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# Synthesis and properties of novel *ortho*-metalated cobalt(I) and iron(II) complexes through $C_{sp2}$ -H bond activation of dibenzylphenylphosphine

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#### ABSTRACT

Dibenzylphenylphosphine in the reaction with CoMe(PMe<sub>3</sub>)<sub>4</sub> afforded complex  $[(Me_3P)_3Co((ortho-C_6H_4) \cap P(C_6H_5)(CH_2C_6H_5))]$  (1) by  $C_{sp2}$ —H activation via *ortho*-metalation with P atom as anchoring group. An unexpected dinitrogen iron(II) complex  $[(Me_3P)_2(N_2)Fe((ortho-C_6H_4)_2 \cap P(C_6H_5))]$  (2) stabilized by two five-membered chelate rings as [CPC]-pincer ligand was formed through the reaction of dibenzylphenylphosphine with FeMe<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub> via double  $C_{sp2}$ —H activation. The reactions of complexes 1 and 2 with carbon monoxide delivered carbonyl complexes  $[(Me_3P)(CO)_2Co((ortho-C_6H_4) \cap P(C_6H_5))]$  (3) and  $[(Me_3P)_2(CO)Fe((ortho-C_6H_4)_2 \cap P(C_6H_5))]$  (4). An iodo methyl cobalt(III) complex  $[(Me_3P)_2(Me)(I)Co((ortho-C_6H_4) \cap P(C_6H_5))]$  (5) was isolated through the reaction of 1 with iodomethane. The structures of 1, 2, 3, 4 and 5 were determined by X-ray diffraction.

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#### 1. Introduction

Carbon-hydrogen bond activation is of great importance not only in the research on fundamental theories but also in industrial applications. Many of these studies have involved C-H bond activation mediated by transition-metal complexes. In the past twenty years some examples on C<sub>sp2</sub>-H bond activation through transition-metal complexes were reported under mild conditions with high selectivity [1–4]. Through C–H activation metal-hydrogen bond is generated. This procedure plays an important role in organometallic chemistry because metal hydrides are indispensable intermediates in many chemical transformations referring to insertion with a wide variety of unsaturated compounds [5]. The possibility of direct introduction of a new C-C bond via C-H bond cleavage is a highly attractive strategy in synthetic chemistry [6]. Klein reported C-H activation of azobenzene [7] and phenyl phosphites [8] using cobalt complexes supported by trimethylphosphine via ortho-metalation.

As a complement to the research of C—H bond activation by the elements of 8th group in the periodic table herein we report our recent progress in the cyclometalation of dibenzylphenylphosphine with cobalt and iron complexes supported by trimethylphosphine.

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#### 2. Results

#### 2.1. Reaction of CoMe(PMe<sub>3</sub>)<sub>4</sub> with dibenzylphenylphosphine

Reaction of  $CoMe(PMe_3)_4$  with dibenzylphenylphosphine delivered the *ortho*-metalated cobalt(I) complex **1** through C–H bond activation via *ortho*-metalation with the escape of methane (Eq. (1)).



Crystallization at 0 °C afforded red crystals of complex **1** in the yield of 44%. In <sup>1</sup>H NMR spectra PMe<sub>3</sub> group resonances appear at 0.95 and 1.51 ppm. The singlet at 3.40 ppm is assigned to the "free" PCH<sub>2</sub> group, while another singlet at 4.12 ppm belongs to the PCH<sub>2</sub> group within the chelate ring. The resonance for the two PCH<sub>2</sub> groups in free dibenzylphenylphosphine ligand is registered at 3.10 ppm as a singlet [9]. In <sup>31</sup>P NMR spectra a singlet with a resonance at 9.2 ppm was found for two PMe<sub>3</sub> ligands. The third PMe<sub>3</sub>





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ligand shows a singlet at 22.7 ppm. The phosphor resonance of PCH<sub>2</sub> group appears at 70.1 ppm.

The molecular structure of complex **1** (Fig. 1) shows a trigonal bipyramidal configuration around cobalt with C25 and P3 on axial direction with the bond angle of C25–Co1–P3 172.73(5)° bending toward the chelate ring. A five-membered metallacycle is formed through the coordination of the P atom of dibenzylphenylphosphine and the *ortho*-chelated carbon atom. The bite angle (C25–Co1–P4) of the chelate ligand is 79.87(5)°, which is significantly larger than that (71.48(10)° in the similar Co(I) complex with the four-membered chelate ring [8]. The five-membered chelate ring (Co1P4C23C24C25) is nonplanar because the sum of the bond angles is 524.57°.

A proposed reaction mechanism is described in Scheme 1. The reaction likely begins with the coordination of dibenzylphenyl phosphine-P atom by substituting one of the trimethylphosphine ligand, which brings the metal closer to the *ortho*-( $C_{sp2}$ -H) bond of the benzyl group. This chelation results in an easier and selective  $C_{sp2}$ -H bond cleavage of benzyl group to give an active methyl hydrido cobalt(III) intermediate, which affords cobalt(I) complex **1** with the escape of methane via reductive elimination.

#### 2.2. Reaction of $Fe(Me)_2(PMe_3)_4$ with dibenzylphenylphosphine

Under similar reaction conditions, instead of CoMe(PMe<sub>3</sub>)<sub>4</sub>, Fe(Me)<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub> was used in the reaction of dibenzylphenylphosphine (eq. (2)). A dinitrogen iron(II) complex **2** as yellow crystals was isolated from diethyl ether in the yield of 26%. Complex **2** was formed through double  $C_{sp2}$ –H bond activation of two benzyl groups under elimination of two methane molecules via double *ortho*-metalation.





**Fig. 1.** Molecular structure of **1** and selected bond distances (Å) and angles (deg): Co1–C25 2.0164(15), Co1–P1 2.2054(6), Co1–P2 2.1923(6), Co1–P3 2.1751(6), Co1–P4 2.1473(6); C25–Co1–P3 172.73(5), C25–Co1–P4 79.87(5), C25–Co1–P2 82.50(5).



Scheme 1. Proposed formation mechanism of complex 1.

In the IR spectra  $\nu$ (N^N) absorption was found at 2078 cm<sup>-1</sup>, which is in the range of infrared stretching frequencies of dinitrogen iron complex [10–14]. In <sup>1</sup>H NMR spectra two PMe<sub>3</sub> groups resonate at 0.89 ppm as a singlet. Two sets of PCH<sub>2</sub> were recorded at 2.91 and 3.47 ppm.

The molecular structure of complex 2 is shown in Fig. 2. The configuration of complex 2 about the iron atom is close to octahedral with a [CPC]-pincer ligand. C5 and P3 atoms are transorientated in axial positions with the bond angle C5-Fe1-P3 (177.76(11)°). Two five-membered metallacycles are formed through the coordination of the P atom in the chelate ligand and the two ortho-metalated C atoms. Both of the chelate rings are almost perpendicular to each other. The sum of internal bond angles (539.3°) of one chelate ring (Fe1P1C13C6C5) indicates ideal planarity of the five atoms, while another metallacycle (Fe1P1C14C15C16) with the sum of internal angles (527.53°) is remarkably distorted. The bond length of terminal coordinate dinitrogen (N1-N2 = 1.113(4) Å) is close to that found in related iron complexes [15]. This bond distance is a little bit longer than the distance (1.0976 Å) in free  $N_2$ . This implies that the triple bond is weakly activated [10].

The interaction of iron with nitrogen is of significant practical and theoretical importance in many fields, such as catalysis, biology and atmospheric chemistry [16]. In the Haber process the dissociation of  $N_2$  over iron is critical in the formation of ammonia. Many articles have been published in the field of activation of dinitrogen by iron complexes [17,18]. We are making our efforts to explore the chemical properties of dinitrogen iron complex **2**.

#### 2.3. Reaction of complexes 1 and 2 with carbon monoxide

Stirring a solution of **1** in CO atmosphere (1 bar) gave rise to complex **3** (eq. (3)). Complex **3** was formed through substitution of two trimethylphosphine groups by two carbonyl ligands. An expected insertion of CO into the Co–C bond as the case of the cobalt complex in the literature [8] did not occur, because the complex with five-membered chelate ring is more stable than that with four-membered chelate ring. The tension of four-membered ring is relieved by transferring to five-membered chelate ring via carbonylation [8].



Fig. 2. Molecular structure of 2 and selected bond distances (Å) and angles (deg): Fe1-C5 2.024(4), Fe1-C16 2.053(4), Fe1-P1 2.1935(11), Fe-P3 2.2739(13), Fe-P4 2.2777(12), Fe1-N1 1.803(3), N1-N2 1.113(4); C5-Fe1-P3 177.76(11), P4-Fe1-C16 169.44(11), P1-Fe1-N1 168.19(11), Fe1-N1-N2 179.1(4), C5-Fe1-C16 84.55(15), C13-P1-C14 104.17(18).



Crystallization at 0 °C afforded yellow crystals of complex **3**. The IR spectra contain two bands at 1898 and 1958 cm<sup>-1</sup> assigned to the two terminal carbonyl ligands. In the <sup>31</sup>P NMR spectra the signals at 56.9 and 12.0 ppm belong to dibenzylphenylphosphine and trimethylphosphine ligand. In the <sup>1</sup>H NMR spectra the trimethylphosphine group appears as doublet at 1.10 ppm.

The molecular structure of complex **3** (Fig. 3) confirms the trigonal bipyramidal coordination geometry in the crystal. The bond angle C1–Co–P2 (178.11(8)°) in the axial direction deviates from 180°. The sum of internal bond angles (535.4°) of this chelate ring indicates little deviation from planarity of the five atoms (CoC1C6C7P1). The chelate bite angle (C1–Co–P1 = 83.20(9)°) is comparable with that (83.97(12)°) in the related cobalt(I) complex [19]. The Co–CO bond distances (Co–C21 = 1.742(2) and Co–C22 = 1.750(3) Å) are in the region of those for carbonyl cobalt(I) complexes [20], but both of them are remarkably shorter than Co–C1 bond distance (2.014(3) Å) because of the enhancement of  $\pi$ -backbonding of the coordinate carbonyl ligands. As expected, the carbon–oxygen distances (C21–O1 1.148(3) and C22–O2 1.145(3) Å) are longer than that (1.1282 Å) in free CO molecule [21] due to the activation of carbonyl bond.

Under the same reaction conditions the reaction of **2** with CO afforded complex **4**. In this process complex **4** was formed through a simple substitution of  $N_2$  by CO. In the IR spectra the stretching

vibration (2078 cm<sup>-1</sup>) of N^N in complex **2** is replaced by the corresponding vibration (1941 cm<sup>-1</sup>) of C^O in complex **4**. In the <sup>1</sup>H NMR spectra two PMe<sub>3</sub> ligands appear as doublet at 0.78 ppm. The PCH<sub>2</sub> groups resonate at 3.35 and 3.44 ppm as doublets. In the <sup>31</sup>P NMR spectra the PCH<sub>2</sub> resonates at 82.8 ppm as triplets ( $^{2}J_{P,P} = 50.0$  Hz). The PMe<sub>3</sub> groups appear at 11.6 ppm as doublets ( $^{2}J_{P,P} = 50.0$  Hz). IR and NMR data support the structure assigned for complex **4**.



Complex **4** crystallizes from diethyl ether at 0 °C as yellow plates. The molecular structure of complex **4** (Fig. 4) shows an octahedral coordination geometry. Fe–CO distance (Fe1–C23 = 1.7332(18) Å) is significantly shorter than Fe–C<sub>ortho</sub> bond distances (Fe1–C1 = 2.0554(17) and Fe1–C7 = 2.0246(17) Å) reflects the strong interaction between iron center and carbonyl ligands as an  $\sigma$ -donor/ $\pi$ -acceptor ligand. The bond distance C23–O1 (1.158(2) Å) is comparable with those (C21–O1 1.148(3) and C22–O2 1.145(3) Å) in complex **3** and much longer than the bond distance in free CO molecule.

#### 2.4. Reaction of complex 1 with iodomethane

Cobalt(I) complex **1** generated in situ through the reaction of  $CoMe(PMe_3)_4$  and dibenzylphenylphosphine reacted with iodo



**Fig. 3.** Molecular structure of **3** and selected bond distances (Å) and angles (deg): C1–Co 2.014(3), Co–C21 1.742(2), Co–C22 1.750(3), Co–P1 2.1892(6), Co–P2 2.2044(8); C21–O1 1.148(3). C22–O2 1.145(3); C1–Co–P2 178.11(8), P1–Co–C21 117.29(8), C1–Co–C22 89.56(16), P2–Co–C22 92.14(14).



**Fig. 4.** Molecular structure of **4** and selected bond distances (Å) and angles (deg): Fe1–C1 2.0554(17), Fe1–C7 2.0246(17), Fe1–C23 1.7332(18), Fe1–P2 2.2292(4), C23–O1 1.158(2), C23–Fe1–P2 168.24(7), C1–Fe1–P4 168.93(5), P3–Fe1–C7 177.27(5), Fe1–C23–O1 178.87(19).

methane to afford cobalt(III) complex **5** by undergoing an oxidative addition reaction (eq. (5)).



Orange crystals of complex **5** are obtained from pentane at 0 °C. The molecular structure of **5** (Fig. 5) shows a slightly distorted octahedral frame of donor atoms centered by a cobalt atom bearing one I-, two C- and three P-atoms. Owing to *trans*-influence iodine



atom is situated in *trans*-position of the *ortho*-metalated C26 atom, while the methyl ligand occupies the opposite location to the chelate P atom. The sum of the internal bond angle of the five-membered chelate ring (Co–P3C25C14C26) is 521.47<sup>0</sup> indicates that the five atoms are not coplanar. The bond distance Co–P3 (2.2813(12) Å) is a little bit longer than the other two Co–P distances (Co–P1 2.2564(14) and Co–P2 2.2574(13) Å). This is caused by the strong *trans*-influence of the methyl ligand. The length of (Co–I1 = 2.7051(7) Å) is close to that in related compound [22].

#### 3. Conclusion

Dibenzylphenylphosphine in the reaction with  $CoMe(PMe_3)_4$ afforded complex **1** by  $C_{sp2}$ —H activation via *ortho*-metalation with P atom as anchoring group. An unexpected dinitrogen iron(II) complex **2** stabilized by two five-membered chelate rings as [CPC]pincer ligand was formed through the reaction of dibenzylphenylphosphine with FeMe<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub>. The reactions of complexes **1** and **2** with carbon monoxide delivered carbonyl complexes **3** and **4**. The iodo methyl cobalt(III) complex **5** was isolated through the reaction of complex **1** with iodomethane. The structures of complexes **1**, **2**, **3**, **4** and **5** were determined by single crystal X-ray diffraction.

#### 4. Experimental section

#### 4.1. General procedures and materials

All air-sensitive materials were handled either in vacuo or under nitrogen by using standard Schlenk techniques. Dibenzylphenylphosphine and CoMe(PMe<sub>3</sub>)<sub>4</sub> and FeMe<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub> were prepared according to published procedures [23,24]. All solvents were dehydrated and degassed before use. Infrared spectra (4000–400 cm<sup>-1</sup>), as obtained from Nujol mulls between KBr disks, were recorded on a Bruker alpha FT-IR. <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR (300, 75, and 121 MHz, respectively) spectra were recorded on a Bruker Avance 300 spectrometer. <sup>13</sup>C and <sup>31</sup>P NMR resonances were obtained with broadband proton decoupling.

#### 4.2. Synthesis of 1

The solution of CoMe(PMe<sub>3</sub>)<sub>4</sub> (0.58 g, 1.54 mmol) in 20 ml of THF was added dibenzylphenylphosphine (0.45 g, 1.55 mmol) in 20 ml of THF. After stirring at room temperature for 48 h, the color of the solution turned to deep red. THF was evaporated in vacuo and the residue was extracted by pentane. Crystallization at 0 °C afforded the deep red plates which are suitable for X-ray diffraction analysis. Yield: 0.36 g of **1** (40.4%). Analysis for **1** C<sub>29</sub>H<sub>45</sub>CoP<sub>4</sub>, [found (calculated)]: C, 60.13 (60.42); H, 7.52 (7.88). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 673.2 K, ppm): 0.95 (s, 18H, PCH<sub>3</sub>), 1.51 (s, 9H, PCH<sub>3</sub>), 3.40 (s, 2H, PhCH<sub>2</sub>), 4.12 (s, 2H, PhCH<sub>2</sub>), 6.47–7.33 (m, 14H, Ar–H). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 673.2 K, ppm): 70.1 (s, 1P, PhCH<sub>2</sub>P), 9.2 (s, 2P, PMe<sub>3</sub>), 22.7 (s, 1P, PMe<sub>3</sub>).

#### 4.3. Synthesis of 2

The solution of FeMe<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub> (0.65 g, 1.68 mmol) in 20 ml THF was added dibenzylphenylphosphine (0.49 g, 1.70 mmol) in 20 ml THF. After stirring at room temperature for 48 h, the color of the solution turned brown. THF was evaporated in vacuo and the residue was extracted by pentane and diethyl ether. Crystallization at 0 °C afforded the yellow plates which are suitable for X-ray diffraction analysis. Yield: 0.23 g of **2** (26.0%). Analysis for **2**  $C_{26}H_{35}FeN_2P_3$ , [found (calculated)]: C, 59.26 (59.56); H, 6.42 (6.73); N 5.03 (5.34). m.p. 110–112 °C (dec.). IR (Nujol):  $\nu = 2078$  (N<sup>N</sup>) cm<sup>-1</sup>.<sup>1</sup>H NMR (CDCl<sub>3</sub>, 292.4 K, ppm): 0.89 (s, 18H, PCH<sub>3</sub>), 2.91 (s, 2H,

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Crystallographic	Data for	Complexes	1–5

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	1	2	3	4	5
Empirical formula	C <sub>29</sub> H <sub>45</sub> CoP <sub>4</sub>	C <sub>26</sub> H <sub>35</sub> FeN <sub>2</sub> P <sub>3</sub>	C <sub>25</sub> H <sub>27</sub> CoO <sub>2</sub> P <sub>2</sub>	C <sub>27</sub> H <sub>35</sub> FeOP <sub>3</sub>	C <sub>27</sub> H <sub>39</sub> CoIP <sub>3</sub>
fw	576.46	524.34	480.37	526.43	642.18
Cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
Space group	P2(1)/c	P2(1)/n	P2(1)/n	P2(1)/n	P-1
a, Å	9.788(2)	9.2974(17)	12.9608(9)	9.2884(5)	11.0447(13)
b, Å	13.260(3)	19.069(3)	14.5619(10)	19.0589(11)	11.2627(14)
<i>c,</i> Å	23.416(5)	14.792(3)	13.7839(10)	14.7526(9)	14.1430(17)
$\alpha$ , deg	90	90	90	90	78.835(2)
β, deg	93.26(3)	90.377(3)	108.1630(10)	90.8110(10)	80.412(2)
γ, deg	90	90	90	90	69.715(2)
<i>V</i> , Å <sup>3</sup>	3034.2(11)	2622.5(8)	2471.9(3)	2611.3(3)	1609.5(3)
Ζ	4	4	4	4	2
$D_{\rm c}$ , g cm <sup>-3</sup>	1.262	1.328	1.291	1.309	1.325
No. of rflns collected	13762	10423	14291	15096	9433
No. of unique data	6062	3463	5565	5845	6934
R <sub>int</sub>	0.0220	0.0476	0.0206	0.0166	0.0149
$\theta_{max}$ , deg	26.73	22.64	27.53	27.50	27.54
$R_1 (I > 2\sigma(I))$	0.0290	0.0400	0.0382	0.0317	0.0512
wR <sub>2</sub> (all data)	0.0784	0.0986	0.1097	0.0902	0.1981

PhCH<sub>2</sub>), 3.47 (s, 2H, PhCH<sub>2</sub>), 6.41–8.02 (m, 14H, Ar–H). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 292.4 K, ppm): 71.3 (s, 1P, PhCH<sub>2</sub>P), 4.5 (s, 1P, PMe<sub>3</sub>), 8.2 (d,  ${}^{2}J_{P,P} = 86.8$  Hz, 1P, PMe<sub>3</sub>).

#### 4.4. Synthesis of 3

The solution of complex **1** (0.21 g, 0.36 mmol) in 20 ml diethyl ether was stirred under 1 bar CO for 12 h. The color of the solution turned light yellow. Diethyl ether was evaporated in vacuo and the residue was extracted by pentane. Crystallization at 0 °C afforded complex **3** as yellow cubic crystals suitable for X-ray diffraction analysis. Yield: 0.067 g of **3** (40%). Analysis for **3** C<sub>25</sub>H<sub>27</sub>CoO<sub>2</sub>P<sub>2</sub>, [found (calculated)]: C, 62.53 (62.51); H, 5.32 (5.67). m.p. 92–94 °C (dec.). IR (Nujol):  $\nu = 1898$ , 1958 (C]O) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 295.5 K, ppm): 1.10 (d, <sup>2</sup>J<sub>PH</sub> = 8.4 Hz, 9H, PCH<sub>3</sub>), 3.52 (t, |<sup>2</sup>J<sub>PH</sub> + <sup>3</sup>J<sub>H,H</sub>| = 15.90 Hz, 2H, PhCH<sub>2</sub>), 3.41 (t, |<sup>2</sup>J<sub>P,H</sub> + <sup>3</sup>J<sub>H,H</sub>| = 13.20 Hz, 2H, PhCH<sub>2</sub>), 7.62–6.82 (m, 14H, Ar–H). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 295.6 K, ppm): 56.9 (s, 1P, PhCH<sub>2</sub>P), 12.0 (s, 1P, PMe<sub>3</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 300.1 K, ppm): 19.7 (dd, <sup>1</sup>J<sub>P,C</sub> = 39.4 Hz, PCH<sub>2</sub>), 123.3 (s, CH), 125.0 (s, CH), 125.3 (s, CH), 125.8 (s, CH), 129.2 (s, CH), 130.1 (s, CH), 131.0 (d, <sup>2</sup>J<sub>P,C</sub> = 9.8 Hz, C), 135.7 (d, <sup>2</sup>J<sub>P,C</sub> = 6.0 Hz, C), 146.5 (d, <sup>2</sup>J<sub>P,C</sub> = 3.0 Hz), 146.8 (d, <sup>2</sup>J<sub>P,C</sub> = 3.0 Hz, C).

#### 4.5. Synthesis of 4

The solution of FeMe<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub> (0.80 g, 2.05 mmol) in 20 ml THF was added dibenzylphenylphosphine (0.60 g, 2.07 mmol) in 20 ml THF. After stirring at room temperature for 48 h, the color of the solution turned brown. The solution was stirred under 1 bar CO for 12 h. The color of the solution turned black. THF was evaporated in vacuo and the residue was extracted by pentane and diethyl ether. Crystallization at 0 °C afforded complex 4 as yellow cubic crystals suitable for X-ray diffraction analysis. Yield: 0.39 g of 4 (32.8%). Analysis for 4 C<sub>27</sub>H<sub>35</sub>FeOP<sub>3</sub>, [found (calculated)]: C, 61.73 (61.60); H, 8.92 (8.99). m.p. 96–98 °C (dec.). IR (Nujol):  $\nu = 1941$  (C]O) cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 673.2 K, ppm): 0.78 (d,  ${}^{2}J_{P,H} = 5.7$  Hz, 18H, PCH<sub>3</sub>), 3.35 (d,  ${}^{2}J_{P,H} = 13.5$  Hz, 2H, PhCH<sub>2</sub>), 3.44 (d,  ${}^{2}J_{P,H} = 6.0$  Hz, 2H, PhCH<sub>2</sub>), 6.87–7.41 (m, Ar–H, 13H). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>, 673.2 K, ppm): 11.6 (d,  ${}^{2}J_{P,P} = 50.0$  Hz, 2P, PMe<sub>3</sub>), 82.8 (t,  ${}^{2}J_{P,P} = 50.0$  Hz, 1P, PhCH<sub>2</sub>P).  ${}^{13}C$ NMR (C<sub>6</sub>D<sub>6</sub>, 673.2 K, ppm): 20.7 (s, PCH<sub>3</sub>), 20.9 (s, PCH<sub>3</sub>), 21.0 (s, PCH<sub>3</sub>), 45.4 (s, PCH<sub>2</sub>), 45.8 (m, PCH<sub>2</sub>), 121.5 (s, CH), 125.6 (s, CH), 131.8 (d,  ${}^{2}J_{P,C} = 8.3$  Hz, C), 139.6 (s, CH), 142.8 (d,  ${}^{2}J_{P,C} = 4.5$  Hz, C), 145.5 (s, CH), 145.8 (s, CH), 171.3 (s, Fe-C), 261.9 (s, C).

#### 4.6. Synthesis of 5

The solution of CoMe(PMe<sub>3</sub>)<sub>4</sub> (0.46 g, 1.22 mmol) in 20 ml of THF was added dibenzylphenylphosphine (0.35 g, 1.21 mmol) in 20 ml of THF. After stirring at room temperature for 48 h, CH<sub>3</sub>I (0.2 g, 1.41 mmol) was added. The solution turned orange. THF was evaporated in vacuo and the residue was extracted by pentane. Crystallization at 0 °C afforded complex **5** as orange crystals suitable for X-ray diffraction analysis. Yield: 0.10 g of **5** (32%). Analysis for **5** C<sub>27</sub>H<sub>39</sub>CoIP<sub>3</sub>, [found (calculated)]: C, 50.13 (50.50); H, 6.32 (6.12). m.p. 101–103 °C (dec.). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 294.8 K, ppm): 0.48 (d, <sup>3</sup>*J*<sub>P,H</sub> = 6.3 Hz, 3H, CoCH<sub>3</sub>), 1.25 (d, <sup>2</sup>*J*<sub>P,H</sub> = 3.9 Hz, 18H, PCH<sub>3</sub>), 2.13 (s, 4H, PCH<sub>2</sub>), 6.51–7.42 (m, 14H, CH). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 294.8 K, ppm): 12.5 (s, 2P, PMe<sub>3</sub>), –4.9 (s, P, PCH<sub>2</sub>).

#### 4.7. X-ray structure determinations

Intensity data were collected on a Bruker SMART diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$ ) 0.71073 Å). Crystallographic data for complexes **1–5** 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.

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#### Appendix A. Supplementary materials

CCDC-737241 (1), CCDC-737238 (2), CCDC-737243 (3), CCDC-737239 (4) and CCDC-737242 (5) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

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