

Synthesis and Characterization of Diorganocobalt Chlorides by Aliphatic Vinylic C–Cl Bond Activation

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Abstract. Three diorganocobalt chlorides $[\text{CoClMe}(\text{PMe}_3)_2-\{\text{(C}_5\text{H}_6)-\text{CH=O}\}]$ (**4**), $[\text{CoClMe}(\text{PMe}_3)_2-\{\text{(C}_6\text{H}_8)-\text{CH=O}\}]$ (**5**), and $[\text{CoClMe}(\text{PMe}_3)_2-\{\text{(C}_6\text{H}_7\text{Memeta})-\text{CH=O}\}]$ (**6**) were synthesized through cyclometalation reactions with aldehyde as an anchoring group involving aliphatic vinylic C–Cl bond activation. Complexes **4–6** were characterized by IR and NMR spectroscopy. The crystal and molecular

structures of complexes **4** and **5** were determined by single-crystal X-ray diffraction. Complexes **4–6** are stable in solution at room temperature, but they decompose at above 30 °C affording C,C-coupling products with the formation of $[\text{Co}(\text{PMe}_3)_3\text{Cl}]$. The results of this work will be important for people to deepen the understanding of the C–Cl bond activation mechanism.

1 Introduction

Organic chloride as one kind of important starting materials can be widely used in many cross-coupling reactions, such as the Heck reaction, Suzuki coupling, Kumada coupling, Sonogashira coupling, and Stille coupling. C–Cl bond activation is the key step in these reactions. Therefore, the study on the C–Cl bond activation and functionalization mediated by transition metal complexes is always the research topic in organic synthesis and organometallic chemistry. Density functional theory calculations have been employed to model the double C–Cl bond activation of CH_2Cl_2 at $[\text{CoCl}(\text{PR}_3)_3]$ to give $[\text{CoCl}_3(\text{CH}_2\text{PR}_3)(\text{PR}_3)_2]$.^[11] The C–Cl bond activation of CH_2Cl_2 with cobalt was studied by Pierre Braunstein and co-workers.^[2] A practical coupling between aryl chlorides and arylmagnesium halides was developed with $\text{Co}(\text{acac})$ as pre-catalyst in 2013.^[3]

The research interest was focused on the C–Cl bond activation mediated by electron-rich cobalt, nickel, and iron com-

plexes supported by trimethylphosphine ligands. A series of organoiron, organonickel, and organocobalt complexes were synthesized via C–Cl bond activation in the past years.^[4–13] Recently, the activation of vinylic C–Cl bonds in chloroalkenes by nickel complexes was reported. Seven organonickel(II) complexes were synthesized and characterized by oxidative addition of the vinylic C–Cl bonds.^[14] As the continuation of the research on C–Cl bond activation, in this paper the results on C–Cl bond activation with cobalt complex are disclosed. Three novel organocobalt chlorides were synthesized through cyclometalation reactions with aldehyde as an anchoring group involving aliphatic vinylic C–Cl bond activation. These complexes are stable in solution at room temperature and decompose at above 30 °C affording C,C-coupling products with the formation of $[\text{Co}(\text{PMe}_3)_3\text{Cl}]$. The results of this work will be important for people to deepen the understanding of the C–Cl bond activation mechanism.

2 Results and Discussion

$[\text{CoMe}(\text{PMe}_3)_4]$ reacted with β-chlorinated vinylic aldehydes **1–3** to give rise to three cobalt(III) chlorides **4–6** by oxidative addition of the C–Cl bond with aldehyde as an anchoring group (Scheme 1). Crystallization in *n*-pentane at –20 °C afforded complexes **4–6** as red crystals in yields of 74%, 76%, and 72%, respectively. Complexes **4–6** in solid state are quite stable in air and they decompose at above 135–146 °C.

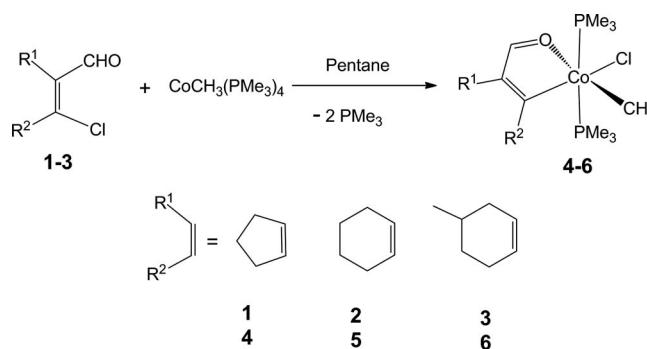
The selected IR and NMR spectroscopic data of complexes **4–6** are collected in Table 1. Compared with the (C=O) band (1667–1679 cm^{–1}) and the [C(=O)–H] band (3321–3352 cm^{–1}) of compounds **1–3**, the related characteristic bands of complexes **4–6** have a large red shift. These substantial red shifts upon coordination of the C=O and O-donor atom acted as an-

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Table 1. Selected spectroscopic data of complexes **4–6**.

	IR /cm ⁻¹ v[C(O)-H]	v(C=O)	v(C=C)	ρ (PMe ₃)	¹ H NMR /ppm PCH ₃	CoCH ₃	C(=O)H	³¹ P NMR /ppm PMe ₃
4	3220	1618	1540	941	0.99(t)	0.38(t)	8.61(s)	5.9(s, br)
5	3123	1594	1562	944	0.94(s)	0.22(s,br)	8.46(s)	5.2(s, br)
6	3239	1608	1561	931	1.04(m)	0.34(t)	8.58(s)	19.5(s, br)



Scheme 1. Synthesis of complexes **4**, **5**, and **6**.

ching moiety indicate a weakening of these bonds. In the ^{13}C NMR spectrum of complex **5**, it was found that the PMe_3 group gives rise to a virtual triplet signal between $\delta = 10.9$ and 11.3 ppm with $|^1\text{J}(\text{P},\text{C}) + ^3\text{J}(\text{P},\text{C})| = 27.0$ Hz. All the spectroscopic data of the three complexes are in agreement with an octahedral configuration around the central cobalt(III) atom consisting of a P-Co-P axis and equatorial coordination of C, Cl, and O donor atoms. The crystal and molecular structures of complexes **4** and **5** were confirmed by single-crystal X-ray diffraction analysis.

The molecular structures of complexes **4** and **5** are shown in Figure 1 and Figure 2. The selected bond lengths and angles are listed in the figure captions. The molecular structures of the complexes **4** and **5** confirmed a hexa-coordinate octahedral arrangement in the crystal.

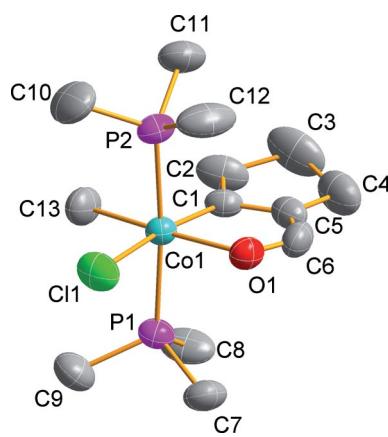


Figure 1. Molecular structure of **4**, selected distances /Å and angles /°: O1–C6 1.236(4), C₆–C1 1.825(3), C₆–C13 1.975(3), C₆–O1 2.039(2), C₆–P1 2.1937(9), C₆–P2 2.1947(9), C₆–C11 2.312(1), C1–C5 1.352(5); C13–C₆–O1 175.3(1), P1–C₆–P2 174.84(4), C1–C₆–C11 169.8(1), C5–C1–C₆ 114.6(2), C1–C₆–O1 82.0(1), C6–O1–C₆ 109.5(2), C1–C5–C6 114.6(3), O1–C6–C5 119.2(4).

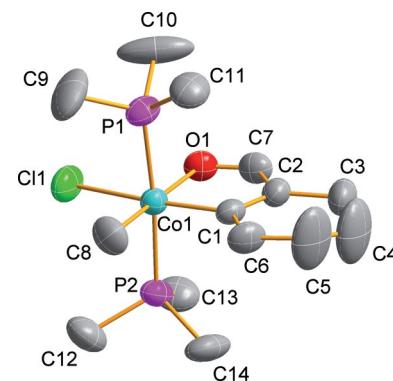


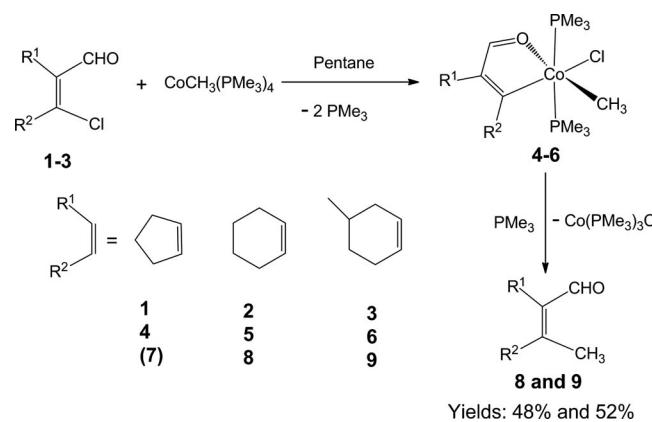
Figure 2. Molecular structure of **5**, selected distances /Å and angles /°: Co1–O1 2.020(2), Co1–C11 2.3470(9), Co1–C1 1.879(3), Co1–C8 1.996(3), Co1–P1 2.2250(9), Co1–P2 2.2197(9), O1–C7 1.249(4), C1–C2 1.375(4); O1–Co1–C11 87.18(7), C1–Co1–C8 95.0(1), C8–Co1–C11 94.8(1), C1–Co1–O1 83.1(1), P2–Co1–P1 175.06(4).

Complex **4** shows an orthorhombic crystal structure. In the distorted octahedral coordination, two *trans*-phosphine ligands are in the axial direction, while the two coordination atoms (C13, C11) and the chelate ring with [C1, O1] are in the equatorial plane. This is consistent with the observation in the ^{31}P NMR spectra. A five-membered metallacycle is formed through cyclometalation with the coordination of the O atom of the aldehyde group and the *ortho*-chelated C atom. The sum of internal bond angles (539.88°) of this chelate ring indicates ideal planarity. Typically, the Cl atom is *trans*-oriented to the vinylic-C atom, which is well understood in terms of mutual *trans* influence.^[7–9] The bite angle of the chelating ligand [$\text{C1}-\text{Co1}-\text{O1} = 81.98(13)^\circ$] is close to that in a related complex [$\text{C1}-\text{Co}-\text{O1} = 80.27(10)^\circ$.^[7] The two axial trimethylphosphine ligands are positioned [$\text{P1}-\text{Co1}-\text{P2} = 174.84(4)^\circ$] toward the space between Co–Me and Co–Cl bonds for steric reasons. However, both of the Co–C(13) [$1.975(3)$ Å] and Co–Cl(1) [$2.312(1)$ Å] bond lengths are shorter than the related bond lengths [$\text{Co1}-\text{C8} = 2.044(2)$, $\text{Co1}-\text{Cl1} = 2.3679(8)$ Å] in the *ortho*-metalated cobalt(III) complex with the imine nitrogen atom as anchoring group.^[8] This can be explained by the stronger coordination ability of N-donor atom than that of O-donor atom.

In complex **5**, the cobalt atom attains an octahedral coordination with one chloro ligand and a Me group [$C_8\text{--Co1--Cl1} = 94.77(12)^\circ$], opposite to the planar [$C\text{:}O$]-chelate ring ligand with a bite angle of [$C1\text{--Co1--O1} = 83.12(10)^\circ$]. The two axial trimethylphosphine ligands are also slightly displaced [$P2\text{--Co1--P1} = 175.06(4)^\circ$] toward the space between the Co-Me and Co-Cl group for steric reasons. The sum (360.02°) of the four angles [$O1\text{--Co1--Cl1} = 87.18(7)$, $C1\text{--Co1--C8} =$

94.95(14), C8–Co1–Cl1 = 94.77(12) and C1–Co1–O1 = 83.12(10°] around the central cobalt atom in the equatorial plane proves that the five atoms [Co1 O1 C1 C8 Cl1] are co-planar. The five-membered chelate ring and the cyclohexene ring are almost in one plane. The C=O bond length [O1–C7 = 1.249(4) Å], is longer than that of the uncoordinated C=O (1.20 Å). This indicates a significant bond weakening upon coordination of the O-donor atom. The formal C=C double bond [C1–C2 (1.375(4) Å] of the cyclohexene ring in complex **5** is longer than that of the related C1–C5 bond [1.352(5) Å] in complex **4**. This suggests that the cyclopentene ring in complex **4** possesses stronger transannular strain than that of cyclohexene in complex **5**.

Complexes **4–6** are stable in solutions at room temperature. No spontaneous elimination of chloromethane was observed at room temperature. However, when the reactions were heated at 30 °C for 2 h, violet crystals, [CoCl(PMe₃)₃], were found in these three reactions. The C,C-coupling products, compounds **8** and **9**, were isolated and characterized by ¹H NMR spectroscopy. The isolation of compound **7** failed (Scheme 2). With imine as anchoring group the similar C,C-coupling reaction was also observed at the central cobalt atom in 2008.^[8] It is suggested that high temperatures could accelerate the reductive elimination reaction. It seems that initial coordination of the O-donor should be the key step in the formation of complexes **4–6**. With aldehyde-O as an anchoring group the oxidative addition reactions proceed smoothly. The cyclometalated products **4–6** are quite air-stable at room temperature due to the chelate effect.



Scheme 2. The formation of methylation C,C-coupling products.

3 Conclusions

Three *ortho*-metallated diorgano cobalt(III) chlorides **4–6** were obtained via the reactions of [CoMe(PMe₃)₄] with β -chlorinated vinylic aldehydes **1–3**. These cyclometalated complexes **4–6** formed via activation of the aliphatic vinylic C–Cl bond have octahedral coordination arrangements. Complexes **4–6** were characterized by IR and NMR spectroscopy. Potential routes of formation of complexes **4–6** were discussed. In solutions, complexes **4–6** showed a trend to undergo subsequent reductive elimination accompanied by C,C-coupling to

give methylated cycloolefine aldehyde derivatives. The structures of complexes **4** and **5** were determined by single-crystal X-ray diffraction.

4 Experimental Section

4.1 General Procedures and Materials

All reactions were carried out in an atmosphere of nitrogen using standard Schlenk and vacuum-line techniques. These standard vacuum techniques were used in manipulations of volatile and air-sensitive materials. All the solvents were distilled from Na/benzophenone in a nitrogen atmosphere. [CoMe(PMe₃)₄]^[15] was prepared according to the literature method. *ortho*-Chlorinated cycloalkenyl aldehydes (**1–3**) were synthesized by published procedures.^[16] All other chemicals were purchased from Aldrich or Acros and used as received without further purification. Infrared spectra, as obtained from Nujol mulls between KBr disks, were performed within the 4000–400 cm⁻¹ region with a Bruker ALPHA FT-IR Spectrometer. ¹H, ¹³C, and ³¹P NMR spectra (300, 75, and 121 MHz, respectively) were recorded with a Bruker Avance 300 spectrometer with C₆D₆ as the solvent. ¹³C and ³¹P NMR resonances were obtained with broadband proton decoupling. Melting points were measured in capillaries sealed in a nitrogen atmosphere and are uncorrected. X-ray crystallography was performed with a Bruker Smart 1000 diffractometer. Elemental analyses were carried out with an Elementar Vario EL III.

4.2 Synthesis of 4

[CoMe(PMe₃)₄] (0.60 g, 1.59 mmol) in pentane (30 mL) was combined with 2-chlorocyclopent-1-enecarbaldehyde (**1**) (0.20 g, 1.53 mmol) in pentane (20 mL) at -80 °C. The reaction mixture was allowed to warm to ambient temperature and stirred for 16 h. During this period, the reaction mixture turned brown-red in color and a little brown solid precipitated. After filtering in vacuo, the resulting solid was extracted with Et₂O (30 mL). Crystallization from pentane at -20 °C afforded red crystals suitable for single-crystal X-ray diffraction analysis. Yield: 0.40 g, 74%. C₁₃H₂₈ClCoOP₂, (356.67 g·mol⁻¹): calcd. C 43.78, H 7.91%; found: C: 44.18, H 8.11%. Dec > 135 °C. **IR** (Nujol mull, 4000–400 cm⁻¹): $\tilde{\nu}$ = 3220 v[Co–O–H], 1618 v(C=O), 1540 v(C=C), 941 ρ (PMe₃). **1H NMR** (300 MHz, C₆D₆, 297 K, ppm): δ = 0.38 [t, ³J(P,H) = 9.3 Hz, 3 H, CH₃], 0.99 [t', ¹J(P,H) + ⁴J(P,H) = 8.1 Hz, 18 H, PCH₃], 1.79–1.89 (m, 2 H, cyclopent-H), 2.44 [t, ²J(H,H) = 7.5, ³J(H,H) = 7.2 Hz, 4 H, Cyclopent-H], 8.61 [s, 1 H, C(O)-H]. **³¹P NMR** (121 MHz, C₆D₆, 297 K, ppm): δ = 5.9 (s, PCH₃).

4.3 Synthesis of 5

A sample of [CoMe(PMe₃)₄] (0.65 g, 1.72 mmol) in pentane (30 mL) was combined with 2-chlorocyclohex-1-enecarbaldehyde (**2**) (0.25 g, 1.72 mmol) in pentane (20 mL) at -80 °C. The reaction mixture was allowed to warm to ambient temperature and stirred for 16 h. During this period, the reaction mixture turned brown-red in color and a little brown-red solid precipitated. After filtering in vacuo, the resulting solid was extracted with Et₂O (30 mL). Crystallization from pentane at -20 °C afforded brown-red crystals suitable for single-crystal X-ray diffraction analysis. Yield: 0.48 g, 76%. C₁₄H₃₀ClCoOP₂, (370.70 g·mol⁻¹): calcd. C: 45.36, H 8.16%; found: C: 45.74, H 8.31%. Dec > 138 °C. **IR** (Nujol mull, 4000–400 cm⁻¹): $\tilde{\nu}$ = 3123 v[C(O)-H], 1594 v(C=O), 1562 v(C=C), 944 ρ (PMe₃). **1H NMR** (300 MHz, C₆D₆, 297 K, ppm): δ = 0.22 (br. s, 3 H, CH₃), 0.94 (br. s,

18 H, PCH_3), 1.37 (br. s, 4 H, Cyclohex-H), 2.12 (br. s, 2 H, cyclohex-H), 2.30 (br. s, 2 H, cyclohex-H), 8.46 [s, 1 H, C(O)-H]. ^{13}C NMR (75 MHz, $C_6\text{D}_6$, 297 K, ppm): δ = 11.1 [t', $^1J(\text{P},\text{C}) + ^3J(\text{P},\text{C})$] = 27.0 Hz, PCH_3], 23.2 (s, C_{cyclohex}), 24.4 (s, C_{cyclohex}), 24.8 (s, C_{cyclohex}), 38.3 (s, C_{cyclohex}), 100.0 (s, $C=C$), 139.4 (s, $C=C$), 192.8 (s, $C=O$). ^{31}P NMR (121 MHz, $C_6\text{D}_6$, 297 K, ppm): δ = 5.2 (s, PCH_3).

4.4 Synthesis of 6

A sample of $[\text{CoMe}(\text{PMe}_3)_4]$ (0.45 g, 1.19 mmol) in pentane (30 mL) was combined with 2-chloro-5-methylcyclohex-1-enecarbaldehyde (**3**) (0.19 g, 1.19 mmol) in pentane (20 mL) at -80 °C. The reaction mixture was allowed to warm to ambient temperature and stirred for 16 h. During this period, the reaction mixture turned dark brown-red in color and a little brown-red solid precipitated. After filtering in vacuo, the resulting solid was extracted with Et_2O (30 mL). Crystallization from pentane at -20 °C afforded red crystals. Yield: 0.33 g, 72 %. $C_{15}\text{H}_{32}\text{ClCoOP}_2$ (384.71 g·mol⁻¹): calcd. C: 46.83, H 8.38%; found: C: 46.51, H 8.41%. Dec > 146 °C. IR (Nujol mull, 4000–400 cm⁻¹): ν = 3239 v[C(O)-H], 1608 v(C=O), 1561 v(C=C), 931 p(PMe₃). ^1H NMR (300 MHz, $C_6\text{D}_6$, 297 K, ppm): δ = 0.34 [t, $^3J(\text{P},\text{H})$ = 9.0 Hz, 3 H, $CoCH_3$], 0.98 [d, $^2J(\text{H},\text{H})$ = 9.0 Hz, 3 H, Cyclohex- CH_3], 1.04 (m, 18 H, PCH_3), 1.57 (m, 1 H, Cyclohex-H), 1.78 (m, 3 H, Cyclohex-H), 2.29 [d, $^2J(\text{H},\text{H})$ = 12.0 Hz, 2 H, Cyclohex-H], 2.63 [d, $^2J(\text{H},\text{H})$ = 15.0 Hz, 1 H, Cyclohex-H], 8.58 [s, 1 H, C(O)-H]. ^{31}P NMR (121 MHz, $C_6\text{D}_6$, 297 K, ppm): δ = 19.5 (s, PCH_3).

4.5 Isolation of Compounds 8 and 9

Compound 8: A sample of $[\text{CoMe}(\text{PMe}_3)_4]$ (0.65 g, 1.72 mmol) in pentane (30 mL) was combined with 2-chlorocyclohex-1-enecarbaldehyde (**2**) (0.25 g, 1.72 mmol) in pentane (20 mL) at -80 °C. The reaction mixture turned to brown red immediately. After the temperature was raised to 30 °C the reaction solution was stirred for 2 h and the solution became to brown yellow. During this process, a lot of bluish-violet crystals of $\text{CoCl}(\text{PMe}_3)_4$ precipitated. After filtration the filtrate was treated with diluted HCl and extracted with diethyl ether. The organic layer was dried with MgSO_4 . After remove of the solvents compound **8** was isolated as pale yellow oil. Yield: 0.10 g, 48%. ^1H NMR (300 MHz, $C_6\text{D}_6$, 297 K, ppm): δ = 2.10 (s, 3 H, vinylic- CH_3), 1.57 (m, 4 H, cyclohex-H), 2.16 (m, 4 H, cyclohex-H), 10.11 [s, 1 H, C(O)-H].

Compound 9: Compound **9** was isolated with the same method as compound **8**. Yield: 52%. ^1H NMR (300 MHz, $C_6\text{D}_6$, 297 K, ppm): δ = 1.00 [d, $^2J(\text{H},\text{H})$ = 9.0 Hz, 3 H, cyclohex- CH_3], 1.20 (m, 1 H, cyclohex-H), 1.59 (m, 4 H, cyclohex-H), 2.14 (s, 3 H, vinylic- CH_3), 2.26 (m, 2 H, Cyclohex-H), 10.14 [s, 1 H, C(O)-H].

4.6 Crystallographic Data

Complex 4: $C_{13}\text{H}_{28}\text{ClCoOP}_2$, M_r = 356.67, orthorhombic, space group $Pbca$, a = 15.739(3) Å, b = 17.609(4) Å, c = 24.675(5) Å, V = 6839(2) Å³, T = 293 K, Z = 16, D_c = 1.386 g·cm⁻³, μ = 1.335 mm⁻¹.

A total of 24,491 reflections were collected, 7805 unique ($R_{\text{int}} = 0.0577$), $R_1 = 0.0431$ [for 7805 reflections with $I > 2 \sigma(I)$], $wR_2 = 0.1004$ (all data). The structure was solved by direct methods and refined with full-matrix least-squares on all F² (SHELXL-97) with non-hydrogen atoms anisotropic.

Complex 5: $C_{14}\text{H}_{30}\text{ClCoOP}_2$, M_r = 370.70, orthorhombic, space group $Pbca$, a = 15.936(3) Å, b = 18.579(3) Å, c = 25.264(4) Å, V = 7480(2) Å³, T = 273 K, Z = 16, D_c = 1.317 g·cm⁻³, μ = 1.224 mm⁻¹. A total of 46,102 reflections were collected, 9433 unique ($R_{\text{int}} = 0.0338$), $R_1 = 0.0442$ [for 9433 reflections with $I > 2 \sigma(I)$], $wR_2 = 0.1196$ (all data). The structure was solved by direct methods and refined with full-matrix least-squares on all F² (SHELXL-97) with non-hydrogen atoms anisotropic.

4) 和 CCDC-918121 (**5**)（Fax: +44-1223-336-033；E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk）获得。

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