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Effect of anchoring group and valent of cobalt center on the competitive cleavage of C–F *or* C–H bond activation

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ABSTRACT

Treatment of $CoMe(PMe_3)_4$ with 2,6-difluorobenzophenone imine and 2,6-difluorobenzophenone resulted in C–H bond activation complex, $[Co(2\text{-}C_6H_4)\text{-}(C{=}NH)\text{-}(2',6''\text{-}F_2C_6H_3)(PMe_3)_3]$ **(2),** and C–F bond activation complex $[Co(Me)(F)(2\text{-}(6\text{-}FC_6H_3)\text{-}(C{=}O)\text{-}C_6H_5)(PMe_3)_2]$ **(3)** respectively. Using $Co(PMe_3)_4$ instead of $CoMe(PMe_3)_4$ the C–F activation Co(I) complex $[Co(2\text{-}(6\text{-}FC_6H_3)\text{-}(C{=}NH)\text{-}C_6H_5)(PMe_3)_3]$ **(1)**, was obtained by the reaction of $Co(PMe_3)_4$ with 2,6-difluorobenzophenone imine. In the case of mono-fluorinated aromatic ketone, the reaction of $CoMe(PMe_3)_4$ with 2,4′-difluorobenzophenone afforded only C–H bond activation complex, $[Co(2\text{-}(4\text{-}FC_6H_3)\text{-}(C{=}O)\text{-}(2'\text{-}FC_6H_4)(PMe_3)_3]$ **(4)** in comparison with the C–F activation in the di-fluorinated aromatic ketone 2,6-difluorobenzophenone system. The crystal structures of complexes **1, 3** and **4** were determined by X-ray diffraction. The proposed mechanisms were discussed.

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1. Introduction

The intramolecular selective activation of C–F *versus* C–H bond has attracted a great deal of attention in recent years because of the requirements of "molecular surgery" in modern synthetic chemistry. The priority of selective activation of C–F *versus* C–H bond within one molecule is complicated and is related to many factors [1–16]. It has not only thermodynamic but also kinetic reason. A survey of competing C–F activation pathways in the reaction of Pt(0) with fluoropyridines by Perutz was investigated with both computational and experimental methods [17]. In 2008 Klein reported the first regioselective cyclometalation reactions of cobalt in arylketone [18]. It was found that $CoMe(PMe_3)_4$ activates *ortho*-(C–H) and *ortho*-(C–F) bonds of aromatic ketones and the *ortho*-(C–F) activation is preferred over the *ortho*-(C–H) activation in 2,3,4,5,6-pentafluorobenzophenone. Recently Johnson published a combined experimental and computational study of unexpected C–F bond activation intermediates and selectivity in the reaction of pentafluorobenzene with a $(PEt_3)_2Ni$ synthon [19]. Goldman reported addition at the aryl *meta*- and *para*-positions is kinetically more favorable than at the *ortho*-position, although thermodynamics favor the chelated *ortho*-(C–H) addition for three coordinate d^8 metal complexes [20]. Hydrido osmium is capable of producing the triple C–H bond activation of the cyclohexyl group of cyclohexylmethyl ketone [21]. Esteruelas found that the *ortho*-(C–H) bond activation is preferred over the *ortho*-(C–F) bond activation in aromatic ketones with one aromatic ring by phosphine-supported hexahydride osmium complex [22]. Both C–F and C–H bond activations are favored by an increase of the degree of fluorination of the substrates [23]. We obtained the first organo cobalt(III) complex containing a [C–Co–F] fragment through a cyclometalation reaction involving C–F bond activation at a cobalt(I) center with an aldazine-N atom as an anchoring group [24]. In this paper we present competitive cleavage of C–F *versus* C–H bond in the cyclometalation reaction at electron-rich cobalt center with ketone and imine as anchoring group. Through the reaction of $CoMe(PMe_3)_4$ with 2,6-difluorobenzophenone, another example of organo cobalt(III) complex, $[Co(Me)(F)(2\text{-}(6\text{-}FC_6H_3)\text{-}(C{=}O)\text{-}C_6H_5)(PMe_3)_2]$ **(3),** containing a [C–Co–F] fragment was obtained.

2. Results

2.1. Reaction of $Co(PMe_3)_4$ with 2,6-difluorobenzophenone imine

$Co(PMe_3)_4$ was combined with 2,6-difluorobenzophenone imine affording the C–F bond activation complex **1** (eq. (1)).

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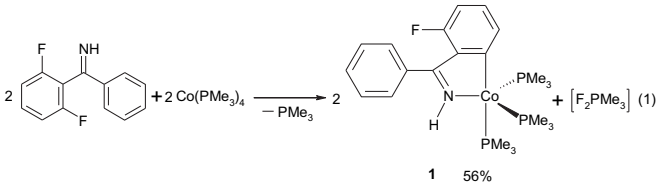


Complex **1** forms purple-blue crystals suitable for X-ray diffraction which decompose above 140 °C. In the IR spectra the characteristic ν(C=N) band was found at 1603 cm^{-1}. The resonance of the N–H proton in the ^{1}H NMR spectrum is registered at 8.36 ppm.

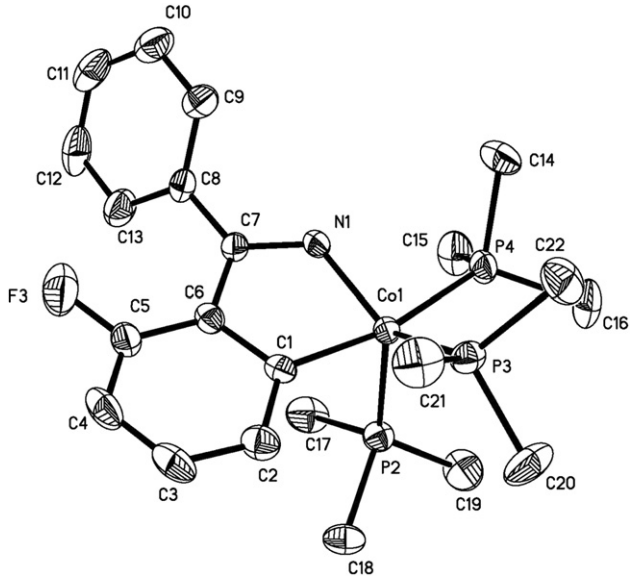


Fig. 1. Molecular structure of **1** and selected bond distances (Å) and angles (°): Co1-N1 1.885(3), Co1-P2 2.1904(13), Co1-P3 2.2002(12), Co1-P4 2.2159(13), C1-Co1 1.936(4), C7-N1 1.336(5); N1-Co1-C1 80.91(16), N1-Co1-P2 114.11(11), C1-Co1-P2 86.68(12), N1-Co1-P3 133.89(11), C1-Co1-P3 93.66(13), P2-Co1-P3 111.18(5), P2-Co1-P4 97.46(5), P3-Co1-P4 96.03(5), N1-Co1-P4 86.41(11), C1-Co1-P4 167.26(13), C7-N1-Co1 120.9(3), N1-C7-C6 110.9(4), C6-C1-Co1 113.8(3), C1-C6-C7 112.7(3).

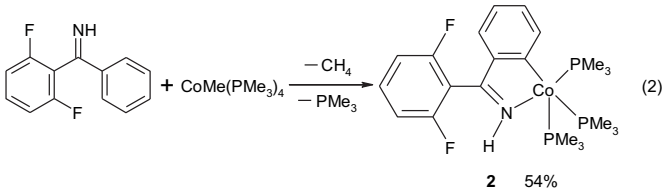
The molecular structure of **1** (Fig. 1) shows a trigonal bipyramidal configuration around cobalt with C1 and P4 on axial direction. The bite angle N1-Co1-C1 80.91(16)° is smaller than that of complex **4**. The sum of internal bond angles of the chelate ring is (539.21°). The distance of C7-N1 (1.336(5) Å) is close to that (1.337(8) Å) in the reported compound [25]. In comparison with the reaction of $Co(PMe_3)_4$ with 2,6-difluorobenzophenone [26], the imine group is a better anchoring group than the keto group. The C–F bond could be activated by the compensation of chelate effect.

In the proposed mechanism (Scheme 1) the π-coordination of C=N double bond to the cobalt(0) center is the first step, which makes closing of cobalt center to the *ortho*-(C–F) bond and the formation of the intermediate **A** possible. Oxidative addition between the C–F bond and the cobalt(0) center delivered cobalt(II) intermediate **B**. **B** was reduced to cobalt(I) product **1**.

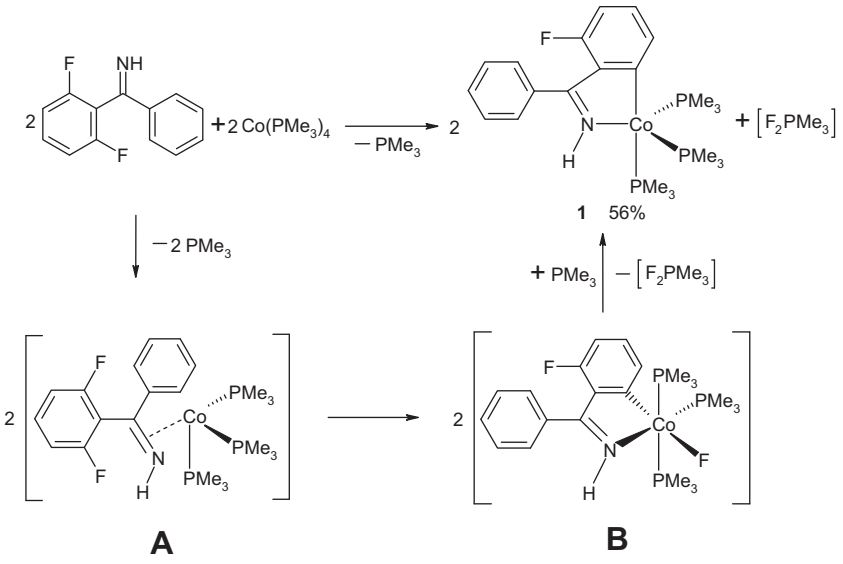
In our early work [27], the formation of F_2PMe_3 in the reaction of perfluorotoluene with $Co(PMe_3)_4$ was confirmed via ^{31}P NMR spectroscopy. The fate of the fluorine atom in reaction (1) is not experimentally identifiable.

2.2. Reaction of $CoMe(PMe_3)_4$ with 2,6-difluorobenzophenone imine

Instead of cobalt(0) complex $Co(PMe_3)_4$, cobalt(I) complex $CoMe(PMe_3)_4$ was combined with 2,6-difluorobenzophenone imine affording deep-green crystals of complex **2** through C–H bond activation (eq. (2)).



In the IR spectra ν(C=N) absorption was found at 1620 cm^{-1}. The signal of the (NH) group is registered at 8.33 ppm. In the ^{31}P NMR spectra there are three signals for PMe_3 ligands at 43.9, 33.5



Scheme 1. Proposed mechanism for reaction (1).

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