Formation of PCP pincer cobalt complexes with cobaltacyclopropane moieties via double C_{sp3}-H bond activation†

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The introduction and changes of the substituents at the middle carbon atom of the preligand dipyrrolmethane have significant impact on the reaction results. When the substituent at the C_{sp3} atom is methyl group, the reaction of the preligand with $CoMe(PMe_3)_4$ delivered cobalt(I) complex **2** as C_{sp3}-H bond activation product. In the case of ethyl, propyl and pentyl group, PCP pincer cobalt complexes **3 – 5** with cobaltacyclopropane moieties were formed via double C_{sp3}-H bond activation. With iso-propyl as the substituent, cobalt(I) complex **6** as C_{sp2}-H activation product was obtained.

Keywords: Dipyrrolmethane / C-H activation / Cobaltacyclopropane / *Trimethyphosphine*

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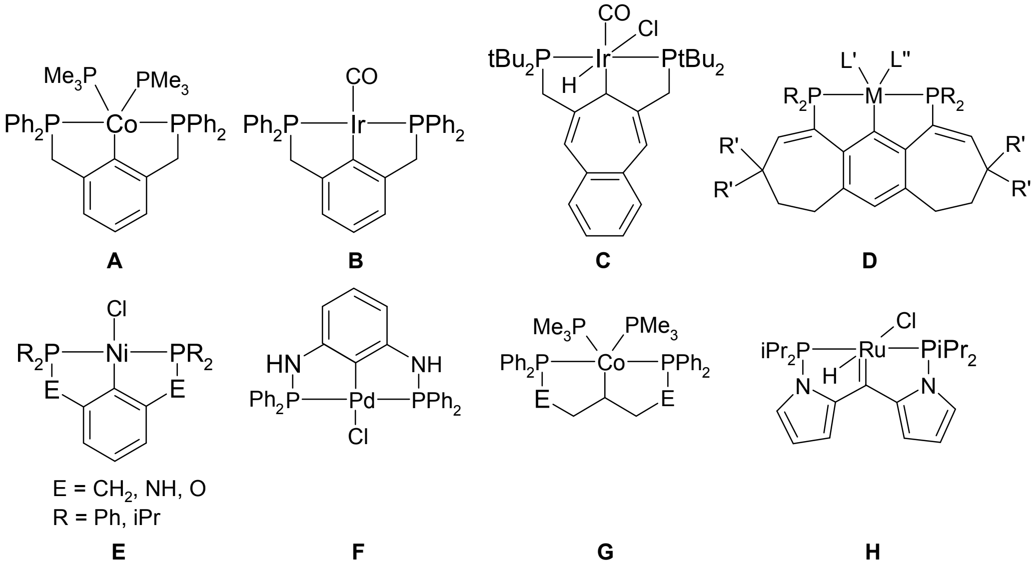
[a] The first two authors contributed to this work equally.

Introduction

A pincer ligand is a type of chelating agent that binds tightly to three adjacent coplanar sites, usually on a transition metal in a meridional configuration.[1] Among the reports on pincer ligands, many of them are related to PCP ligand and its chemistry because, on the one hand, the phosphorus atoms have excellent coordination ability; on the other hand, the formation of carbanion is of importance in the study on C-H bond activation.

According to the different spacer groups between the middle C and the P atoms there are several kinds of PCP pincer ligands (**Scheme 1**). With carbon atom as the spacer group the cobalt PCP pincer complexes type **A** was prepared by a transmetalation reaction between 1-lithio-2,6-bis((diphenylphosphino)methyl)benzene and $[CoCl(PMe_3)_3]$.[2] Acid-catalyzed oxidative addition of a C−H bond was realized by the similar **B** type carbonyl iridium(I) complex.[3] Treatment of the benzo annulated cycloheptatriene PCP pincer ligand with $Ir(CO)_3Cl$ gave the meridional cyclometalated chlorohydrido carbonyl iridium complexes (**C** type).[4] A series of PCP pincer complexes (**D** type, M = Rh and Ir) bearing a novel alkyl–aryl mixed “7-6-7” ring skeleton was synthesized and studied as catalysts for the transfer dehydrogenation of alkanes.[5] Our study also revealed that the PCP pincer nickel complex ([Ph-PNCNP-Ph]-Ni-Cl) showed the highest catalytic activity for the cross-coupling reaction under mild reaction condition (**E** type).[6] The Heck couplings of aryl halides with fluoroalkyl-substituted ethylenes could be catalyzed by PCP pincer palladium complex (**F** type).[7]

In general, C_{sp3}-H bond activation by transition metal complexes is much more difficult than C_{sp2}-H bond activation but there are few examples of the $PC_{sp3}P$ transition metal complexes formed via C_{sp3}-H bond activation. **G** type PCP cobalt(I) complex bearing an aliphatic chain was obtained by the reaction of the preligand with $CoMe(PMe_3)_4$.[8] The reactivity of substituents placed in the central C atom of G type PCP pincer ligands has been thoroughly studied by Milstein.[8b,8c] Ozerov isolated the Ru complexes of a neutral PCP ligand with a central carbene moiety through double C_{sp3}-H bond activation (**H** type).[9] With the similar preligand we disclosed its coordination compounds of iron, cobalt and nickel via C_{sp3}-H bond activation or simple ligand substitution.[10]



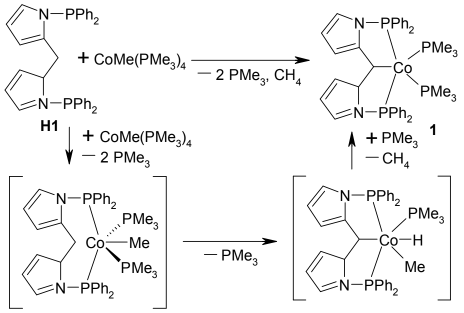
Scheme 1. PCP pincer ligands.

As a continuation we will report the coordination chemistry of the derivatives of preligand dipyrrolmethane with cobalt (**H** type). Double C_{sp3}-H bond activation was also observed but occurred at different carbon atoms. The resulted complexes are with a cobaltacyclopropane moiety.

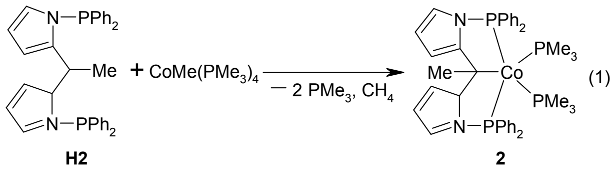
Results and Discussion

1. Reaction of $CoMe(PMe_3)_4$ with H2

We reported the reaction of ligand **H1** with $CoMe(PMe_3)_4$ to afford complex **1**. It is proposed that the reaction proceeds with ligand substitution, oxidative addition via C_{sp3}-H activation and reductive elimination with the escape of methane (Scheme 2).[10] In order to further study the effect of the introduction and changes of the substituents at the middle carbon atom of the preligand dipyrrolmethane on the reaction results and to prepare new pincer complexes via C_{sp3}-H bond activation, in this paper we have prepared a series of new ligands, **H2-H6**, with different alkyl groups at the middle C_{sp3} atom. The reaction of **H2** with $CoMe(PMe_3)_4$ is similar with the reaction of **H1** and $CoMe(PMe_3)_4$ (**Scheme 2**).



Scheme. 2 Reaction of **H1** with $CoMe(PMe_3)_4$



Complex **2** as a derivative of complex **1** was isolated via C-H bond activation (eq. (1)). Complex **2** was characterized by single crystal X-ray diffraction analysis (**Figure 1**). C23 and P1 are in the axial postions of a trigonal bipyramidal coordination geometry with P2, P3 and P4 in the equatorial plane. Co1-C23 (2.209(3) Å) is a little bit longer than the corresponding bond Co1-C35 (2.140(3) Å)[10] in complex **1** due to the influence of the methyl group. No reasonable ^{1}H and ^{31}P NMR spectra could be observed because complex **2** is not stable and dissociates to paramagnetic tetra-coordinate cobalt(I) species and the free PMe_3 ligand.

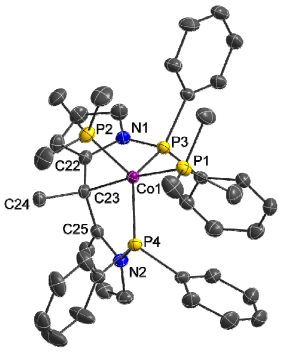


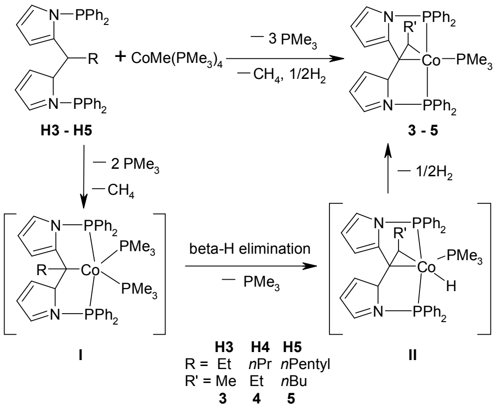
Figure 1. Molecular structure of complex **2**. The thermal ellipsoids are displayed at 30% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles [°]: Co1-C23 2.209(3), Co1 P1 2.2284(9), Co1-P2 2.242(1), Co1-P3 2.1528(9) Co1-P4 2.1497(9), P3-N1 1.729(3), P4-N2 1.730(3), C23-C22 1.494(4), C23-C24 1.541(4), C23-C25 1.500(4), N1-C22 1.376(4), N2-C25 1.366(4); C23-Co1-P1 174.76(9), C23-Co1-P2 89.76(8), C23-Co1-P3 82.13(8), C23-Co1-P4

80.52(9), P1-Co1-P2 94.72(4), P1-Co1-P3 98.48(4), P1-Co1-P4 94.60(4), P2-Co1-P3 113.85(4), P2-Co1-P4 126.72(4), P3-Co1-P4 116.35(4), C24-C23-Co1 117.1(2).

2. Reaction of $CoMe(PMe_3)_4$ with H3-H5

When the substituent at the C_{sp3} atom is ethyl, propyl and pentyl group (preligand **H3** – **H5**), the reaction of the preligands with $CoMe(PMe_3)_4$ delivered cobalt(II) complexes (**3 - 5**) with cobaltacyclopropane moieties as red powder in the yields from 60 - 70% (**Scheme 3**). It is proposed that the C_{sp3}-H bond activation was the first step to afford intermediate **I** which is similar as complexes **1** and **2** with the C_{sp3} coordination to cobalt center. Intermediate **I** transformed to unstable hydrido intermediate **II** via β-H elimination. The final products **3 - 5** were formed through intermolecular reductive elimination or a homolytic hydride dissocitation with the escape of dihydrogen. Unfortunately, the experiments to catch the hydrido signal by *in situ* IR or NMR failed.

Because complexes **3** – **5** are paramagnetic, they are NMR silent, and their characterization relied on X-ray diffraction (**Figure 2** - **Figure 4**). In this process, not only the C-H bond of the central carbon atom was activated but also one C-H bond of the methylene group, adjacent to the central carbon atom, was cleaved to form a cobaltacyclopropane moiety. Cobalt is situated in the center of a strongly deformed tetrahedron. This is a non-symmetrical triangle of the cobaltacyclopropane. Co1-C21 (1.985(7) (**3**), 1.989(6) (**4**) and 2.007(3) (Å) (**5**),) is shorter than Co1-C20 (2.193(9) (**3**), 2.226(6) (**4**) and 2.232(3) (Å) (**5**)). C20-C21 bond lengths ((1.523(10) (**3**), 1.529(8) (**4**) and 1.520(4) (Å) (**5**),)) are within the range for C-C single bond. Two chelate rings are almost planar because the sums of interior angles of them is 538.98^{o} and 539.98^{o}.



Scheme 3 The proposed reaction mechanism of the formation of complexes **3-5.**

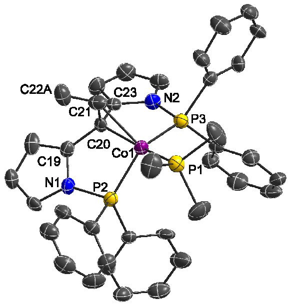


Figure 2. Molecular structure of complex **3**. The thermal ellipsoids are displayed at 30% probability level, and hydrogen atoms are omitted for clarity. Only one disordered position was presented. Selected bond lengths (Å) and angles [°]: Co1-C20 1.985(7), Co1-C21 2.193(9), Co1-P1 2.187(3), Co1-P2 2.103(3), Co1-P3 2.114(3), C20-C21 1.523(10), C21-C22A 1.522(10), C19-C20 1.475(10), C20-C23 1.496(10), C19-N1 1.365(10), C23-N2 1.368(8), N1-P2 1.738(6), N2-P3 1.736(7); C20-Co1-C21 42.4(3), C20-Co1-P1 162.7(2), C20-Co1-P2 85.9(2), C20-Co1-P3 86.7(2), C21-Co1-P1 120.8(2), C21-Co1-P2 105.6(2), C21-Co1-P3 100.9(2), P1-Co1-P2 97.87(10), P1-Co1-P3 103.12(10), P2-Co1-P3 130.76(10), C19-C20-C21 114.2(6), C23-C20-C21 116.2(5), C22A-C20-C21 128.6(13).

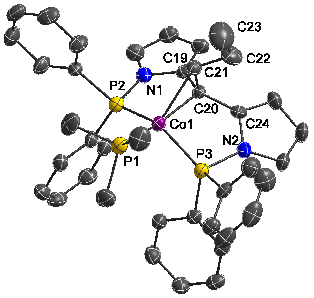


Figure 3. Molecular structure of complex **4**. The thermal ellipsoids are displayed at 30% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles [°]: Co1-C20 1.989(6), Co1-C21 2.226(6), Co1-P1 2.187(2), Co1-P2 2.111(2), Co1-P3 2.111(2), C19-C20 1.482(9), C20-C21 1.529(8), C20-C24 1.500(9), C21-C22 1.516(10), C22-C23 1.496(12), C19-N1 1.371(8), C24-N2 1.381(8), N1-P2 1.731(6), N2-P3 1.732(6); C20-Co1-C21 42.1(2), C20-Co1-P1 162.41(18), C20-Co1-P2 86.54(19), C20-Co1-P3 86.72(18), C21-Co1-P1 120.48(17), C21-Co1-P2 100.36(18), C21-Co1-P3 104.84(19), P1-Co1-P2 101.61(8), P1-Co1-P3 98.41(8), P2-Co1-P3 133.40(8), C19-C20-C21 114.1(5), C22-C21-C20 119.0(6), C24-C20-C21 116.3(5), C23-C22-C21 112.3(8).

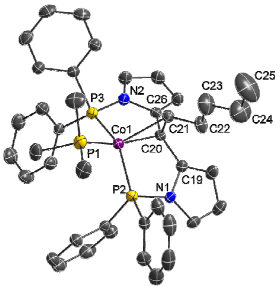


Figure 4. Molecular structure of complex **5.** The thermal ellipsoids are displayed at 30% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles [°]: Co1-C20 2.007(3), Co1-C21 2.232(3), Co1-P1 2.1821(11), Co1-P2 2.1070(10), Co1-P3 2.1177(10), C19-C20 1.487(4), C20-C21 1.520(4), C20-C26 1.481(4), C21-C22 1.520(4), C22-C23 1.503(5), C23-C24 1.522(6), C24-C25 1.447(6), C19-N1 1.390(3), C26-N2 1.383(4), N1-P2 1.735(2), N2-P3 1.741(2); C20-Co1-C21 41.61(11), C20-Co1-P1 163.02(8), C20-Co1-P2 87.08(9), C20-Co1-P3 86.64(8), C21-Co1-P1 121.54(8), C21-Co1-P2 104.48(9), C21-Co1-P3 102.07(9), P1-Co1-P2 102.16(4), P1-Co1-P3 97.41(3), P2-Co1-P3 131.42(4),

C19-C20-C21 115.64(19), C22-C21-C20 117.8(3), C26-C20-C21 115.96(19), C23-C22-C21 113.4(3), C24-C23-C22 113.4(4), C25-C24-C23 113.0(5).

In general, there are two extreme states of Dewar-Chat-Duncanson model for olefin-metal coordination: (**a**)[11] and (**b**)[12] (**Scheme 4**). The former is olefin π-coordination and the characteristics of C=C bond is maintained. This is weak coordination. The latter is that the π-bond of the double bond is cleaved to form a metallacyclopropane moiety. Which model the olefin-metal coordination adopts depends upon how strong the π-backbonding is. Normally, the more electron-rich the metal center, the stronger the π-backbond. In the cobaltacyclopropane extreme model the carbon-carbon interaction is single bond and the hybrid state of the two carbon atom changed from sp^2 to sp^3. In addition, the electron-withdrawing substituents at the alkene carbon atoms are promote the π-backbond. At the same time the metal oxidation state increases two positive charges. Usually, the actual state is in transition state between these two extreme states. It is known that complexes **3 – 5** belong to metallacyclopropane extreme state from their molecular structural parameters because low-valent cobalt center, strong electron-donating trimethylphosphine ligands and electron-withdrawing pyrrol rings enhanced the π-backbond from the cobalt center to the olefin ligand. The metal olefin interaction in complexes **3 - 5** evidences a strong back donation, approaching a metallacyclopropane structure. In olefin coordination chemistry, the examples on carbon-carbon double bond elongation to 1.52 Å by metal center are seldom reported.[13]

In the structures of these three cobalt complexes, Co1-C21 bond is obviously longer than the related Co1-C20 bond because the influence of alkyl group R’. This is different from the averaging of the olefin bond lengths after its coordination. With increase of the steric hindrance of R’ group from complex **3** to **5**, Co1-C20 and Co1-C21 bond lengths are getting longer and longer, but the related bite angles are getting smaller and smaller (42.4(3)^o (**3**)， 42.1(2)^o (**4**) and 41.61(11)^o (**5**))

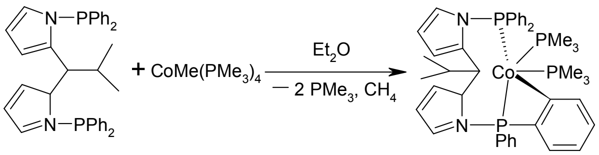
(**a**) (**b**)

Scheme 4 Two extreme states of Dewar-Chat-Duncanson model for olefin-metal coordination.

3. Reaction of CoMe(PMe$_3$)$_4$ with H6

When the substituent at the middle carbon atom is iso-propyl, the reaction of preligand **H6** with CoMe(PMe$_3$)$_4$ in diethyl ether gave rise to a C$_{sp2}$-H activation product (**6**) (eq. (2)). Complex **6** as dark-red club-shaped crystals could be obtained from n-pentane extract solution in the yield of 48%.

The structure of complex **6** was determined by X-ray single structure analysis (**Figure 5**). X-ray diffraction revealed that the ortho-(C$_{sp2}$-H) bond of one phenyl group was activated to form a four-membered chelate ring [Co1P4C31C36].



(2)

H6 **6**

The expected pincer complex with C_{sp3}-H bond activation was not produced. The distance between Co1 and the middle carbon atom (C23) of 3.69 Å is far beyond the scope of normal Co-C bond lengths. This shows that there is no chemical interaction between them. This result might be caused by the steric hindrance of the iso-propyl group. In the molecular structure of **6**, the cobalt is located at a distorted trigonal bipyramidal geometry with C36 and P3 in the axial direction. P1, P2, P4 and Co1 are almost in one plane. Co1-C36 (2.009(8) Å) is within the normal region of the Co-C bond distances.

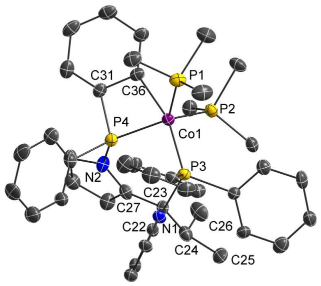


Figure 5 Molecular structure of complex **6.** The thermal ellipsoids are displayed at 30% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles [°]: Co1-C36 2.009(8), Co1-P1 2.211(3), Co1-P2 2.205(3), Co1-P3 2.160(3), Co1-P4 2.146(3), C31-C36 1.401(11), C31-P4 1.776(8), N1-P3 1.810(8), N2-P4 1.730(7); C36-Co1-P3 162.8(2), C36-Co1-P1 84.9(2), C36-Co1-P2 88.2(2), C36-Co1-P2, C36-Co1-P4 70.9(3), C31-C36-Co1, C36-C31-P4, P1-Co1-P2 113.45(11), P1-Co1-P3 98.81(9), P1-Co1-P4 122.91(11), P2-Co1-P3 105.38(9), P2-Co1-P4 116.41(9), P3-Co1-P4 93.33(8).

Conclusion

In summary, the introduction and changes of the substituents at the middle carbon atom of the PCP preligands have significant impact on the reaction results. The impact comes from the electronic properties and the space variation of the substituents in the structure of the PCP preligand. From aforementioned reactions, we have determined three different reaction paths. Reaction 1 (eq. (1)) is with mono C_{sp3}-H bond activation to afford PCP pincer cobalt complex **2**. Reaction 2 (**Scheme 3**) has double C_{sp3}-H bond activation to form complexes **3** – **5** with unusual cobaltacyclopropane moieties. Reaction 3 (eq. (2)) provides C_{sp2}-H bond activation product **6** with a four-membered and an eight-membered chelate ring.

Experimental Section

1. General procedures and materials.

All operations are conducted utilizing standard Schlenk techniques under the nitrogen atmosphere. Toluene, diethyl ether, pentane and THF were dried by distillation from Na-benzophenone. C_6D_6 for NMR testing was degassed and processed with zeolite. $CoMe(PMe_3)_4$ was prepared according to previous report.[14] All other reagent was utilized without further purification. ^1H and ^{31}P NMR spectra were recorded on the Bruker NMR Avance spectrometer at 300 MHz. IR spectra were recorded on a Bruker ALPHA FT-IR from Nujol mulls between KBr disks. Melting points were measured in capillaries sealed under N_2 and were uncorrected. Elemental analyses were carried out on an Elementar Vario ELIII.

2. Synthesis of preligands H2-H6

All of the preligands **H2-H6** were synthesized according to the method for **H1** in the literarure.[15]

***N,N′*-bis(diphenylphohsphino)-5-methyldipyrromethane (H2).**

H2 was isolated as a viscous liquid in the yield of 65%.^{1}H NMR (C_6D_6, 300 MHz): δ_H 1.83 (d, ^3J HH = 6.9 Hz, 3H, -C*H₃*), 5.79 (m, 1H, -C(Me)*H*-), 6.27 (m, 2H, py-*H*), 6.35 (t, ^3J HH = 3.0 Hz, 2H, py-*H*), 6.67 (t, ^3J HH = 1.5 Hz, 2H, py-*H*), 7.06-7.11 (m, 12H, Ar-*H*), 7.33-7.45 (m, 8H, Ar-H). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ_C 22.9 (s, -*C*H₃), 31.7 (t, ^3JPC = 17.8 Hz, -*C*(Me)H), 109.1, 111.8, 124.0, 128.6, 128.9, 129.5, 132.2, 133.1, 137.8, 138.4, 144.1. ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz): δ_P 33.0 (s).

***N,N′*-bis(diphenylphohsphino)-5-ethyldipyrromethane (H3).**

H3 was isolated as a white solid in the yield of 74%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 1.03 (t, ^3J HH = 7.2 Hz, 3H, -C*H₃*), 2.08 (quint, ^3J HH = 7.2 Hz, 2H, -C*H*₂CH₃), 5.23 (m, 2H, -C(Et)*H*-), 6.04 (br s, 2H, py-*H*), 6.19 (t, ^3J HH = 3.0 Hz, 2H, py-*H*), 6.45 (br s, 2H, py-*H*), 7.16-7.20 (m, 4H, Ar-*H*), 7.27-7.36 (m, 10H, Ar-*H*), 7.42 (m, 6H, Ar-*H*). ^{13}C{^{1}H} NMR ($CDCl_3$,75 MHz): δ_C 11.8 (s, *C*H₃), 29.3 (s, -*C*H₂CH₃), 37.0 (t, ^3JPC = 16.8 Hz, -*C*(Et)H-), 107.5, 109.9, 122.5, 127.1, 127.4, 128.1, 130.8-131.5, 136.2, 136.6, 141.4. ^{31}P{^{1}H} NMR ($CDCl_3$, 121 MHz): δ_P 32.7 (s).

N,N′-bis(diphenylphohsphino)-5-propyldipyrromethane (H4).

H4 was isolated as a white solid in the yield of 81%. ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ$_H$ 0.96 (t, ^{3}*J* HH = 7.5 Hz, 3H, -C*H*$_3$), 1.65 (sext, ^{3}*J* HH = 7.5 Hz, 2H, -C*H*$_2$CH$_3$), 2.27 (q, ^{3}*J* HH = 7.5 Hz, 2H, -C*H*$_2$CH$_2$CH$_3$), 5.78 (m, 1H, -C(n-Pr)*H*-), 6.37 (m, 2H, py-*H*), 6.40 (t, ^{3}*J* HH = 3.0 Hz, 2H, py-*H*), 6.67 (br s, 2H, py-H), 7.04-7.12 (m, 12H, Ar-*H*), 7.33-7.44 (m, 8H, Ar-*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75 MHz): δ$_C$ 12.8 (s, -*C*H$_3$), 20.2 (s, -*C*H$_2$CH$_3$), 35.1 (t, ^{3}*J*PC = 16.6 Hz, -*C*(*n*-Pr)H-), 38.6 (s, -*C*H$_2$CH$_2$CH$_3$), 108.0, 110.5, 122.4, 127.1, 127.4, 128.0, 130.9, 131.5, 136.5, 136.8, 141.5. ^{31}P{^{1}H} NMR (C$_6$D$_6$, 121 MHz): δ$_P$ 33.0 (s).

N,N′-bis(diphenylphohsphino)-5-pentyldipyrromethane (H5).

H5 was isolated as a viscous liquid in theyield of 65%.^{1}H NMR (C$_6$D$_6$, 300 MHz): δ$_H$ 0.84 (t, ^{3}*J* HH = 7.2 Hz, 3H, -C*H*$_3$), 1.24 (sext, ^{3}*J* HH = 7.2 Hz, 2H, -C*H*$_2$CH$_3$), 1,33 (m, 2H, -C*H*$_2$CH$_2$CH$_3$), 1.63 (quint, ^{3}*J* HH = 7.5 Hz, 2H, -C*H*$_2$(CH$_2$)$_2$CH$_3$), 2.30 (q, ^{3}*J* HH = 7.5 Hz, -C*H*$_2$(CH$_2$)$_3$CH$_3$), 5.77 (m, 1H, -C(n-pentyl)*H*-), 6.41 (m, 4H, py-*H*), 6.68 (m, 2H, py-*H*), 7.05-7.13 (m, 12H, Ar-H), 7.34-7.45 (m, 8H, Ar-*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75 MHz): δ$_C$ 12.9 (s, -*C*H$_3$), 21.4 (s, -*C*H$_2$CH$_3$), 26.9 (s, -*C*H$_2$(CH$_2$)$_2$CH$_3$), 35.5 (t, ^{3}*J*PC = 17.0 Hz, -*C*(*n*-pentyl)H-), 36.6 (s, -*C*H$_2$(CH$_2$)$_3$CH$_3$), 108.0, 110.5, 122.5, 127.1, 127.4, 128.0, 130.9, 131.5, 136.5, 136.8, 141.6. ^{31}P{^{1}H} NMR (C$_6$D$_6$, 121 MHz): δ$_P$ 32.9 (s).

N,N′-bis(diphenylphohsphino)-5-isopropyldipyrromethane (H6).

H6 was isolated as a viscous liquid in the yield of 71%. ^{1}H NMR (C_6D_6, 300 MHz): δ_H 1.18 (d, ^3J HH = 6.6 Hz, 6H, -CH(C*H*$_3$)$_2$), 2.64 (m, 1H, -C*H*(CH$_3$)$_2$), 5.67 (m, 1H, -C(*i*-Pr)*H*-), 6.44 (t, ^3J HH = 3.2 Hz, 2H, py-*H*), 6.53 (m, 2H, py-*H*), 6.66 (m, 2H, py-*H*), 6.97-7.04 (m, 6H, Ar-H), 7.10-7.12 (m, 6H, Ar-*H*), 7.21-7.26 (m, 4H, Ar-*H*), 7.42-7.48 (m, 4H, Ar-H). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ_C 20.6 (s, -CH(*C*H$_3$)$_2$), 34.7 (s, -*C*H(CH$_3$)$_2$), 42.1 (t, ^3JPC = 16.2 Hz, -*C*(*i*-Pr)H-), 108.4, 110.7, 122.3, 127.1, 127.3, 127.9, 131.2, 136.8, 141.1. ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz): δ_P 32.4 (s).

3. Synthesis of PCP pincer cobalt complexes 2-6

Complex **2**: **H2** (750 mg, 1.42 mmol) in 40 mL of diethyl ether was combined with a solution of CoMe(PMe$_3$)$_4$ (550 mg, 1.45 mmol) in 20 mL of diethyl ether with stirring at -78 °C. The reaction mixture was allowed to warm slowly to room temperature and stirred for 16 h. During this time the color of the solution gradually changed to dark red and a lot of red powder precipitated from the reaction solution. After filtration the red powder was recrystallized with diethyl ether (30 mL x 2). Complex **2** as dark red crystals could be obtained from both the mother and the extraction solution at 0 °C in 64% yield (670 mg). m. p. 46 – 47 °C. Anal. Calcd. for $C_{40}H_{47}CoN_2P_4$ (738.61 g/mol): C, 65.05; H, 6.41. Found: 64.87; H, 6.59. IR (Nujol, KBr): 3053 (Ar-H), 1578 (ArC=C), 932 (PMe$_3$) cm^{-1}. NMR: decomposed in C_6D_6.

Complex **3**: **H3** (830 mg, 1.53 mmol) in 40 mL of diethyl ether was combined with a solution of CoMe(PMe$_3$)$_4$ (580 mg, 1.53 mmol) in 20 mL of diethyl ether with stirring at -78 °C. The reaction mixture was allowed to warm slowly to room temperature and stirred for 24 h. During this time the color of the solution gradually changed to dark red and a lot of red powder precipitated from the reaction solution. After filtration the red powder was recrystallized with diethyl ether (40 mL x 3). Complex **3** as dark red crystals could be obtained from both the mother and the extraction solution at 0 °C in 59% yield (610 mg). m. p. 96 – 98 ^{o}C. Anal. Calcd. for $C_{38}H_{40}CoN_2P_3$ (676.56 g/mol): C, 67.46; H, 5.96. Found: 67.29; H, 6.09. IR (Nujol, KBr): 3053 (Ar-H), 1578, 1523 (ArC=C), 950 (PMe_3) cm^{-1}. NMR: paramagnetic in solution.

Complex **4**: **H4** (780 mg, 1.40 mmol) in 40 mL of diethyl ether was combined with a solution of $CoMe(PMe_3)_4$ (530 mg, 1.40 mmol) in 20 mL of diethyl ether with stirring at -78 °C. The reaction mixture was allowed to warm slowly to room temperature and stirred for 24 h. During this time the color of the solution gradually changed to dark red and a lot of red powder precipitated from the reaction solution. After filtration the red powder was recrystallized with diethyl ether (40 mL x 3). Complex **4** as dark red lumpish crystals could be obtained from both the mother and the extraction solution at 0 °C in 59% yield (610 mg). m. p. 202 – 204 ^{o}C. Anal. Calcd. for $C_{39}H_{41}CoN_2P_3$ (689.58 g/mol): C, 67.93; H, 5.99. Found: 68.17; H, 6.07. IR (Nujol, KBr): 3058 (Ar-H), 1584 (ArC=C), 933 (PMe_3) cm^{-1}. NMR: paramagnetic in solution.

Complex **5**: **H5** (780 mg, 1.40 mmol) in 40 mL of diethyl ether was combined with a solution of $CoMe(PMe_3)_4$ (530 mg, 1.40 mmol) in 20 mL of diethyl ether with stirring at -78 °C. The reaction mixture was allowed to warm slowly to room temperature and stirred for 24 h. During this time the color of the solution gradually changed to dark red and a lot of red powder precipitated from the reaction solution. After filtration the red powder was recrystallized with diethyl ether (40 mL x 2). Complex **5** as dark red lumpish crystals could be obtained from both the mother and the extraction solution at 0 °C in 70% yield (630 mg). m. p. 167 - 169 °C. Anal. Calcd. for $C_{41}H_{45}CoN_2P_3$ (717.63 g/mol): C, 68.62; H, 6.32. Found: 68.80; H, 6.37. IR (Nujol, KBr): 3056 (Ar-H), 1576, 1526 (ArC=C), 944 (PMe_3) cm^{-1}. NMR: paramagnetic in solution.

Complex **6**: **H6** (800 mg, 1.44 mmol) in 40 mL of diethyl ether was combined with a solution of $CoMe(PMe_3)_4$ (550 mg, 1.40 mmol) in 20 mL of diethyl ether with stirring at -78 °C. The reaction mixture was allowed to warm slowly to room temperature and stirred for 24 h. During this time the color of the solution gradually changed to dark red and a lot of red powder precipitated from the reaction solution. After filtration the red powder was recrystallized with *n*-pentane (30 mL x 2) and diethyl ether (30 mL). Complex **6** as dark red club-shaped crystals could be obtained from both the mother and the extraction solution at 0 °C in 48% yield (530 mg). m. p. 191 - 193 °C. Anal. Calcd. for $C_{42}H_{51}CoN_2P_4$ (766.66 g/mol): C, 65.80; H, 6.70. Found: 66.10; H, 6.87. IR (Nujol, KBr): 3051 (Ar-H), 1577, 1526 (ArC=C), 946 (PMe_3) cm^{-1}. NMR: paramagnetic in solution.

4. X-ray single crystal diffraction

The single crystals of all the complexes for X-ray single crystal diffraction were obtained from their *n*-pentane or diethyl ether solutions at low temperature. Diffraction data were collected on a Bruker SMART Apex II CCD diffractometer equipped with graphite monochromated Mo K_α radiation (λ = 0.71073 Å). During collection of the intensity data, no significant decay was observed. The structures were resolved by direct or Patterson methods with the SHELXS-97 program and were refined on F^2 with SHELXTL.[16] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and were refined using a riding model. A summary of crystal data, data collection parameters, and structure refinement details is given in **Table 1**. CCDC 1028669- 1028673 for complexes **2 - 6** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Detailed Information for X-ray Diffraction Studies of All the Structures

complex	**2**	**3**	**4**	**5**	**6**
formula	$C_{40}H_{47}CoN_2P_4$	$C_{38}H_{40}CoN_2P_3$	$C_{39}H_{41}CoN_2P_3$	$C_{41}H_{45}CoN_2P_3$	$C_{42}H_{51}CoN_2P_4$
Fw, g/mol	738.61	676.56	689.58	717.63	766.66
temp, K	273(2)	273(2)	293(2)	293(2)	273(2)
system	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic
space group	P2(1)/c	P121/n1	Pcab	P121/c1	P2(1)/n
a, Å	20.3187(13)	10.890(7)	16.666(2)	10.526(3)	12.548(12)
b, Å	10.3342(6)	16.894(12)	19.745(3)	19.385(5)	10.357(11)
c, Å	18.2160(11)	18.714(14)	21.037(3)	21.235(5)	32.36(3)
α, deg	90.00	90.00	90.00	90.00	90.00
β, deg	100.9230(10)	101.593(14)	90.00	119.716(10)	97.749(19)
γ, deg	90.00	90.00	90.00	90.00	90.00
V, Å^3	3755.7(4)	3374(4)	6922.4(15)	3763.1(17)	4167(7)
Z	4	4	8	4	4
d_{calc}, Mg/m^3	1.306	1.499	1.325	1.267	1.222
abs coeff, mm^{-1}	0.658	0.681	0.665	0.614	0.596
F(000)	1552	768	2896	1508	920

θ range for data collection, deg		1.02 - 27.44	2.27 - 27.40	2.06 – 25.00	1.52 – 25.00	1.83 - 27.82
no. of reflns		21389	15711	32296	18597	24400
no. of indep obs reflns		8336	5783	6096	6609	9602
	R(int)	0.0524	0.2030	0.1789	0.0663	0.1261
I > 2σ(I)	R1	0.0465	0.0756	0.0778	0.0434	0.1003
	wR2	0.1258	0.1314	0.1813	0.1019	0.2801
	GoF on F^2	0.767	0.905	1.037	0.967	0.955

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