

cis-Dichlorido(3-chloro-2-methyliminophenyl- κ^2C^1,N)-*trans*-bis(trimethylphosphine- κP)cobalt(III)

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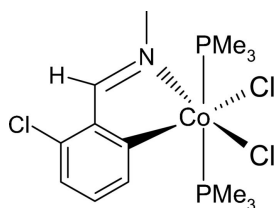
Received 22 November 2007; accepted 23 November 2007

Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(C-C) = 0.002$ Å; R factor = 0.025; wR factor = 0.066; data-to-parameter ratio = 25.8.

In the title compound, $[CoCl_2(C_8H_7ClN)(C_3H_9P)_2]$, the Co atom displays an octahedral coordination, with two *cis* Cl atoms perpendicular to two *trans* trimethylphosphine ligands as well as *trans* to the bidentate 3-chloro-2-methyliminophenyl ligand.

Related literature

For reactions of chlorinated phenyl Schiff bases with $[CoCl(PMe_3)_3]$, see: Chen *et al.* (2007).



Experimental

Crystal data

$[CoCl_2(C_8H_7ClN)(C_3H_9P)_2]$
 $M_r = 434.57$
 Orthorhombic, $P2_12_12_1$
 $a = 8.5530$ (17) Å
 $b = 10.543$ (2) Å
 $c = 21.769$ (4) Å

$V = 1963.0$ (7) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 1.44$ mm⁻¹
 $T = 298$ (2) K
 $0.30 \times 0.30 \times 0.28$ mm

Data collection

Bruker SMART diffractometer
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
 $T_{min} = 0.672$, $T_{max} = 0.689$

16045 measured reflections
 4910 independent reflections
 4868 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.038$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.066$
 $S = 1.07$
 4910 reflections
 190 parameters
 H-atom parameters constrained

$\Delta\rho_{max} = 0.47$ e Å⁻³
 $\Delta\rho_{min} = -0.43$ e Å⁻³
 Absolute structure: Flack (1983),
 with 2082 Friedel pairs
 Flack parameter: -0.001 (9)

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2001); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LN2014).

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supplementary materials

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***cis*-Dichlorido(3-chloro-2-methyliminophenyl- κ^2C^1,N)-*trans*-bis(trimethylphosphine- κP)cobalt(III)**

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Comment

Reaction of chlorinated phenyl Schiff bases with [CoCl(PMe₃)₃] has been reported recently (Chen *et al.*, 2007). *N*-(2,6-Dichlorobenzylidene)methanamine reacts with [CoCl(PMe₃)₃] by a cyclometallation reaction involving C—Cl bond activation at cobalt(I) centers and with imine as pre-chelate ligands to afford the hexacoordinate title cobalt(III) complex as a red solid that is soluble in pentane or diethyl ether.

A view of the molecular structure is given in Fig. 1. The cobalt atom displays an octahedral coordination with two *cis*-chlorine atoms (C11 and C12) perpendicular to two *trans* trimethylphosphine ligands as well as *trans* to the bidentate 3-chloro-2-methyliminophenyl ligand. The P1—Co—P2 angle of 172.71 (2)° implies a slight distortion from an ideal octahedron. The sum of the internal angles (540°) indicates planarity of the chelate ring. The C?N bond length C7—N1 [1.288 (2) Å] is relatively long, indicating significant bond weakening upon coordination of the nitrogen donor atom. The longer Co1—Cl5 bond [2.3471 (6) Å], when compared with Co1—Cl1 [2.2742 (5) Å], reflects the stronger *trans*-influence of the carbon atom (C1) than that of the nitrogen atom (N1).

Experimental

Standard vacuum techniques were used in the manipulations of volatile and air-sensitive materials. Chlorotris(trimethylphosphane)cobalt(I) (1.11 g, 3.44 mmol) was dissolved in 40 ml of tetrahydrofuran (THF). To this solution was added *N*-(2,6-dichlorobenzylidene)methanamine (0.63 g, 3.43 mmol) in 20 ml of THF at 193 K. The mixture was allowed to warm to 293 K and stirred for 18 h to form a red-brown turbid mixture. The filtrate was evaporated *in vacuo*, and the residue was extracted with pentane (60 ml) and diethyl ether (60 ml), respectively. Crystallization in diethyl ether at 246 K afforded the title complex as red crystals in 57% yield.

Refinement

The H atoms were introduced at calculated positions as riding atoms, with C—H bond lengths of 0.93 (CH) or 0.96 Å (CH₃) and with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$, respectively.

Figures

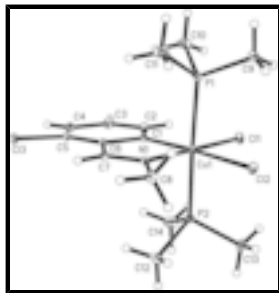


Fig. 1. The molecular structure of the title complex, shown with 30% probability displacement ellipsoids.



Fig. 2. The formation of the title compound.

cis-Dichlorido(3-chloro-2-methyliminophenyl- κ^2C^1, N)-*trans*- bis(trimethylphosphine- κP)cobalt(III)

Crystal data

[CoCl₂(C₈H₇ClN)(C₃H₉P)₂]

$M_r = 434.57$

Orthorhombic, $P2_12_12_1$

$a = 8.5530$ (17) Å

$b = 10.543$ (2) Å

$c = 21.769$ (4) Å

$V = 1963.0$ (7) Å³

$Z = 4$

$F_{000} = 896$

$D_x = 1.470$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 3063 reflections

$\theta = 3.1$ – 20.4°

$\mu = 1.44$ mm⁻¹

$T = 298$ (2) K

Block, red

$0.30 \times 0.30 \times 0.28$ mm

Data collection

Bruker P4
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 298$ (2) K

ω scans

Absorption correction: multi-scan
(SADABS; Sheldrick, 1996)

$T_{\min} = 0.672$, $T_{\max} = 0.689$

16045 measured reflections

4910 independent reflections

4868 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.038$

$\theta_{\max} = 28.5^\circ$

$\theta_{\min} = 1.9^\circ$

$h = -11 \rightarrow 9$

$k = -14 \rightarrow 14$

$l = -29 \rightarrow 26$

2699 standard reflections

every 5 reflections

intensity decay: 0.02%

Refinement

Refinement on F^2

Hydrogen site location: inferred from neighbouring sites

| | |
|--|--|
| Least-squares matrix: full | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.025$ | $w = 1/[\sigma^2(F_o^2) + (0.0416P)^2 + 0.7929P]$ |
| $wR(F^2) = 0.066$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.07$ | $(\Delta/\sigma)_{\max} = 0.001$ |
| 4910 reflections | $\Delta\rho_{\max} = 0.47 \text{ e } \text{\AA}^{-3}$ |
| 190 parameters | $\Delta\rho_{\min} = -0.43 \text{ e } \text{\AA}^{-3}$ |
| Primary atom site location: structure-invariant direct methods | Extinction correction: none |
| Secondary atom site location: difference Fourier map | Absolute structure: Flack (1983), 2082 Friedel pairs |
| | Flack parameter: -0.001 (9) |

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|---------------|----------------------------------|
| N1 | 0.03793 (18) | 0.45205 (14) | 0.18750 (6) | 0.0120 (3) |
| Co1 | 0.21282 (3) | 0.51827 (2) | 0.141359 (10) | 0.00967 (6) |
| Cl1 | 0.41880 (5) | 0.58705 (4) | 0.08431 (2) | 0.01627 (9) |
| Cl2 | 0.23616 (5) | 0.69589 (4) | 0.205711 (19) | 0.01659 (9) |
| Cl3 | -0.14169 (5) | 0.09058 (4) | 0.112040 (19) | 0.01852 (9) |
| P1 | 0.06006 (6) | 0.62472 (4) | 0.07525 (2) | 0.01346 (9) |
| P2 | 0.38816 (5) | 0.41085 (4) | 0.19781 (2) | 0.01276 (9) |
| C1 | 0.1815 (2) | 0.36764 (16) | 0.09372 (8) | 0.0121 (3) |
| C2 | 0.2656 (2) | 0.32345 (17) | 0.04297 (8) | 0.0159 (3) |
| H2A | 0.3464 | 0.3721 | 0.0268 | 0.019* |
| C3 | 0.2291 (2) | 0.20742 (17) | 0.01664 (8) | 0.0170 (3) |
| H3A | 0.2881 | 0.1787 | -0.0164 | 0.020* |
| C4 | 0.1063 (2) | 0.13253 (16) | 0.03839 (8) | 0.0161 (3) |
| H4A | 0.0832 | 0.0549 | 0.0202 | 0.019* |
| C5 | 0.0203 (2) | 0.17679 (16) | 0.08749 (8) | 0.0136 (3) |
| C6 | 0.0574 (2) | 0.29240 (15) | 0.11584 (8) | 0.0122 (3) |
| C7 | -0.0181 (2) | 0.34538 (16) | 0.16892 (8) | 0.0129 (3) |
| H7A | -0.1015 | 0.3055 | 0.1884 | 0.015* |
| C8 | -0.0316 (2) | 0.50993 (18) | 0.24222 (8) | 0.0174 (3) |
| H8A | -0.1168 | 0.4584 | 0.2564 | 0.026* |
| H8B | -0.0696 | 0.5931 | 0.2322 | 0.026* |
| H8C | 0.0460 | 0.5163 | 0.2739 | 0.026* |

supplementary materials

| | | | | |
|------|-------------|--------------|--------------|------------|
| C9 | 0.0955 (3) | 0.79342 (18) | 0.07302 (10) | 0.0258 (4) |
| H9A | 0.0261 | 0.8322 | 0.0439 | 0.039* |
| H9B | 0.2018 | 0.8089 | 0.0610 | 0.039* |
| H9C | 0.0774 | 0.8290 | 0.1130 | 0.039* |
| C10 | 0.0760 (3) | 0.5799 (2) | -0.00478 (8) | 0.0227 (4) |
| H10A | 0.0061 | 0.6308 | -0.0289 | 0.034* |
| H10B | 0.0489 | 0.4920 | -0.0093 | 0.034* |
| H10C | 0.1814 | 0.5930 | -0.0185 | 0.034* |
| C11 | -0.1493 (2) | 0.6155 (2) | 0.08898 (10) | 0.0258 (4) |
| H11A | -0.2035 | 0.6640 | 0.0583 | 0.039* |
| H11B | -0.1726 | 0.6492 | 0.1289 | 0.039* |
| H11C | -0.1824 | 0.5286 | 0.0869 | 0.039* |
| C12 | 0.3113 (3) | 0.3308 (2) | 0.26513 (9) | 0.0243 (4) |
| H12A | 0.3947 | 0.2879 | 0.2861 | 0.036* |
| H12B | 0.2337 | 0.2702 | 0.2528 | 0.036* |
| H12C | 0.2648 | 0.3920 | 0.2922 | 0.036* |
| C13 | 0.5434 (3) | 0.5051 (2) | 0.23006 (12) | 0.0293 (5) |
| H13A | 0.6122 | 0.4516 | 0.2533 | 0.044* |
| H13B | 0.4998 | 0.5688 | 0.2565 | 0.044* |
| H13C | 0.6009 | 0.5452 | 0.1976 | 0.044* |
| C14 | 0.4966 (3) | 0.2879 (2) | 0.15854 (10) | 0.0260 (4) |
| H14A | 0.5677 | 0.2484 | 0.1868 | 0.039* |
| H14B | 0.5543 | 0.3246 | 0.1252 | 0.039* |
| H14C | 0.4252 | 0.2256 | 0.1428 | 0.039* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|---------------|---------------|---------------|
| N1 | 0.0100 (6) | 0.0149 (6) | 0.0111 (6) | 0.0009 (5) | 0.0003 (5) | 0.0007 (5) |
| Co1 | 0.00910 (11) | 0.00863 (10) | 0.01127 (10) | -0.00028 (8) | 0.00087 (8) | -0.00067 (7) |
| Cl1 | 0.01429 (18) | 0.01469 (17) | 0.01983 (19) | -0.00287 (15) | 0.00548 (15) | 0.00055 (15) |
| Cl2 | 0.0190 (2) | 0.01338 (18) | 0.01734 (19) | -0.00129 (15) | -0.00002 (15) | -0.00514 (14) |
| Cl3 | 0.0213 (2) | 0.01699 (19) | 0.01728 (18) | -0.00885 (16) | -0.00267 (16) | 0.00191 (15) |
| P1 | 0.0146 (2) | 0.01225 (19) | 0.0135 (2) | 0.00196 (15) | -0.00023 (16) | 0.00098 (14) |
| P2 | 0.0109 (2) | 0.01100 (18) | 0.0164 (2) | -0.00005 (15) | -0.00138 (15) | 0.00015 (16) |
| C1 | 0.0133 (8) | 0.0113 (7) | 0.0116 (7) | 0.0004 (6) | -0.0009 (6) | 0.0013 (5) |
| C2 | 0.0153 (8) | 0.0150 (7) | 0.0173 (8) | -0.0011 (6) | 0.0024 (6) | -0.0009 (6) |
| C3 | 0.0200 (9) | 0.0144 (7) | 0.0166 (8) | 0.0021 (7) | 0.0016 (7) | -0.0038 (6) |
| C4 | 0.0204 (9) | 0.0113 (7) | 0.0166 (8) | 0.0007 (6) | -0.0037 (7) | -0.0025 (6) |
| C5 | 0.0144 (8) | 0.0116 (7) | 0.0147 (7) | -0.0035 (6) | -0.0026 (6) | 0.0020 (6) |
| C6 | 0.0129 (8) | 0.0123 (7) | 0.0113 (7) | 0.0006 (6) | -0.0019 (6) | 0.0015 (6) |
| C7 | 0.0115 (7) | 0.0157 (7) | 0.0116 (7) | -0.0008 (6) | -0.0010 (6) | 0.0013 (6) |
| C8 | 0.0164 (8) | 0.0204 (8) | 0.0153 (8) | -0.0002 (7) | 0.0047 (6) | -0.0039 (6) |
| C9 | 0.0352 (12) | 0.0126 (8) | 0.0296 (10) | 0.0023 (8) | -0.0070 (9) | 0.0045 (7) |
| C10 | 0.0277 (10) | 0.0263 (9) | 0.0141 (8) | 0.0070 (8) | -0.0023 (7) | -0.0008 (7) |
| C11 | 0.0154 (9) | 0.0350 (11) | 0.0271 (10) | 0.0054 (8) | -0.0009 (8) | 0.0060 (8) |
| C12 | 0.0231 (10) | 0.0274 (9) | 0.0224 (9) | 0.0053 (8) | 0.0013 (7) | 0.0113 (7) |
| C13 | 0.0226 (10) | 0.0209 (9) | 0.0444 (12) | -0.0048 (8) | -0.0165 (9) | 0.0012 (8) |

C14 0.0260 (10) 0.0282 (10) 0.0239 (9) 0.0162 (8) -0.0008 (8) -0.0016 (7)

Geometric parameters (Å, °)

| | | | |
|-------------|-------------|---------------|-------------|
| N1—C7 | 1.288 (2) | C6—C7 | 1.437 (2) |
| N1—C8 | 1.465 (2) | C7—H7A | 0.9300 |
| N1—Co1 | 1.9323 (15) | C8—H8A | 0.9600 |
| Co1—C1 | 1.9155 (17) | C8—H8B | 0.9600 |
| Co1—P1 | 2.2444 (6) | C8—H8C | 0.9600 |
| Co1—P2 | 2.2455 (5) | C9—H9A | 0.9600 |
| Co1—Cl1 | 2.2742 (5) | C9—H9B | 0.9600 |
| Co1—Cl2 | 2.3471 (6) | C9—H9C | 0.9600 |
| Cl3—C5 | 1.7411 (18) | C10—H10A | 0.9600 |
| P1—C9 | 1.805 (2) | C10—H10B | 0.9600 |
| P1—C10 | 1.8105 (19) | C10—H10C | 0.9600 |
| P1—C11 | 1.818 (2) | C11—H11A | 0.9600 |
| P2—C13 | 1.801 (2) | C11—H11B | 0.9600 |
| P2—C14 | 1.808 (2) | C11—H11C | 0.9600 |
| P2—C12 | 1.814 (2) | C12—H12A | 0.9600 |
| C1—C2 | 1.398 (2) | C12—H12B | 0.9600 |
| C1—C6 | 1.410 (2) | C12—H12C | 0.9600 |
| C2—C3 | 1.386 (2) | C13—H13A | 0.9600 |
| C2—H2A | 0.9300 | C13—H13B | 0.9600 |
| C3—C4 | 1.397 (3) | C13—H13C | 0.9600 |
| C3—H3A | 0.9300 | C14—H14A | 0.9600 |
| C4—C5 | 1.379 (3) | C14—H14B | 0.9600 |
| C4—H4A | 0.9300 | C14—H14C | 0.9600 |
| C5—C6 | 1.403 (2) | | |
| C7—N1—C8 | 117.90 (15) | C1—C6—C7 | 113.23 (15) |
| C7—N1—Co1 | 116.15 (12) | N1—C7—C6 | 115.12 (16) |
| C8—N1—Co1 | 125.91 (12) | N1—C7—H7A | 122.4 |
| C1—Co1—N1 | 82.74 (7) | C6—C7—H7A | 122.4 |
| C1—Co1—P1 | 89.20 (5) | N1—C8—H8A | 109.5 |
| N1—Co1—P1 | 93.63 (5) | N1—C8—H8B | 109.5 |
| C1—Co1—P2 | 88.36 (5) | H8A—C8—H8B | 109.5 |
| N1—Co1—P2 | 92.88 (5) | N1—C8—H8C | 109.5 |
| P1—Co1—P2 | 172.71 (2) | H8A—C8—H8C | 109.5 |
| C1—Co1—Cl1 | 94.41 (5) | H8B—C8—H8C | 109.5 |
| N1—Co1—Cl1 | 177.13 (5) | P1—C9—H9A | 109.5 |
| P1—Co1—Cl1 | 86.64 (2) | P1—C9—H9B | 109.5 |
| P2—Co1—Cl1 | 86.69 (2) | H9A—C9—H9B | 109.5 |
| C1—Co1—Cl2 | 175.19 (5) | P1—C9—H9C | 109.5 |
| N1—Co1—Cl2 | 92.52 (5) | H9A—C9—H9C | 109.5 |
| P1—Co1—Cl2 | 91.91 (2) | H9B—C9—H9C | 109.5 |
| P2—Co1—Cl2 | 91.09 (2) | P1—C10—H10A | 109.5 |
| Cl1—Co1—Cl2 | 90.33 (2) | P1—C10—H10B | 109.5 |
| C9—P1—C10 | 102.64 (10) | H10A—C10—H10B | 109.5 |
| C9—P1—C11 | 102.83 (11) | P1—C10—H10C | 109.5 |
| C10—P1—C11 | 102.61 (10) | H10A—C10—H10C | 109.5 |

supplementary materials

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|------------|-------------|---------------|-------|
| C9—P1—Co1 | 114.36 (7) | H10B—C10—H10C | 109.5 |
| C10—P1—Co1 | 116.27 (7) | P1—C11—H11A | 109.5 |
| C11—P1—Co1 | 116.19 (7) | P1—C11—H11B | 109.5 |
| C13—P2—C14 | 101.64 (11) | H11A—C11—H11B | 109.5 |
| C13—P2—C12 | 102.05 (11) | P1—C11—H11C | 109.5 |
| C14—P2—C12 | 103.56 (11) | H11A—C11—H11C | 109.5 |
| C13—P2—Co1 | 115.30 (7) | H11B—C11—H11C | 109.5 |
| C14—P2—Co1 | 116.43 (7) | P2—C12—H12A | 109.5 |
| C12—P2—Co1 | 115.76 (7) | P2—C12—H12B | 109.5 |
| C2—C1—C6 | 118.00 (15) | H12A—C12—H12B | 109.5 |
| C2—C1—Co1 | 129.22 (13) | P2—C12—H12C | 109.5 |
| C6—C1—Co1 | 112.76 (12) | H12A—C12—H12C | 109.5 |
| C3—C2—C1 | 120.33 (17) | H12B—C12—H12C | 109.5 |
| C3—C2—H2A | 119.8 | P2—C13—H13A | 109.5 |
| C1—C2—H2A | 119.8 | P2—C13—H13B | 109.5 |
| C2—C3—C4 | 121.86 (17) | H13A—C13—H13B | 109.5 |
| C2—C3—H3A | 119.1 | P2—C13—H13C | 109.5 |
| C4—C3—H3A | 119.1 | H13A—C13—H13C | 109.5 |
| C5—C4—C3 | 118.20 (16) | H13B—C13—H13C | 109.5 |
| C5—C4—H4A | 120.9 | P2—C14—H14A | 109.5 |
| C3—C4—H4A | 120.9 | P2—C14—H14B | 109.5 |
| C4—C5—C6 | 120.97 (16) | H14A—C14—H14B | 109.5 |
| C4—C5—C13 | 119.07 (13) | P2—C14—H14C | 109.5 |
| C6—C5—C13 | 119.90 (14) | H14A—C14—H14C | 109.5 |
| C5—C6—C1 | 120.59 (16) | H14B—C14—H14C | 109.5 |
| C5—C6—C7 | 126.16 (16) | | |

Fig. 1

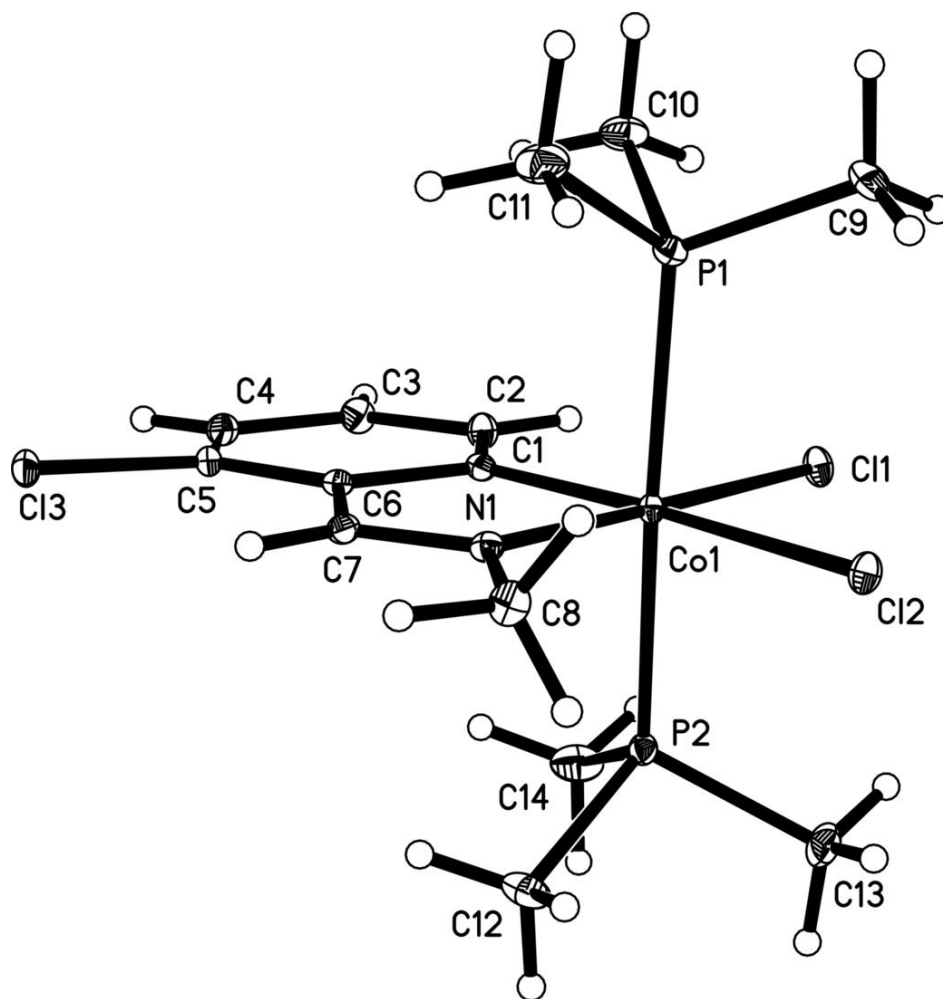


Fig. 2

