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利用碳氢键活化合成钴的钳式配合物及其性质研究

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摘要　利用 $CoMe(PMe_3)_4$ 或者 $CoMe_3(PMe_3)_3$ 与[PCP]-钳式配体, $[Ph_2P(ortho\text{-}C_6H_4)]_2CH_2$ (**1**), 室温下反应, 在实现碳氢键活化的同时, 合成了钴的钳式配合物 [PCP]Co(I)(PMe_3) (**2**). 配合物 **2** 与卤代烃 C_6Cl_6, EtBr, *n*-BuBr 以及 CH_3I 反应, 分别生成了单电子氧化加成产物**3**～**5**, [PCP]Co(II)X(PMe_3) [X＝Cl (**3**), Br (**4**), I (**5**)]. X 射线衍射分析测定了配合物**2**～**6**的结构.

关键词　碳氢键活化; 钳式配合物; 钴配合物

Synthesis and Reactivity of Cobalt Pincer Complexes Formed by Carbon-Hydrogen Bond Activation

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Abstract　By treating diphosphinito [PCP]-pincer ligand, $(Ph_2P(ortho\text{-}C_6H_4))_2CH_2$ (**1**) with $CoMe(PMe_3)_4$ or $CoMe_3(PMe_3)_3$ the same C_{sp3}—H bond activation product [PCP]Co(I)(PMe_3) (**2**) was obtained at room temperature. Treatment of **2** with C_6Cl_6, EtBr or *n*-BuBr and CH_3I gave rise to the single electron oxidation addition products [PCP]Co(II)X(PMe_3) [X＝Cl (**3**), Br (**4**) and I (**5**)]. The molecular structures of **2**～**6** were confirmed by X-ray diffraction analysis.

Keywords　C_{sp3}—H activation; pincer complex; cobalt complex

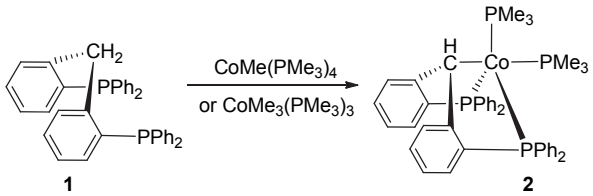
1 Introduction

Over the past decades, the study on C—H bond activation and functionalization especially on C_{sp3}—H bond is becoming one of the main chemical challenges in organic synthesis.[1] Among numerous strategies to realize the activation of C_{sp3}—H bond, oxidative addition at low-valent metal center assisted by chelate ligand(s) is still playing an important role.[2] [ZCZ]-type (Z＝N, P, O, S…) pincer ligand possessing two donating groups can facilitate the process of selective activation of C_{sp3}—H bond.[3] An early example was a pincer rhodium complex formed by stoichiometric activation of C_{sp3} — H bond with $(t\text{-}Bu)_2PCH_2CH_2CH_2CH_2CH_2P(t\text{-}Bu)_2$ in the late 1970s.[4]

Although many pincer ligands were designed to conduct C_{sp3}—H bond activation, noble metals were used in the related publications in most cases[5] and only in a few studies inexpensive iron and cobalt compounds were chosen to activate C_{sp3}—H bond.[6] In the exploration of C_{sp3} — H bond activation of [PCP]-type ligand $[Ph_2P(ortho\text{-}C_6H_4)]_2CH_2$ (**1**), there were almost no successful reports except the electrophilic substitution reaction assisted by $RhCl_3$.[7] We reported the C_{sp3}—H bond activation of (**1**) by using $Fe(PMe_3)_4$ and $FeMe_2(PMe_3)_4$ under a mild condition.[8] This result prompted us to extend this study to electron-rich Co complexes. In this paper, we describe the reaction route realizing the C_{sp3}—H bond activation with $CoMe(PMe_3)_4$ to isolate Co(I) complex **2**. By the reaction of **2** with RX (RX＝C_6Cl_6, EtBr, *n*-BuBr or MeI), we obtained the single-electron oxidative addition products **3**, **4** and **5**. The crystal and molecular structures of complexes **2**～**6** were determined by single crystal X-ray diffraction.

2 Results and discussion

The reaction of **1** with $CoMe(PMe_3)_4$ or $CoMe_3(PMe_3)_3$ at room temperature afforded the same C_{sp3}—H bond activation product complex **2** as a red solid in over 60% yield. Complex **2** could be recrystallized from diethyl ether at 0 ℃ (Eq. 1). **2** in solid state was stable in air for several hours.



1　　2　　(1)

From the ^1H NMR spectrum of complex **2** in C_6D_6, we

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could easily find the presence of the CH group at δ 4.04. The proton resonances of two types of PMe_3 groups are recorded as two doublets at δ 0.84 and 1.05 with the coupling constants ^2J(PH)=6.0 and 3.9 Hz. The ^{31}P NMR spectrum shows a triplets of doublets for one PMe_3 at δ −14.0 with the coupling constants ^2J(PP)=99.7 Hz and ^2J(PP)=30.1 Hz, a quartet for another PMe_3 at δ 9.6 and a broaden singlet for the two diphenylphosphanyl groups at δ 48.4. In the molecular structure of **2**, the cobalt atom is situated in a distorted trigonal bipyramidal coordination sphere and makes up the equatorial plane with [Co(1)P(1)P(3)P(9)] (Figure 1). One PMe_3 ligand and the central C_{sp3} atom are located in the axial positions with an angle of C(46)-Co(1)-P(8)=177.5(2)°. Co(1)—C(46) distance and the four Co—P bond lengths are well matched with the other structural features.[6,9]

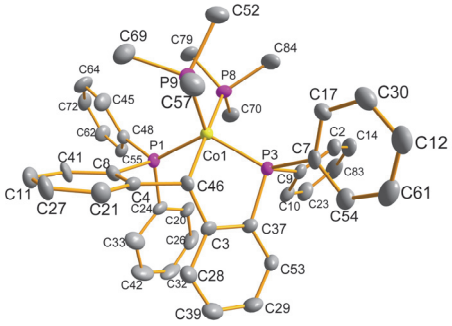
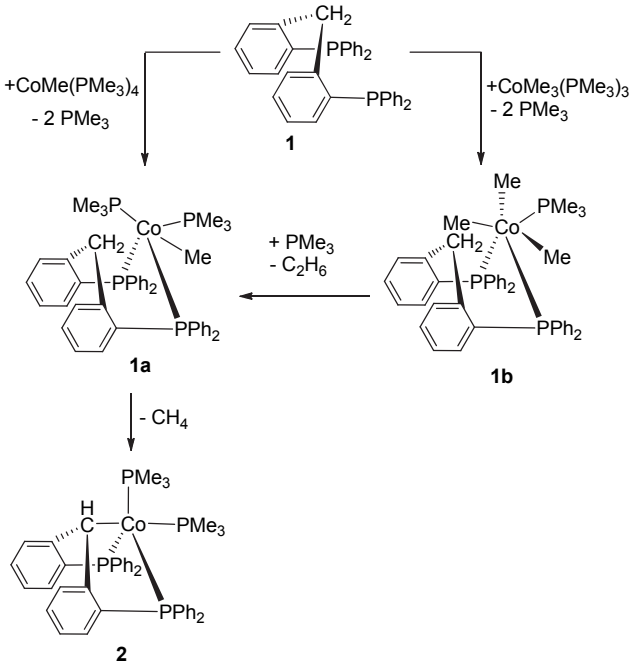


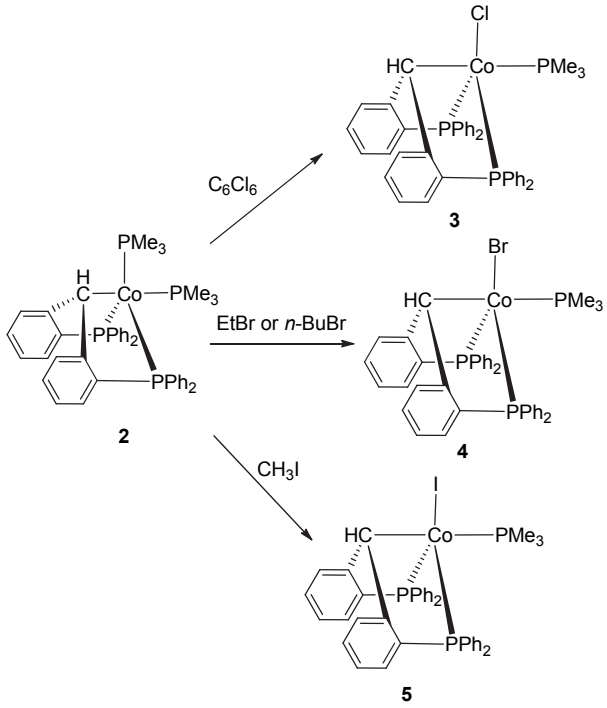
Figure 1 Molecular structure of **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Co(1)—C(46) 2.085(6), Co(1)—P(3) 2.153(2), Co(1)—P(1) 2.173(2), Co(1)—P(8) 2.188(2), Co(1)—P(9) 2.224(2); C(46)-Co(1)-P(8) 177.5(2), C(46)-Co(1)-P(3) 80.6(2), C(46)-Co(1)-P(1) 79.8(2), C(46)-Co(1)-P(9) 87.7(2), P(3)-Co(1)-P(1) 120.79(7), P(1)-Co(1)-P(9) 113.28(7), P(3)-Co(1)-P(9) 121.03(7).

It is proposed that the reaction of **1** with $CoMe(PMe_3)_4$ begins with ligand substitution to form intermediate **1a** (Scheme 1). The C_{sp3}—H bond activation of **1a** is realized by the interaction of the acidic hydrogen atom of the central methylene group and the basic coordinated methyl group. As an alternative to form a hydrido methyl organocobalt(III) intermediate from **1a** to **2** through oxidative addition was excluded because the *in situ* IR and NMR confirmation of the Co—H functionality failed. Similarly, the reaction of **1** with $CoMe_3(PMe_3)_3$ begins with the ligand substitution, too. Because the PPh_2 group is less basic than the trimethylphosphine ligand, the transformation of **1b** to **1a** proceeds via reductive elimination of the two *cis*-methyl groups at the cobalt(III) center with the liberation of one molecule of ethane. Therefore, a cobalt(I) intermediate **1a** is formed.

By the reaction of complex **2** with excess C_6Cl_6 in THF at room temperature, we isolated **3** as red crystals from diethyl ether (Scheme 2). The molecular structure of **3** was confirmed by X-ray diffraction (Figure 2). Complex **3** has a trigonal bipyramidal coordination geometry with the angle C(22)-Co-P(1) (176.12(6)°) in the axial position. The four equatorial atoms [Co(1)Cl(1)P(2)P(3)] are not completely coplanar because the sum of the three bond angles [Cl(1)-Co(1)-P(2)=112.43(2)°, Cl(1)-Co(1)-P(3)=132.82° and P(2)-Co(1)-P(3)=111.63(2)°] around the



Scheme 1 Proposed mechanism of formation of complex **2**.



Scheme 2 Reactions of complex **2** with halogenated alkanes.

cobalt center is 356.88°. Both strongly deformed 5-membered chelate rings orientate in the axial direction.

When **2** was treated with excess EtBr or *n*-BuBr in THF at room temperature for 12 h, the same complex **4** as red crystals was obtained from diethyl ether (Scheme 2). The X-ray diffraction study on complex **4** revealed that the central cobalt atom was coordinated by five coordination

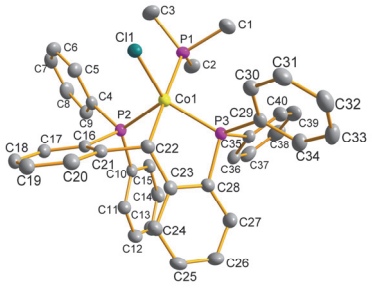


Figure 2 Molecular structure of **3**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Cl(1)—Co(1) 2.2907(5), Co(1)—C(22) 2.077(2), Co(1)—P(3) 2.1941(5), Co(1)—P(1) 2.2493(5), Co(1)—P(2) 2.2722(5); C(22)-Co(1)-P(3) 81.10(5), C(22)-Co(1)-P(1) 176.12(6), C(22)-Co(1)-P(2) 82.92(5), C(22)-Co(1)-Cl(1) 88.32(5), Cl(1)-Co(1)-P(2) 112.43(2), Cl(1)-Co(1)-P(3) 132.82(2), P(2)-Co(1)-P(3) 111.63(2).

atoms [BrCPPP] with a distorted trigonal bipyramidal geometry (Figure 3). The steric requirements of the coordinated ligands of **4** cause the axial bond angle C(22)-Co(1)-P(1) to bend to 177.0(2)° from the ideal 180°. The sum (358.29°) of the three bond angel around the Co atom [P(3)-Co(1)-Br(1)=127.35(5)°; P(2)-Co(1)-Br(1)=120.39(6)° and P(3)-Co(1)-P(2) = 110.54(7)°] indicates that the four atoms [Co(1)Br(1)P(2)P(3)] are not exactly coplanar. The distance of Co—C(22) (2.074(6) Å) is in the normal range.[6,9]

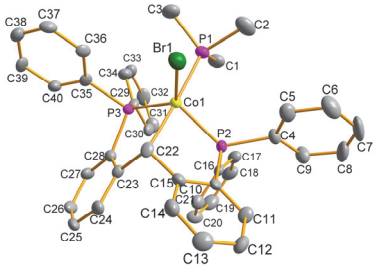


Figure 3 Molecular structure of **4**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Br(1)—Co(1) 2.432(1), Co(1)—C(22) 2.074(6), Co(1)—P(3) 2.197(2), Co(1)—P(2) 2.231(2), Co(1) — P(1) 2.250(2); C(22)-Co(1)-P(3) 83.2(2), C(22)-Co(1)-P(2) 84.0(2), C(22)-Co(1)-Br(1) 89.4(2), C(22)-Co(1)-P(1) 177.0(2), P(3)-Co(1)-P(2) 110.54(7), P(3)-Co(1)-Br(1) 127.35(5), P(2)-Co(1)-Br(1) 120.39(6).

The iodo complex **5** as a derivative of complexes **3** and **4** was also synthesized through the reaction of complex **2** with excess CH_3I in THF (Scheme 2). Complex **5** has a similar structure with complexes **3** and **4**. The cobalt atom is centered by a slightly distorted trigonal bipyramidal geometry (Figure 4). The axial bond angle [C-Co-X= 176.12(6)° (**3**, X=Cl), 177.0(2)° (**4**, X=Br), 178.35(8)° (**5**, X=I)] increases with the increase of the atomic size while no trend could be found out if we compare the three bond angles P(2)-Co(1)-P(3) [111.63(2)° (**3**), 110.54(7)° (**4**), 113.40(3)° (**5**)] in the equatorial coordination plane in the three complexes. However, the variation trend of Co—X bond lengths [Co(1)—Cl(1)=2.2907(5) Å (**3**), Co(1)—Br(1)=2.432(1) Å (**4**), Co(1)—I(1)=2.6362(4) Å (**5**)] is reasonable.

In the studies of reaction mechanism of reactions of

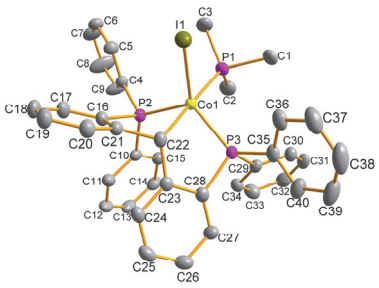
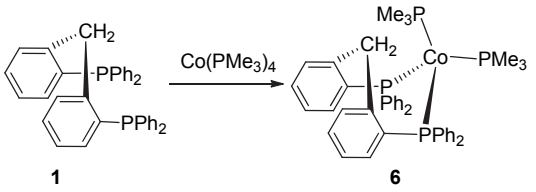


Figure 4 Molecular structure of **5**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Co(1)—C(22) 2.067(3), Co(1)—P(3) 2.2070(8), Co(1)—P(2) 2.2292(8), Co(1)—P(1) 2.2405(8), Co(1) — I(1) 2.6362(4); P(3)-Co(1)-P(2) 113.40(3), P(3)-Co(1)-I(1) 129.95(2), P(2)-Co(1)-I(1) 113.53(2), C(22)-Co(1)-P(1) 178.35(8), C(22)-Co(1)-P(3) 81.41(7), C(22)-Co(1)-P(2) 80.79(7), C(22)-Co(1)-I(1) 89.75(7).

complex **2** with halogenated alkanes, we hypothesized that these reactions underwent the single electron oxidative addition mechanism similar as our early reported work[10,11], but we failed to isolate the alkyl metal complexes.

Unexpectedly, complex **6** as a ligand replacement product could be obtained by the reaction of **1** with $Co(PMe_3)_4$ in THF at room temperature (Eq. 2). In this process, no C—H bond activation occurred. Complex **6** was isolated as red crystals from diethyl ether in over 60% yield at 0 ℃. The NMR measurement shows that complex **6** is paramagnetic. The seriously distorted tetrahedral molecular structure of complex **6** was confirmed by X-ray diffraction analysis (Figure 5).



(2)

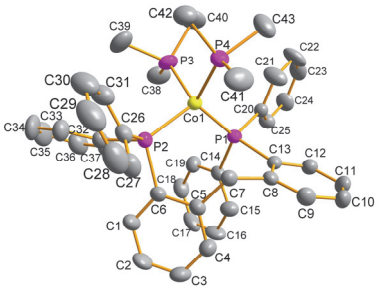


Figure 5 Molecular structure of **6**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Co(1)—P(2) 2.188(1), Co(1)—P(1) 2.192(1), Co(1)—P(4) 2.206(1), Co(1)—P(3) 2.217(1); P(2)-Co(1)-P(1) 111.51(4), P(2)-Co(1)-P(4) 113.46(4), P(1)-Co(1)-P(4) 118.76(4), P(2)-Co(1)-P(3) 104.97(4), P(1)-Co(1)-P(3) 107.44(4), P(4)-Co(1)-P(3) 98.70(4).

3 Conclusions

In summary, the reactions of diphosphinito PCP ligand, $[Ph_2P(ortho\text{-}C_6H_4)]_2CH_2$ (**1**), with $CoMe(PMe_3)_4$ or $CoMe_3(PMe_3)_3$ afforded the same product **2** via C_{sp3}-H ac-

tivation at room temperature. Treatment of **2** with halogeno alkanes (C_6Cl_6, EtBr or *n*-BuBr and CH_3I) furnished cobalt(II) products **3**, **4** and **5** by the single electron oxidation addition. Only ligand substitution product, complex **6** was isolated from the reaction of **1** with $Co(PMe_3)_4$. It can be concluded that the reactivity of $CoMe(PMe_3)_4$ toward the [PCP]-pincer ligands is more stronger than that of $Co(PMe_3)_4$. The molecular structures of complexes **2**～**6** were determined by X-ray single crystal diffraction analysis.

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