** as a C–H bond activation product was obtained from the reaction of pentafluorobenzene, C_6F_5H, with $Co(PMe_3)_4$. The byproducts, hydrodefluorination product 1,2,4,5-$C_6F_4H_2$ and F_2PMe_3 from the reaction of C_6F_5H and $Co(PMe_3)_4$ were also observed. The reaction mechanism of C_6F_5H with $Co(PMe_3)_4$ is proposed and partly-experimentally verified. The reaction of C_6F_5H with $Co(PMe_3)_4$ under 1 bar of CO at room temperature afforded hydrido dicarbonyl cobalt(II) complex $(C_6F_5)Co(H)(CO)_2(PMe_3)_2$ (**11**). Treatment of the mixtures of $C_6F_5H/Co(PMe_3)_4$ with hexachlorobenzene, C_6Cl_6, resulted in $(C_6F_5)CoCl(PMe_3)_3$ (**12**) *via* C–H bond cleavage with the hydrodechlorination product pentachlorobenzene, C_6Cl_5H, and 1,2,4,5-tetrachlorobenzene, $C_6Cl_4H_2$. The structures of complexes **1**, **2**, **6**, **7**, **8**, **11** and **12** were determined by X-ray diffraction.

Acknowledgements

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