Supplementary Material (ESI) for Dalton Transactions


**Supporting Information**

# Regioselective Cyclometalation Reactions of Cobalt in Arylketones: C-H versus C-F Activation

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**General Remarks.** All manipulations were done under an atmosphere of purified argon (BTS - Catalyst) by using standard vacuum techniques.[1-2] Solvents were dried according to known procedures and freshly distilled prior to use. Deutorated tetrahydrofuran were freeze-pump-thaw degassed , dried from sodium/potassium alloy and distilled. Purchased reagents were used without any further purification. Literature methods were applied for the preparation of $[CoCH_3(PMe_3)_4]$[3] and $PMe_3$.[4]

Air-sensitive samples were provided in capillaries sealed under vacuum and were analyzed by H. Kolbe Microanalytical Laboratory, Mülheim/Ruhr. C, H, N analyses identification of contents of air stable substances were performed in the microanalysis laboratory of Clemens-Schöpf-Institut for Organic Chemistry and Biochemistry in TU-Darmstadt using Perkin-Elmer CHN 240 A and CHN 240 B devices. The melting and decomposition points were measured on a Büchi 510 Melting point apparatus and are uncorrected. Air-sensitives substances were sealed in capillaries under 1 bar of Argon.

IR spectra were obtained from as Nujol mulls between KBr plates using a Bruker FRA 106 spectrophotometer and recorded in the range 4000 - 400 $cm^{-1}$. $^{1}H$ and $^{13}C$ NMR spectra (500 MHz and 125 MHz, respectively) were recorded on a Bruker ARX-300 or Bruker DRX 500 spectrometers at the Organic Chemistry Institute of TU Darmstadt , $^{31}P$ NMR spectra (202 MHz) were recorded on a Bruker AM-200 instrument. $^{1}H$ and $^{13}$ C NMR chemical shifts were referenced to external TMS and $^{31}P$ chemical shifts were referenced to external $H_3PO_4$ 85%. $^{13}C$ and $^{31}P$ resonances were obtained with broad-band proton decoupling. Magnetic suscepitbility data were obtained by the Faraday method using a Cahn D 200 torsion balance (Bruker) at 1.5 Tesla. Crystallographic data were collected on STOE–IPDS (Eduard-Zintl Institute of TU-Darmstadt) and Bruker AXS SMART APEX CCD (University of Paderborn) diffractometer. Structures were solved by Direct and Patterson methods using SHELXTL program library.[5]

**Synthesis of [2-(Benzoyl-κO)phenyl-κC]tris(trimethylphosphine)cobalt(I) – (1)**

920 mg (2.43 mmol) of $CoCH_3(PMe_3)_4$ in THF were combined with 443 mg (2.43 mmol) of benzophenone at –70 °C. The mixture was warmed to 20 °C and kept stirring for 16 h. The volatiles were then removed in vacuo. The residue was extracted with pentane and combined solutions were cooled to afford brown crystals of **1** at 4 °C. Yield 924 mg (81%); m. p. 111-113 °C. IR (Nujol): $\tilde{\nu}$ = 3057 $cm^{-1}$ (ν H–C=C); 1582 $cm^{-1}$ m (ν C=C); 1484 $cm^{-1}$ m (ν C=O), 1422 $cm^{-1}$ w ($\delta_{as}$ $PCH_3$ ), 1273 $cm^{-1}$ m ($\delta_s$ $PCH_3$ ), 935 $cm^{-1}$ vs ($\rho_1$ $PCH_3$), 842 $cm^{-1}$ m ($\rho_2$ $PCH_3$), 753 vw (γ C–$H_{arom}$), 701 $cm^{-1}$ m ($\nu_{as}$ $PC_3$ ), 661 $cm^{-1}$ vs ($\nu_s$ $PC_3$ ). $^1$H NMR (500 MHz, THF-$d_8$, 300 K, ppm): δ = 1.30 (d, $^2J_{P,H}$ = 6.5 Hz, 27H, $PCH_3$); 6.61 (dt, $^4J_{H,H}$ = 0.8 Hz, $^3J_{H,H}$ = 7.8 Hz, 1H, Ar–H); 7.12 (t, $^3J_{H,H}$ = 7.8 Hz, 2H, Ar–H); 7.33 (tt, $^4J_{H,H}$ = 1.2 Hz, $^3J_{H,H}$ = 8.0 Hz, 1H, Ar–H); 7.46 (dt, $^4J_{H,H}$ = 0.9 Hz, $^3J_{H,H}$ = 7.4 Hz, 1H, Ar–H); 8.11 (d, $^3J_{H,H}$ = 8.1 Hz, 2H, Ar–H); 8.19 ($d_{br}$, $^3J_{H,H}$ = 8.1 Hz, 1H, Ar–H); 8.22 (d, $^3J_{H,H}$ = 8.2 Hz, 1H, Ar–H). $^{13}$C{$^1$H} NMR (125 MHz, THF-$d_8$, 300 K, ppm): δ = 21.3 (m, $PCH_3$); 118.3 (q, $^4J_{P,C}$ = 4.6 Hz, CH); 121.9 (s, CH); 122.6 (s, CH); 123.7 (d, $^5J_{P,C}$= 2.4 Hz, CH); 124.2 (dd, $^4J_{P,C}$ = 3.4 Hz, $^4J_{P,C}$ = 2.2 Hz, CH); 130.4 (s, CH); 145.2 (q, $^4J_{P,C}$ = 4.6 Hz, C); 146.2 (s, C); 147.8 (q, $^5J_{P,C}$ = 2.2 Hz, CH); 170.8 (q, $^3J_{P,C}$ = 11.8 Hz; C=O), 173.9 (m, Co–C). $^{31}$P{$^1$H} NMR (202 MHz, THF-$d_8$, 300 K, ppm): δ = 5.1 ($s_{br}$ , $PCH_3$). Anal. Calcd. for $C_{22}H_{36}CoOP_3$: C 56.42; H 7.75; P 19.84. Found: C 56.95; H 7.53; P 20.68 %.

**Synthesis of [2-(Benzoyl-κO)benzyl-κC]tris(trimethylphosphine)cobalt(I) - (2)**

1.15 g (3.04 mmol) of $CoCH_3(PMe_3)_4$ in THF were combined with 0.60 g (3.04 mmol) of benzylphenylketone at –70 °C. The mixture was warmed to 20 °C and kept stirring for 16 h. The volatiles were then removed in vacuo. The residue was extracted with pentane and combined solutions were cooled to afford brown crystals of **2** at -27 °C. Yield 970 mg (66 %); m. p. 107-109 °C. IR (Nujol): $\tilde{\nu}$ = 3023 $cm^{-1}$ m (ν H–C=C), 1547 $cm^{-1}$ s (ν C=C), 1483 $cm^{-1}$ m (ν C=O), 1421 s ($\delta_{as}$ $PCH_3$ ), 1278 $cm^{-1}$ m ($\delta_s$ $PCH_3$ ), 937 $cm^{-1}$ vs ($\rho_1$ $PCH_3$); 874 $cm^{-1}$ m ($\rho_2$ $PCH_3$), 748 $cm^{-1}$ (γ C–$H_{arom}$), 698 $cm^{-1}$ vs ($\nu_{as}$ $PC_3$ ), 657 $cm^{-1}$ vs ($\nu_s$ $PC_3$ ). $^1$H NMR (500 MHz, THF-$d_8$, 300 K, ppm): δ = 1.05 ($s_{br}$, 27H, $PCH_3$); 4.20 (s, 2H, $CH_2$); 7.25–7.55 (m, 6H, Ar–H); 8.03 (m, 1H, Ar–H); 8.95 (m,

1H, Ar–H); 9.19 (m, 1H, Ar–H). $^{13}C\{^{1}H\}$ NMR (125 MHz, THF-$d_8$, 300 K, ppm): δ = 20.9 (m, $PCH_3$); 46.1 (s, $CH_2$); 127.5 (s, CH); 129.4 (s, CH); 129.6 (d, $^{3}J_{P,C}$ = 8.2 Hz, CH); 130.6 (s, CH); 133.8 (s, CH); 136.5 (s, CH); 138.2 (s, C); 151.2 (m, C); 158.4 (s, CH); 166.1 (s, Co–C=O); 183.7 (m, Co–C). $^{31}P\{^{1}H\}$ NMR (202 MHz, THF-$d_8$, 300 K, ppm): δ = 1.5 ($s_{br}$, 3P, $PCH_3$). Anal. Calcd. for $C_{23}H_{38}CoOP_3$: C 57.27; H 7.94; P 19.26. Found: C 56.49; H 7.39; P 19.53 %.

**Synthesis of [2-(3,4,5,6-Tetrafluoro-benzoyl-κO)phenyl-κC]tris-(trimethylphosphine) cobalt(I) - (3)**

1.20 g (3.17 mmol) of $CoCH_3(PMe_3)_4$ in THF were combined with 0.86 g (3.17 mmol) of 2,3,4,5,6-pentafluorobenzophenone at -70 °C. The mixture was warmed to 20 °C and kept stirring for 16 h. The volatiles were then removed in vacuo. The residue was extracted with pentane and combined solutions were cooled to afford brown crystals of **3** at -27 °C. Yield: 1.08 g (63 %); m. p. 152 -154 °C. IR (Nujol): $\tilde{\nu}$ = 3077 $cm^{-1}$ vw (ν H–C=C); 1617 $cm^{-1}$ m (ν C=C); 1590 $cm^{-1}$ m (ν C=C); 1490 $cm^{-1}$ m (ν C=O), 1420 $cm^{-1}$ w ($\delta_{as}$ $PCH_3$ ); 1339 $cm^{-1}$ s (ν F–C=C), 1277 $cm^{-1}$ s ($\delta_s$ $PCH_3$ ), 939 $cm^{-1}$ vs ($\rho_1$ $PCH_3$); 830 $cm^{-1}$ m ($\rho_2$ $PCH_3$), 760 m (γ C–$H_{arom}$), 701 $cm^{-1}$ m ($\nu_{as}$ $PC_3$ ), 665 $cm^{-1}$ m ($\nu_s$ $PC_3$ ). $^{1}H$ NMR (500 MHz, THF-$d_8$, 300 K, ppm): δ = 1.32 (d, $^{2}J_{P,H}$ = 6.1 Hz, 27H, $PCH_3$); 7.09 (t, $^{3}J_{H,H}$ = 7.2 Hz, 2H, Ar–H); 7.48 (t, $^{3}J_{H,H}$ = 7.0 Hz, 1H, Ar–H); 7.81 (t, $^{3}J_{H,H}$ = 6.5 Hz, 2H, Ar–H). $^{13}C\{^{1}H\}$ NMR (125 MHz, THF-$d_8$, 300 K, ppm): δ = 20.5 (d, $^{1}J_{P,C}$ = 20.5 Hz, $PCH_3$); 124.0 (s, CH); 124.3 (s, CH); 128.5 (m, CF); 128.8 (m, CF); 129.1 (s, CH); 129.4 (m, CF); 134.5 (m, CF); 141.5 (m, C); 147.4 (s, C); 167.9 (s, C=O); 168.7 (m, Co–C). $^{31}P\{^{1}H\}$ NMR (202 MHz, THF-$d_8$, 300 K, ppm): δ = 3.6 ($s_{br}$ , $PCH_3$). Anal. Calcd. for $C_{22}H_{32}CoF_4OP_3$: C 48.90; H 5.97; P 17.20. Found: C 48.58; H 5.70; P 16.88 %.

**Synthesis of (2-Fluoro-benzophenone-$\eta^2$-C,O)tris(trimethylphosphine)cobalt(0) - (4)**

1.05 g (2.79 mmol) of $CoCH_3(PMe_3)_4$ in THF were combined with 0.56 g (2.79 mmol) of 2-fluorobenzophenone at -70 °C. The mixture was warmed to 20 °C and kept stirring for 16 h. The

volatiles were then removed in vacuo. The residue was extracted with pentane and combined solutions were cooled to afford brown crystals of **4** at -27 $^{o}$C. Yield: 1.05 g (77 %); m. p. 98 -102 $^{o}$C. IR (Nujol): $\tilde{\nu}$ = 3000 cm$^{-1}$ vw (ν H–C=C); 1878 cm$^{-1}$ s (ν C=O); 1604 cm$^{-1}$ m (ν C=C); 1587 cm$^{-1}$ m (ν C=C), 1423 cm$^{-1}$ w ($\delta_{as}$ $PCH_3$ ), 1274 cm$^{-1}$ s ($\delta_s$ $PCH_3$ ), 933 cm$^{-1}$ vs ($\rho_1$ $PCH_3$), 841cm$^{-1}$ m ($\rho_2$ $PCH_3$), 765 m (γ C–$H_{arom}$), 695cm$^{-1}$ m ($\nu_{as}$ $PC_3$ ), 656 cm$^{-1}$ m ($\nu_s$ $PC_3$ ). Anal. Calcd. for $C_{22}H_{36}CoFOP_3$: C 54.22; H 7.45; P 19.07. Found: C 54.19; H 7.43; P 18.55 %.

**References:**

(1) Schulze, M. *Angew. Chem.* **1958**, *70*, 697.

(2) Strohmeier, W. *Chem. Ber*. **1955**, *88*, 1218.

(3) Klein, H.-F.; Karsch, H. H. *Chem. Ber.* **1975**, *108*, 944.

(4) Wolfsberger, W.; Schmidbaur, H. *Syn. React. Inorg. Metal-Org. Chem.* **1974**, *4*, 149.

(5) Sheldrick, G. M.; Krüger, C.; Goddard, R. *SHELXS-97* and *SHELXL-97*, Universität Göttingen, **1997**.

## Crystallographic Data

**Table 1.** Crystal data and structure refinement for **1**

| | |
|---|---|
| Identification code | k1096 |
| Empirical formula | C22 H36 Co O P3 |

| | | |
|---|---|---|
| Formula weight | 468.35 | |
| Temperature | 298(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | Pna2(1) | |
| Unit cell dimensions | a = 16.4913(9) Å | α= 90°. |
| | b = 9.5041(5) Å | β= 90°. |
| | c = 15.8471(9) Å | γ = 90°. |
| Volume | 2483.8(2) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.252 $Mg/m^3$ | |
| Absorption coefficient | 0.893 $mm^{-1}$ | |
| F(000) | 992 | |
| Crystal size | 0.50 x 0.45 x 0.40 $mm^3$ | |
| Theta range for data collection | 2.47 to 28.30°. | |
| Index ranges | -21<=h<=21, -12<=k<=12, -19<=l<=21 | |
| Reflections collected | 23133 | |
| Independent reflections | 5960 [R(int) = 0.0234] | |
| Completeness to theta = 28.30° | 99.8 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.983 and 0.699 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 5960 / 1 / 254 | |
| Goodness-of-fit on $F^2$ | 1.051 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0295, wR2 = 0.0705 | |
| R indices (all data) | R1 = 0.0339, wR2 = 0.0727 | |
| Absolute structure parameter | 0.005(9) | |
| Extinction coefficient | 0.0011(3) | |
| Largest diff. peak and hole | 0.256 and -0.266 e.$Å^{-3}$ | |

**Table 2.** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **1**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Co(1) | 2849(1) | 2035(1) | 2493(1) | 35(1) |
| P(1) | 1810(1) | 1023(1) | 3086(1) | 49(1) |
| P(2) | 2264(1) | 4111(1) | 2216(1) | 44(1) |
| P(3) | 3010(1) | 1283(1) | 1201(1) | 46(1) |
| O(1) | 3423(1) | 3165(1) | 3287(1) | 39(1) |
| C(1) | 3556(1) | 581(2) | 2927(1) | 44(1) |
| C(2) | 3662(2) | -840(2) | 2708(2) | 59(1) |
| C(3) | 4258(2) | -1679(2) | 3066(2) | 68(1) |
| C(4) | 4777(2) | -1125(2) | 3667(2) | 65(1) |
| C(5) | 4681(1) | 222(2) | 3927(2) | 56(1) |
| C(6) | 4065(1) | 1088(2) | 3591(1) | 43(1) |
| C(7) | 3921(1) | 2532(2) | 3795(1) | 39(1) |
| C(8) | 4264(1) | 3355(2) | 4485(1) | 43(1) |
| C(9) | 4551(2) | 2751(3) | 5239(2) | 58(1) |
| C(10) | 4896(2) | 3586(3) | 5861(2) | 74(1) |
| C(11) | 4964(2) | 5003(3) | 5761(2) | 76(1) |
| C(12) | 4658(2) | 5626(3) | 5048(2) | 66(1) |
| C(13) | 4310(1) | 4814(2) | 4420(1) | 49(1) |
| C(14) | 1818(2) | 1313(4) | 4227(2) | 89(1) |
| C(15) | 1673(2) | -880(3) | 3052(2) | 84(1) |
| C(16) | 773(2) | 1559(3) | 2814(2) | 75(1) |
| C(17) | 1382(2) | 4418(4) | 1535(2) | 90(1) |
| C(18) | 2983(2) | 5412(3) | 1813(2) | 73(1) |
| C(19) | 1939(2) | 5006(3) | 3178(2) | 69(1) |
| C(20) | 4060(2) | 882(4) | 903(2) | 92(1) |
| C(21) | 2493(2) | -319(3) | 843(2) | 72(1) |
| C(22) | 2740(3) | 2414(4) | 307(2) | 97(1) |

**Table 3.** Bond lengths [Å] and angles [°] for **1.**

| | |
|---|---|
| Co(1)-O(1) | 1.9051(12) |
| Co(1)-C(1) | 1.9339(18) |
| Co(1)-P(1) | 2.1786(6) |
| Co(1)-P(3) | 2.1852(6) |
| Co(1)-P(2) | 2.2401(5) |
| P(1)-C(15) | 1.823(2) |
| P(1)-C(14) | 1.830(3) |
| P(1)-C(16) | 1.835(3) |
| P(2)-C(19) | 1.826(3) |
| P(2)-C(18) | 1.828(3) |
| P(2)-C(17) | 1.834(3) |
| P(3)-C(22) | 1.834(3) |
| P(3)-C(20) | 1.835(3) |
| P(3)-C(21) | 1.835(2) |
| O(1)-C(7) | 1.297(2) |
| C(1)-C(2) | 1.405(3) |
| C(1)-C(6) | 1.430(3) |
| C(2)-C(3) | 1.386(3) |
| C(3)-C(4) | 1.385(4) |
| C(4)-C(5) | 1.355(3) |
| C(5)-C(6) | 1.411(3) |
| C(6)-C(7) | 1.430(3) |
| C(7)-C(8) | 1.460(3) |
| C(8)-C(13) | 1.393(3) |
| C(8)-C(9) | 1.407(3) |
| C(9)-C(10) | 1.387(4) |
| C(10)-C(11) | 1.360(4) |
| C(11)-C(12) | 1.372(4) |
| C(12)-C(13) | 1.384(3) |
| O(1)-Co(1)-C(1) | 82.49(7) |
| O(1)-Co(1)-P(1) | 110.84(5) |
| C(1)-Co(1)-P(1) | 90.33(6) |
| O(1)-Co(1)-P(3) | 137.94(5) |

| | |
|---|---|
| C(1)-Co(1)-P(3) | 91.46(6) |
| P(1)-Co(1)-P(3) | 110.77(2) |
| O(1)-Co(1)-P(2) | 81.21(4) |
| C(1)-Co(1)-P(2) | 163.52(6) |
| P(1)-Co(1)-P(2) | 97.73(2) |
| P(3)-Co(1)-P(2) | 99.01(2) |
| C(15)-P(1)-C(14) | 100.32(16) |
| C(15)-P(1)-C(16) | 98.84(15) |
| C(14)-P(1)-C(16) | 101.36(17) |
| C(15)-P(1)-Co(1) | 121.54(10) |
| C(14)-P(1)-Co(1) | 110.66(11) |
| C(16)-P(1)-Co(1) | 120.63(10) |
| C(19)-P(2)-C(18) | 99.62(14) |
| C(19)-P(2)-C(17) | 100.60(15) |
| C(18)-P(2)-C(17) | 101.62(17) |
| C(19)-P(2)-Co(1) | 111.90(9) |
| C(18)-P(2)-Co(1) | 112.62(10) |
| C(17)-P(2)-Co(1) | 126.68(11) |
| C(22)-P(3)-C(20) | 98.76(19) |
| C(22)-P(3)-C(21) | 97.70(16) |
| C(20)-P(3)-C(21) | 100.74(16) |
| C(22)-P(3)-Co(1) | 120.21(11) |
| C(20)-P(3)-Co(1) | 115.09(13) |
| C(21)-P(3)-Co(1) | 120.32(10) |
| C(7)-O(1)-Co(1) | 117.51(11) |
| C(2)-C(1)-C(6) | 115.63(18) |
| C(2)-C(1)-Co(1) | 132.40(16) |
| C(6)-C(1)-Co(1) | 111.97(13) |
| C(3)-C(2)-C(1) | 122.7(2) |
| C(4)-C(3)-C(2) | 120.1(2) |
| C(5)-C(4)-C(3) | 119.7(2) |
| C(4)-C(5)-C(6) | 121.4(2) |
| C(5)-C(6)-C(7) | 126.45(18) |
| C(5)-C(6)-C(1) | 120.25(18) |
| C(7)-C(6)-C(1) | 113.08(16) |
| O(1)-C(7)-C(6) | 114.23(16) |

| | |
|---|---|
| O(1)-C(7)-C(8) | 117.51(17) |
| C(6)-C(7)-C(8) | 128.25(17) |
| C(13)-C(8)-C(9) | 116.84(18) |
| C(13)-C(8)-C(7) | 119.94(18) |
| C(9)-C(8)-C(7) | 123.22(19) |
| C(10)-C(9)-C(8) | 120.5(2) |
| C(11)-C(10)-C(9) | 121.2(2) |
| C(10)-C(11)-C(12) | 119.5(2) |
| C(11)-C(12)-C(13) | 120.3(2) |
| C(12)-C(13)-C(8) | 121.6(2) |

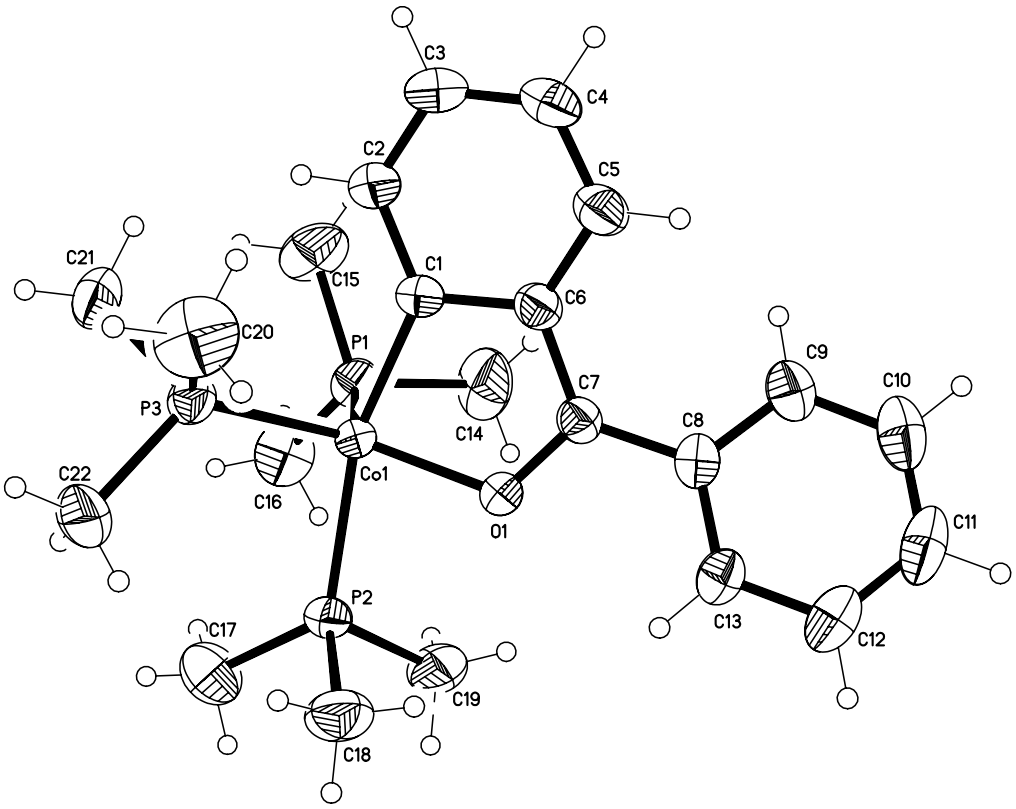
**Table 4.** Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12} ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Co(1) | 40(1) | 29(1) | 34(1) | 0(1) | -3(1) | 0(1) |
| P(1) | 58(1) | 45(1) | 43(1) | 0(1) | 9(1) | -11(1) |
| P(2) | 48(1) | 36(1) | 49(1) | 2(1) | -5(1) | 5(1) |
| P(3) | 59(1) | 42(1) | 38(1) | -3(1) | 6(1) | 0(1) |
| O(1) | 44(1) | 34(1) | 40(1) | -1(1) | -6(1) | -1(1) |
| C(1) | 50(1) | 34(1) | 48(1) | 2(1) | -6(1) | 4(1) |
| C(2) | 76(2) | 39(1) | 64(2) | -3(1) | -19(1) | 5(1) |
| C(3) | 88(2) | 39(1) | 76(2) | -1(1) | -8(1) | 14(1) |
| C(4) | 69(1) | 53(1) | 74(2) | 10(1) | -16(1) | 17(1) |
| C(5) | 54(1) | 51(1) | 62(1) | 7(1) | -12(1) | 6(1) |
| C(6) | 43(1) | 41(1) | 44(1) | 5(1) | -4(1) | -1(1) |
| C(7) | 38(1) | 40(1) | 38(1) | 3(1) | -1(1) | -1(1) |
| C(8) | 37(1) | 53(1) | 37(1) | -4(1) | 1(1) | -4(1) |
| C(9) | 61(1) | 70(1) | 44(1) | 5(1) | -6(1) | -1(1) |
| C(10) | 71(2) | 106(2) | 46(1) | -6(1) | -12(1) | 2(2) |
| C(11) | 65(2) | 100(2) | 63(2) | -37(1) | -9(1) | -10(1) |
| C(12) | 66(2) | 66(1) | 66(2) | -24(1) | 4(1) | -11(1) |
| C(13) | 52(1) | 52(1) | 43(1) | -9(1) | 2(1) | -6(1) |
| C(14) | 117(3) | 106(2) | 43(1) | 3(1) | 18(2) | -28(2) |
| C(15) | 102(2) | 54(1) | 95(2) | 3(1) | 24(2) | -30(1) |
| C(16) | 45(1) | 94(2) | 84(2) | -5(2) | 11(1) | -10(1) |
| C(17) | 79(2) | 89(2) | 101(2) | 4(2) | -40(2) | 26(2) |
| C(18) | 93(2) | 46(1) | 80(2) | 9(1) | 6(2) | -11(1) |
| C(19) | 83(2) | 52(1) | 72(2) | -13(1) | 7(1) | 21(1) |
| C(20) | 73(2) | 107(2) | 96(2) | -4(2) | 42(2) | 3(2) |
| C(21) | 99(2) | 60(1) | 55(2) | -12(1) | -14(1) | -12(2) |
| C(22) | 176(4) | 78(2) | 38(1) | 7(1) | -4(2) | 22(2) |

**Table 5.** Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x $10^3$) for **1**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2A) | 3319 | -1234 | 2307 | 71 |
| H(3A) | 4308 | -2614 | 2902 | 81 |
| H(4A) | 5191 | -1676 | 3891 | 78 |
| H(5A) | 5028 | 585 | 4336 | 67 |
| H(9A) | 4509 | 1785 | 5320 | 70 |
| H(10A) | 5084 | 3170 | 6354 | 89 |
| H(11A) | 5215 | 5545 | 6174 | 91 |
| H(12A) | 4685 | 6598 | 4986 | 79 |
| H(13A) | 4101 | 5254 | 3943 | 59 |
| H(14A) | 1378 | 808 | 4481 | 133 |
| H(14B) | 1760 | 2300 | 4342 | 133 |
| H(14C) | 2323 | 985 | 4457 | 133 |
| H(15A) | 2159 | -1334 | 3243 | 125 |
| H(15B) | 1558 | -1167 | 2484 | 125 |
| H(15C) | 1229 | -1141 | 3412 | 125 |
| H(16A) | 395 | 899 | 3049 | 112 |
| H(16B) | 714 | 1581 | 2212 | 112 |
| H(16C) | 668 | 2479 | 3040 | 112 |
| H(17A) | 964 | 3752 | 1670 | 135 |
| H(17B) | 1538 | 4308 | 955 | 135 |
| H(17C) | 1182 | 5356 | 1624 | 135 |
| H(18A) | 2712 | 6298 | 1739 | 109 |
| H(18B) | 3195 | 5100 | 1281 | 109 |
| H(18C) | 3420 | 5523 | 2208 | 109 |
| H(19A) | 1790 | 5958 | 3047 | 104 |
| H(19B) | 2375 | 5007 | 3579 | 104 |
| H(19C) | 1480 | 4524 | 3413 | 104 |
| H(20A) | 4080 | 633 | 316 | 138 |
| H(20B) | 4255 | 109 | 1236 | 138 |

| | | | | |
|---|---|---|---|---|
| H(20C) | 4394 | 1693 | 1000 | 138 |
| H(21A) | 1918 | -202 | 902 | 107 |
| H(21B) | 2668 | -1103 | 1178 | 107 |
| H(21C) | 2623 | -489 | 262 | 107 |
| H(22A) | 2917 | 1982 | -209 | 146 |
| H(22B) | 2998 | 3313 | 369 | 146 |
| H(22C) | 2162 | 2538 | 291 | 146 |




Molecular structure of **1**

**Table 1.** Crystal data and structure refinement for **3**.

| | | |
|---|---|---|
| Empirical formula | C22 H32 Co F4 O P3 | |
| Formula weight | 540.32 | |
| Temperature | 150(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P21/c | |
| Unit cell dimensions | a = 12.7954(16) Å | α= 90°. |
| | b = 14.830(2) Å | β= 130.890(8)°. |
| | c = 17.434(2) Å | γ = 90°. |
| Volume | 2500.9(5) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.435 $Mg/m^3$ | |
| Absorption coefficient | 0.920 $mm^{-1}$ | |
| F(000) | 1120 | |
| Crystal size | 0.12 x 0.10 x 0.09 $mm^3$ | |
| Theta range for data collection | 2.07 to 26.88°. | |
| Index ranges | -16<=h<=16, -18<=k<=18, -22<=l<=21 | |
| Reflections collected | 34404 | |
| Independent reflections | 5329 [R(int) = 0.1791] | |
| Completeness to theta = 26.88° | 98.7 % | |
| Absorption correction | None | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 5329 / 0 / 289 | |
| Goodness-of-fit on $F^2$ | 1.049 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0564, wR2 = 0.1067 | |
| R indices (all data) | R1 = 0.0916, wR2 = 0.1162 | |
| Largest diff. peak and hole | 0.525 and -0.623 $e.Å^{-3}$ | |

**Table 2.** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **3**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 4033(4) | 681(2) | -2807(3) | 23(1) |
| C(2) | 3606(4) | 193(2) | -2372(3) | 24(1) |
| C(3) | 2259(4) | 142(2) | -2768(3) | 26(1) |
| C(4) | 1229(4) | 580(3) | -3672(3) | 27(1) |
| C(5) | 1559(4) | 1048(3) | -4153(3) | 26(1) |
| C(6) | 2929(4) | 1090(2) | -3774(3) | 22(1) |
| C(7) | 3413(4) | 1545(2) | -4211(3) | 20(1) |
| C(8) | 2596(3) | 1919(2) | -5239(3) | 20(1) |
| C(9) | 1417(4) | 1486(3) | -6093(3) | 26(1) |
| C(10) | 700(4) | 1853(3) | -7051(3) | 31(1) |
| C(11) | 1126(4) | 2650(3) | -7181(3) | 32(1) |
| C(12) | 2294(4) | 3078(3) | -6350(3) | 30(1) |
| C(13) | 3034(4) | 2713(3) | -5391(3) | 25(1) |
| C(14) | 5697(5) | 1552(3) | -478(4) | 37(1) |
| C(15) | 7879(5) | 405(3) | 146(3) | 40(1) |
| C(16) | 7919(5) | 2254(3) | -162(3) | 41(1) |
| C(17) | 5551(6) | -1388(3) | -2250(4) | 41(1) |
| C(18) | 7890(5) | -880(3) | -1907(4) | 47(1) |
| C(19) | 5264(6) | -695(3) | -3864(4) | 49(1) |
| C(20) | 9373(4) | 1311(3) | -1192(3) | 34(1) |
| C(21) | 7413(5) | 1229(3) | -3332(3) | 37(1) |
| C(22) | 7503(4) | 2738(3) | -2354(3) | 31(1) |
| Co(1) | 5829(1) | 964(1) | -2366(1) | 18(1) |
| F(1) | 4556(3) | -252(2) | -1467(2) | 32(1) |
| F(2) | 1928(3) | -312(2) | -2274(2) | 38(1) |
| F(3) | -87(2) | 563(2) | -4025(2) | 40(1) |
| F(4) | 514(2) | 1508(2) | -5006(2) | 38(1) |
| O(1) | 4744(2) | 1617(2) | -3612(2) | 19(1) |
| P(1) | 6772(1) | 1277(1) | -794(1) | 23(1) |
| P(2) | 7543(1) | 1516(1) | -2255(1) | 22(1) |

| | | | | |
|---|---|---|---|---|
| P(3) | 6163(1) | -449(1) | -2536(1) | 24(1) |

**Table 3.** Bond lengths [Å] and angles [°] for **3**.

| | |
|---|---|
| C(1)-C(2) | 1.393(5) |
| C(1)-C(6) | 1.444(5) |
| C(1)-Co(1) | 1.932(4) |
| C(2)-F(1) | 1.376(4) |
| C(2)-C(3) | 1.378(6) |
| C(3)-F(2) | 1.361(4) |
| C(3)-C(4) | 1.387(6) |
| C(4)-C(5) | 1.352(5) |
| C(4)-F(3) | 1.363(4) |
| C(5)-F(4) | 1.364(4) |
| C(5)-C(6) | 1.413(5) |
| C(6)-C(7) | 1.428(5) |
| C(7)-O(1) | 1.293(4) |
| C(7)-C(8) | 1.470(5) |
| C(8)-C(9) | 1.401(5) |
| C(8)-C(13) | 1.402(5) |
| C(9)-C(10) | 1.386(6) |
| C(10)-C(11) | 1.381(6) |
| C(11)-C(12) | 1.378(6) |
| C(12)-C(13) | 1.383(5) |
| C(14)-P(1) | 1.832(4) |
| C(15)-P(1) | 1.824(4) |
| C(16)-P(1) | 1.830(4) |
| C(17)-P(3) | 1.820(4) |
| C(18)-P(3) | 1.823(5) |
| C(19)-P(3) | 1.825(5) |
| C(20)-P(2) | 1.824(4) |
| C(21)-P(2) | 1.825(4) |
| C(22)-P(2) | 1.817(4) |
| Co(1)-O(1) | 1.907(2) |
| Co(1)-P(3) | 2.1962(11) |
| Co(1)-P(1) | 2.2026(11) |
| Co(1)-P(2) | 2.2273(11) |

| | |
|---|---|
| C(2)-C(1)-C(6) | 114.9(3) |
| C(2)-C(1)-Co(1) | 133.1(3) |
| C(6)-C(1)-Co(1) | 112.0(2) |
| F(1)-C(2)-C(3) | 115.0(3) |
| F(1)-C(2)-C(1) | 120.5(3) |
| C(3)-C(2)-C(1) | 124.4(4) |
| F(2)-C(3)-C(2) | 121.1(4) |
| F(2)-C(3)-C(4) | 119.6(3) |
| C(2)-C(3)-C(4) | 119.3(3) |
| C(5)-C(4)-F(3) | 121.6(4) |
| C(5)-C(4)-C(3) | 119.7(3) |
| F(3)-C(4)-C(3) | 118.6(3) |
| C(4)-C(5)-F(4) | 116.8(3) |
| C(4)-C(5)-C(6) | 121.9(4) |
| F(4)-C(5)-C(6) | 121.2(3) |
| C(5)-C(6)-C(7) | 127.6(3) |
| C(5)-C(6)-C(1) | 119.6(3) |
| C(7)-C(6)-C(1) | 112.7(3) |
| O(1)-C(7)-C(6) | 114.2(3) |
| O(1)-C(7)-C(8) | 117.6(3) |
| C(6)-C(7)-C(8) | 128.2(3) |
| C(9)-C(8)-C(13) | 118.0(3) |
| C(9)-C(8)-C(7) | 122.3(3) |
| C(13)-C(8)-C(7) | 119.6(3) |
| C(10)-C(9)-C(8) | 120.2(4) |
| C(11)-C(10)-C(9) | 120.8(4) |
| C(12)-C(11)-C(10) | 119.7(4) |
| C(11)-C(12)-C(13) | 120.2(4) |
| C(12)-C(13)-C(8) | 121.0(4) |
| O(1)-Co(1)-C(1) | 82.35(13) |
| O(1)-Co(1)-P(3) | 113.06(8) |
| C(1)-Co(1)-P(3) | 91.45(11) |
| O(1)-Co(1)-P(1) | 135.02(8) |
| C(1)-Co(1)-P(1) | 94.65(11) |
| P(3)-Co(1)-P(1) | 111.87(4) |
| O(1)-Co(1)-P(2) | 81.58(8) |

| | |
|---|---|
| C(1)-Co(1)-P(2) | 163.92(12) |
| P(3)-Co(1)-P(2) | 95.47(4) |
| P(1)-Co(1)-P(2) | 96.20(4) |
| C(7)-O(1)-Co(1) | 118.1(2) |
| C(15)-P(1)-C(16) | 100.1(2) |
| C(15)-P(1)-C(14) | 100.5(2) |
| C(16)-P(1)-C(14) | 96.1(2) |
| C(15)-P(1)-Co(1) | 116.04(15) |
| C(16)-P(1)-Co(1) | 119.09(15) |
| C(14)-P(1)-Co(1) | 120.93(15) |
| C(22)-P(2)-C(20) | 101.6(2) |
| C(22)-P(2)-C(21) | 99.0(2) |
| C(20)-P(2)-C(21) | 101.4(2) |
| C(22)-P(2)-Co(1) | 113.18(13) |
| C(20)-P(2)-Co(1) | 124.30(15) |
| C(21)-P(2)-Co(1) | 113.79(15) |
| C(17)-P(3)-C(18) | 97.8(2) |
| C(17)-P(3)-C(19) | 99.6(2) |
| C(18)-P(3)-C(19) | 101.7(2) |
| C(17)-P(3)-Co(1) | 122.43(15) |
| C(18)-P(3)-Co(1) | 121.33(16) |
| C(19)-P(3)-Co(1) | 110.22(17) |

---

Symmetry transformations used to generate equivalent atoms:

**Table 4.** Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 28(2) | 19(2) | 25(2) | -3(1) | 18(2) | -6(2) |
| C(2) | 34(2) | 17(2) | 26(2) | -1(2) | 21(2) | -3(2) |
| C(3) | 42(2) | 18(2) | 39(2) | -7(2) | 36(2) | -10(2) |
| C(4) | 24(2) | 24(2) | 36(2) | -8(2) | 22(2) | -7(2) |
| C(5) | 22(2) | 28(2) | 27(2) | -2(2) | 16(2) | -3(2) |
| C(6) | 22(2) | 18(2) | 25(2) | -3(2) | 15(2) | -2(1) |
| C(7) | 19(2) | 17(2) | 21(2) | -2(1) | 12(2) | 0(1) |
| C(8) | 15(2) | 20(2) | 23(2) | 2(1) | 12(2) | 3(1) |
| C(9) | 24(2) | 28(2) | 23(2) | -2(2) | 14(2) | -1(2) |
| C(10) | 22(2) | 43(2) | 22(2) | -4(2) | 13(2) | -2(2) |
| C(11) | 24(2) | 47(3) | 22(2) | 10(2) | 14(2) | 10(2) |
| C(12) | 31(2) | 30(2) | 31(2) | 8(2) | 21(2) | 2(2) |
| C(13) | 23(2) | 27(2) | 25(2) | 3(2) | 15(2) | 0(2) |
| C(14) | 38(2) | 39(2) | 42(3) | -13(2) | 30(2) | -4(2) |
| C(15) | 44(3) | 41(3) | 25(2) | 5(2) | 19(2) | 12(2) |
| C(16) | 37(2) | 50(3) | 30(2) | -14(2) | 20(2) | -14(2) |
| C(17) | 66(3) | 23(2) | 53(3) | -1(2) | 48(3) | -3(2) |
| C(18) | 58(3) | 27(2) | 69(4) | 4(2) | 47(3) | 13(2) |
| C(19) | 78(4) | 34(2) | 38(3) | -11(2) | 40(3) | -15(2) |
| C(20) | 27(2) | 32(2) | 39(3) | 6(2) | 20(2) | 6(2) |
| C(21) | 45(3) | 43(3) | 33(2) | 3(2) | 29(2) | -3(2) |
| C(22) | 25(2) | 26(2) | 38(2) | 5(2) | 19(2) | 1(2) |
| Co(1) | 18(1) | 16(1) | 18(1) | 2(1) | 11(1) | 1(1) |
| F(1) | 45(1) | 27(1) | 30(1) | 7(1) | 27(1) | 0(1) |
| F(2) | 60(2) | 29(1) | 55(2) | -4(1) | 51(2) | -11(1) |
| F(3) | 32(1) | 44(1) | 60(2) | -10(1) | 37(1) | -11(1) |
| F(4) | 22(1) | 46(2) | 38(2) | 11(1) | 17(1) | 6(1) |
| O(1) | 17(1) | 19(1) | 19(1) | 3(1) | 10(1) | 1(1) |
| P(1) | 24(1) | 23(1) | 21(1) | -1(1) | 14(1) | 3(1) |
| P(2) | 18(1) | 21(1) | 24(1) | 4(1) | 13(1) | 2(1) |
| P(3) | 36(1) | 18(1) | 25(1) | 0(1) | 22(1) | 0(1) |

**Table 5.** Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for **3**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(9A) | 1115 | 950 | -6016 | 31 |
| H(10A) | -78 | 1558 | -7614 | 37 |
| H(11A) | 627 | 2897 | -7825 | 38 |
| H(12A) | 2585 | 3614 | -6434 | 36 |
| H(13A) | 3836 | 2998 | -4839 | 30 |
| H(14A) | 6276 | 1747 | 216 | 55 |
| H(14B) | 5186 | 1028 | -569 | 55 |
| H(14C) | 5065 | 2026 | -914 | 55 |
| H(15A) | 7362 | -144 | -48 | 60 |
| H(15B) | 8206 | 596 | 797 | 60 |
| H(15C) | 8654 | 303 | 185 | 60 |
| H(16A) | 8256 | 2299 | 516 | 61 |
| H(16B) | 7417 | 2792 | -532 | 61 |
| H(16C) | 8684 | 2184 | -140 | 61 |
| H(17A) | 6052 | -1404 | -1534 | 61 |
| H(17B) | 5694 | -1942 | -2454 | 61 |
| H(17C) | 4583 | -1313 | -2612 | 61 |
| H(18A) | 7828 | -1499 | -2094 | 71 |
| H(18B) | 8447 | -838 | -1185 | 71 |
| H(18C) | 8305 | -531 | -2110 | 71 |
| H(19A) | 4298 | -563 | -4271 | 73 |
| H(19B) | 5379 | -1321 | -3934 | 73 |
| H(19C) | 5643 | -331 | -4086 | 73 |
| H(20A) | 9918 | 1618 | -1310 | 51 |
| H(20B) | 9555 | 676 | -1130 | 51 |
| H(20C) | 9610 | 1533 | -578 | 51 |
| H(21A) | 7589 | 597 | -3315 | 56 |
| H(21B) | 8081 | 1571 | -3297 | 56 |
| H(21C) | 6501 | 1369 | -3952 | 56 |

| | | | | |
|---|---|---|---|---|
| H(22A) | 7687 | 3001 | -1773 | 47 |
| H(22B) | 6607 | 2926 | -2959 | 47 |
| H(22C) | 8193 | 2931 | -2382 | 47 |

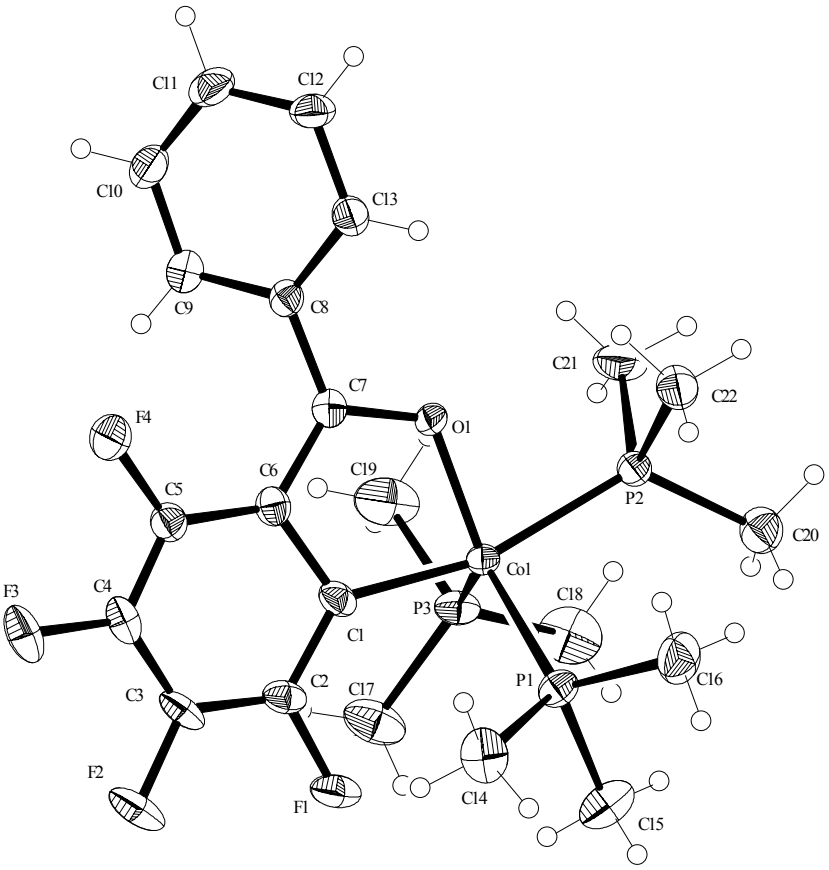
**Table 6.** Torsion angles [°] for **3**.

| | |
|---|---|
| C(6)-C(1)-C(2)-F(1) | 177.9(3) |
| Co(1)-C(1)-C(2)-F(1) | -4.2(6) |
| C(6)-C(1)-C(2)-C(3) | -4.7(5) |
| Co(1)-C(1)-C(2)-C(3) | 173.1(3) |
| F(1)-C(2)-C(3)-F(2) | 0.8(5) |
| C(1)-C(2)-C(3)-F(2) | -176.7(3) |
| F(1)-C(2)-C(3)-C(4) | 179.2(3) |
| C(1)-C(2)-C(3)-C(4) | 1.7(6) |
| F(2)-C(3)-C(4)-C(5) | 178.5(3) |
| C(2)-C(3)-C(4)-C(5) | 0.1(6) |
| F(2)-C(3)-C(4)-F(3) | 1.9(5) |
| C(2)-C(3)-C(4)-F(3) | -176.5(3) |
| F(3)-C(4)-C(5)-F(4) | 0.4(6) |
| C(3)-C(4)-C(5)-F(4) | -176.1(3) |
| F(3)-C(4)-C(5)-C(6) | 178.0(3) |
| C(3)-C(4)-C(5)-C(6) | 1.5(6) |
| C(4)-C(5)-C(6)-C(7) | 179.0(4) |
| F(4)-C(5)-C(6)-C(7) | -3.4(6) |
| C(4)-C(5)-C(6)-C(1) | -4.8(6) |
| F(4)-C(5)-C(6)-C(1) | 172.7(3) |
| C(2)-C(1)-C(6)-C(5) | 6.1(5) |
| Co(1)-C(1)-C(6)-C(5) | -172.2(3) |
| C(2)-C(1)-C(6)-C(7) | -177.2(3) |
| Co(1)-C(1)-C(6)-C(7) | 4.5(4) |
| C(5)-C(6)-C(7)-O(1) | 167.5(4) |
| C(1)-C(6)-C(7)-O(1) | -8.9(4) |
| C(5)-C(6)-C(7)-C(8) | -13.5(6) |
| C(1)-C(6)-C(7)-C(8) | 170.1(3) |
| O(1)-C(7)-C(8)-C(9) | 140.8(3) |
| C(6)-C(7)-C(8)-C(9) | -38.2(5) |
| O(1)-C(7)-C(8)-C(13) | -36.0(5) |
| C(6)-C(7)-C(8)-C(13) | 145.0(4) |
| C(13)-C(8)-C(9)-C(10) | -1.5(5) |

| | |
|---|---|
| C(7)-C(8)-C(9)-C(10) | -178.3(3) |
| C(8)-C(9)-C(10)-C(11) | -0.4(6) |
| C(9)-C(10)-C(11)-C(12) | 1.3(6) |
| C(10)-C(11)-C(12)-C(13) | -0.1(6) |
| C(11)-C(12)-C(13)-C(8) | -1.8(6) |
| C(9)-C(8)-C(13)-C(12) | 2.6(5) |
| C(7)-C(8)-C(13)-C(12) | 179.5(3) |
| C(2)-C(1)-Co(1)-O(1) | -177.7(4) |
| C(6)-C(1)-Co(1)-O(1) | 0.2(2) |
| C(2)-C(1)-Co(1)-P(3) | 69.2(4) |
| C(6)-C(1)-Co(1)-P(3) | -112.9(2) |
| C(2)-C(1)-Co(1)-P(1) | -42.9(4) |
| C(6)-C(1)-Co(1)-P(1) | 135.0(2) |
| C(2)-C(1)-Co(1)-P(2) | -175.2(2) |
| C(6)-C(1)-Co(1)-P(2) | 2.7(6) |
| C(6)-C(7)-O(1)-Co(1) | 9.5(4) |
| C(8)-C(7)-O(1)-Co(1) | -169.6(2) |
| C(1)-Co(1)-O(1)-C(7) | -5.5(3) |
| P(3)-Co(1)-O(1)-C(7) | 82.8(2) |
| P(1)-Co(1)-O(1)-C(7) | -94.5(3) |
| P(2)-Co(1)-O(1)-C(7) | 175.2(2) |
| O(1)-Co(1)-P(1)-C(15) | -173.9(2) |
| C(1)-Co(1)-P(1)-C(15) | 102.3(2) |
| P(3)-Co(1)-P(1)-C(15) | 8.85(19) |
| P(2)-Co(1)-P(1)-C(15) | -89.60(19) |
| O(1)-Co(1)-P(1)-C(16) | -54.2(2) |
| C(1)-Co(1)-P(1)-C(16) | -138.0(2) |
| P(3)-Co(1)-P(1)-C(16) | 128.52(19) |
| P(2)-Co(1)-P(1)-C(16) | 30.07(19) |
| O(1)-Co(1)-P(1)-C(14) | 64.2(2) |
| C(1)-Co(1)-P(1)-C(14) | -19.7(2) |
| P(3)-Co(1)-P(1)-C(14) | -113.11(18) |
| P(2)-Co(1)-P(1)-C(14) | 148.44(18) |
| O(1)-Co(1)-P(2)-C(22) | 55.78(18) |
| C(1)-Co(1)-P(2)-C(22) | 53.3(4) |
| P(3)-Co(1)-P(2)-C(22) | 168.33(16) |

| | |
|---|---|
| P(1)-Co(1)-P(2)-C(22) | -78.91(16) |
| O(1)-Co(1)-P(2)-C(20) | 179.5(2) |
| C(1)-Co(1)-P(2)-C(20) | 177.0(4) |
| P(3)-Co(1)-P(2)-C(20) | -67.90(19) |
| P(1)-Co(1)-P(2)-C(20) | 44.86(18) |
| O(1)-Co(1)-P(2)-C(21) | -56.25(18) |
| C(1)-Co(1)-P(2)-C(21) | -58.8(4) |
| P(3)-Co(1)-P(2)-C(21) | 56.30(17) |
| P(1)-Co(1)-P(2)-C(21) | 169.06(17) |
| O(1)-Co(1)-P(3)-C(17) | -118.2(2) |
| C(1)-Co(1)-P(3)-C(17) | -35.9(2) |
| P(1)-Co(1)-P(3)-C(17) | 59.7(2) |
| P(2)-Co(1)-P(3)-C(17) | 158.6(2) |
| O(1)-Co(1)-P(3)-C(18) | 116.6(2) |
| C(1)-Co(1)-P(3)-C(18) | -161.1(2) |
| P(1)-Co(1)-P(3)-C(18) | -65.5(2) |
| P(2)-Co(1)-P(3)-C(18) | 33.5(2) |
| O(1)-Co(1)-P(3)-C(19) | -1.8(2) |
| C(1)-Co(1)-P(3)-C(19) | 80.5(2) |
| P(1)-Co(1)-P(3)-C(19) | 176.10(19) |
| P(2)-Co(1)-P(3)-C(19) | -84.97(19) |

Symmetry transformations used to generate equivalent atoms:




Molecular structure of **3**.

**Table 1.** Crystal data and structure refinement for **4**.

| | | |
|---|---|---|
| Identification code | 4 | |
| Empirical formula | C22 H36 Co F O P3 | |
| Formula weight | 487.35 | |
| Temperature | 150(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P21/n | |
| Unit cell dimensions | a = 9.7220(12) Å | α= 90.000(12)°. |
| | b = 17.1350(13) Å | β= 101.030(12)°. |
| | c = 15.4390(11) Å | γ = 90.000(12)°. |
| Volume | 2524.4(4) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.282 $Mg/m^3$ | |
| Absorption coefficient | 0.887 $mm^{-1}$ | |
| F(000) | 1028 | |
| Crystal size | 0.12 x 0.10 x 0.08 $mm^3$ | |
| Theta range for data collection | 4.16 to 26.37°. | |
| Index ranges | -12<=h<=12, -21<=k<=21, -19<=l<=19 | |
| Reflections collected | 30970 | |
| Independent reflections | 5112 [R(int) = 0.1130] | |
| Completeness to theta = 26.37° | 99.0 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9324 and 0.9010 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 5112 / 0 / 253 | |
| Goodness-of-fit on $F^2$ | 1.048 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0450, wR2 = 0.1153 | |
| R indices (all data) | R1 = 0.0522, wR2 = 0.1191 | |
| Largest diff. peak and hole | 0.717 and -1.107 $e.Å^{-3}$ | |

**Table 2.** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **4**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 6744(2) | 2556(1) | 4360(2) | 20(1) |
| C(2) | 7325(2) | 3323(1) | 4107(2) | 22(1) |
| C(3) | 7365(3) | 3577(1) | 3252(2) | 26(1) |
| C(4) | 7842(3) | 4305(2) | 3060(2) | 37(1) |
| C(5) | 8322(3) | 4818(2) | 3749(2) | 43(1) |
| C(6) | 8305(3) | 4595(2) | 4612(2) | 40(1) |
| C(7) | 7816(3) | 3860(2) | 4784(2) | 30(1) |
| C(8) | 7479(2) | 1807(1) | 4212(2) | 22(1) |
| C(9) | 8181(2) | 1674(1) | 3514(2) | 26(1) |
| C(10) | 8777(3) | 950(2) | 3400(2) | 32(1) |
| C(11) | 8749(3) | 352(2) | 3998(2) | 38(1) |
| C(12) | 8106(3) | 485(2) | 4714(2) | 40(1) |
| C(13) | 7466(3) | 1194(2) | 4820(2) | 31(1) |
| C(14) | 4211(3) | 4472(2) | 3960(2) | 40(1) |
| C(15) | 3604(3) | 3703(2) | 2315(2) | 44(1) |
| C(16) | 1692(3) | 3644(2) | 3458(2) | 39(1) |
| C(17) | 3356(3) | 3155(2) | 5948(2) | 40(1) |
| C(18) | 4153(3) | 1579(2) | 6033(2) | 40(1) |
| C(19) | 1494(3) | 2009(2) | 5079(2) | 41(1) |
| C(20) | 4727(3) | 1550(2) | 2213(2) | 46(1) |
| C(21) | 4200(5) | 571(2) | 3567(3) | 61(1) |
| C(22) | 2077(3) | 1565(2) | 2656(2) | 53(1) |
| Co(1) | 4637(1) | 2480(1) | 4214(1) | 17(1) |
| F(1) | 6844(2) | 3098(1) | 2548(1) | 35(1) |
| O(1) | 6248(2) | 2593(1) | 5113(1) | 23(1) |
| P(1) | 3934(1) | 1588(1) | 3196(1) | 26(1) |
| P(2) | 3332(1) | 2302(1) | 5230(1) | 23(1) |
| P(3) | 3582(1) | 3525(1) | 3493(1) | 26(1) |

**Table 3.** Bond lengths [Å] and angles [°] for **4**.

| | |
|---|---|
| C(1)-O(1) | 1.343(3) |
| C(1)-C(8) | 1.507(3) |
| C(1)-C(2) | 1.511(3) |
| C(1)-Co(1) | 2.022(2) |
| C(2)-C(3) | 1.397(3) |
| C(2)-C(7) | 1.406(3) |
| C(3)-F(1) | 1.378(3) |
| C(3)-C(4) | 1.382(3) |
| C(4)-C(5) | 1.390(4) |
| C(5)-C(6) | 1.390(5) |
| C(6)-C(7) | 1.389(4) |
| C(8)-C(9) | 1.401(3) |
| C(8)-C(13) | 1.410(3) |
| C(9)-C(10) | 1.394(3) |
| C(10)-C(11) | 1.383(4) |
| C(11)-C(12) | 1.389(4) |
| C(12)-C(13) | 1.388(4) |
| C(14)-P(3) | 1.834(3) |
| C(15)-P(3) | 1.849(3) |
| C(16)-P(3) | 1.839(3) |
| C(17)-P(2) | 1.832(3) |
| C(18)-P(2) | 1.825(3) |
| C(19)-P(2) | 1.828(3) |
| C(20)-P(1) | 1.831(3) |
| C(21)-P(1) | 1.838(3) |
| C(22)-P(1) | 1.838(3) |
| Co(1)-O(1) | 1.8938(17) |
| Co(1)-P(1) | 2.2043(7) |
| Co(1)-P(2) | 2.2189(7) |
| Co(1)-P(3) | 2.2492(7) |
| O(1)-C(1)-C(8) | 115.47(19) |
| O(1)-C(1)-C(2) | 113.38(18) |
| C(8)-C(1)-C(2) | 119.35(19) |

| | |
|---|---|
| O(1)-C(1)-Co(1) | 64.87(12) |
| C(8)-C(1)-Co(1) | 115.33(15) |
| C(2)-C(1)-Co(1) | 116.63(15) |
| C(3)-C(2)-C(7) | 115.5(2) |
| C(3)-C(2)-C(1) | 126.5(2) |
| C(7)-C(2)-C(1) | 117.9(2) |
| F(1)-C(3)-C(4) | 117.1(2) |
| F(1)-C(3)-C(2) | 119.1(2) |
| C(4)-C(3)-C(2) | 123.7(2) |
| C(3)-C(4)-C(5) | 119.0(3) |
| C(6)-C(5)-C(4) | 119.7(2) |
| C(7)-C(6)-C(5) | 119.9(3) |
| C(6)-C(7)-C(2) | 122.1(3) |
| C(9)-C(8)-C(13) | 117.2(2) |
| C(9)-C(8)-C(1) | 124.7(2) |
| C(13)-C(8)-C(1) | 118.0(2) |
| C(10)-C(9)-C(8) | 121.1(2) |
| C(11)-C(10)-C(9) | 120.9(3) |
| C(10)-C(11)-C(12) | 118.6(2) |
| C(13)-C(12)-C(11) | 121.1(3) |
| C(12)-C(13)-C(8) | 120.9(2) |
| O(1)-Co(1)-C(1) | 39.93(8) |
| O(1)-Co(1)-P(1) | 133.91(5) |
| C(1)-Co(1)-P(1) | 107.07(7) |
| O(1)-Co(1)-P(2) | 90.04(5) |
| C(1)-Co(1)-P(2) | 129.36(7) |
| P(1)-Co(1)-P(2) | 105.51(3) |
| O(1)-Co(1)-P(3) | 121.06(5) |
| C(1)-Co(1)-P(3) | 111.11(7) |
| P(1)-Co(1)-P(3) | 98.60(3) |
| P(2)-Co(1)-P(3) | 100.99(3) |
| C(1)-O(1)-Co(1) | 75.20(13) |
| C(20)-P(1)-C(21) | 99.70(18) |
| C(20)-P(1)-C(22) | 98.99(16) |
| C(21)-P(1)-C(22) | 100.90(18) |
| C(20)-P(1)-Co(1) | 119.53(10) |

| | |
|---|---|
| C(21)-P(1)-Co(1) | 115.43(11) |
| C(22)-P(1)-Co(1) | 118.78(10) |
| C(18)-P(2)-C(19) | 100.95(14) |
| C(18)-P(2)-C(17) | 100.20(15) |
| C(19)-P(2)-C(17) | 101.23(14) |
| C(18)-P(2)-Co(1) | 109.79(9) |
| C(19)-P(2)-Co(1) | 128.69(10) |
| C(17)-P(2)-Co(1) | 112.07(10) |
| C(14)-P(3)-C(16) | 99.78(14) |
| C(14)-P(3)-C(15) | 100.03(16) |
| C(16)-P(3)-C(15) | 98.80(14) |
| C(14)-P(3)-Co(1) | 115.10(10) |
| C(16)-P(3)-Co(1) | 117.47(10) |
| C(15)-P(3)-Co(1) | 121.87(10) |

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Symmetry transformations used to generate equivalent atoms:

**Table 4.** Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 19(1) | 23(1) | 18(1) | 0(1) | 1(1) | -2(1) |
| C(2) | 19(1) | 23(1) | 25(1) | 1(1) | 6(1) | -1(1) |
| C(3) | 26(1) | 26(1) | 29(1) | -1(1) | 11(1) | 3(1) |
| C(4) | 43(2) | 28(1) | 48(2) | 10(1) | 28(1) | 7(1) |
| C(5) | 42(2) | 21(1) | 75(2) | 3(1) | 32(2) | -5(1) |
| C(6) | 32(2) | 31(1) | 60(2) | -15(1) | 16(1) | -10(1) |
| C(7) | 25(1) | 32(1) | 32(1) | -6(1) | 5(1) | -7(1) |
| C(8) | 16(1) | 23(1) | 24(1) | 1(1) | -2(1) | -1(1) |
| C(9) | 20(1) | 26(1) | 31(1) | -1(1) | 3(1) | 0(1) |
| C(10) | 23(1) | 32(1) | 40(2) | -8(1) | 4(1) | 3(1) |
| C(11) | 28(1) | 26(1) | 55(2) | -6(1) | -3(1) | 7(1) |
| C(12) | 36(2) | 29(1) | 52(2) | 12(1) | 3(1) | 6(1) |
| C(13) | 29(1) | 32(1) | 32(1) | 8(1) | 5(1) | 2(1) |
| C(14) | 40(2) | 24(1) | 56(2) | 1(1) | 9(1) | 5(1) |
| C(15) | 44(2) | 56(2) | 32(2) | 16(1) | 7(1) | 21(1) |
| C(16) | 32(2) | 42(2) | 40(2) | -1(1) | 3(1) | 12(1) |
| C(17) | 48(2) | 43(2) | 31(1) | -8(1) | 14(1) | -3(1) |
| C(18) | 42(2) | 44(2) | 37(2) | 15(1) | 17(1) | 4(1) |
| C(19) | 27(2) | 57(2) | 41(2) | -2(1) | 11(1) | -9(1) |
| C(20) | 37(2) | 66(2) | 35(2) | -27(1) | 7(1) | 0(1) |
| C(21) | 87(3) | 26(1) | 62(2) | -10(1) | -5(2) | -12(2) |
| C(22) | 24(2) | 69(2) | 62(2) | -35(2) | -1(1) | -6(1) |
| Co(1) | 18(1) | 18(1) | 16(1) | -1(1) | 2(1) | -1(1) |
| F(1) | 45(1) | 37(1) | 26(1) | 3(1) | 9(1) | 5(1) |
| O(1) | 21(1) | 31(1) | 15(1) | -1(1) | 1(1) | -5(1) |
| P(1) | 22(1) | 28(1) | 28(1) | -11(1) | 1(1) | -3(1) |
| P(2) | 23(1) | 26(1) | 22(1) | -1(1) | 7(1) | -2(1) |
| P(3) | 26(1) | 26(1) | 24(1) | 4(1) | 3(1) | 7(1) |

**Table 5.** Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x $10^3$) for **4**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(5A) | 7840 | 4449 | 2479 | 44 |
| H(11A) | 8655 | 5309 | 3632 | 52 |
| H(7A) | 8620 | 4938 | 5075 | 48 |
| H(6A) | 7813 | 3719 | 5365 | 36 |
| H(2A) | 8251 | 2076 | 3119 | 31 |
| H(4A) | 9199 | 868 | 2916 | 38 |
| H(9A) | 9152 | -129 | 3922 | 45 |
| H(12A) | 8103 | 92 | 5130 | 48 |
| H(10A) | 7024 | 1265 | 5297 | 37 |
| H(15A) | 5194 | 4521 | 3956 | 48 |
| H(15B) | 4061 | 4509 | 4555 | 48 |
| H(15C) | 3709 | 4883 | 3612 | 48 |
| H(18C) | 3102 | 4175 | 2128 | 53 |
| H(18B) | 3166 | 3273 | 1969 | 53 |
| H(18A) | 4556 | 3753 | 2236 | 53 |
| H(13A) | 1521 | 3684 | 4049 | 46 |
| H(13B) | 1199 | 3200 | 3172 | 46 |
| H(13C) | 1368 | 4109 | 3136 | 46 |
| H(21A) | 3002 | 3601 | 5599 | 48 |
| H(21B) | 4300 | 3255 | 6246 | 48 |
| H(21C) | 2779 | 3055 | 6376 | 48 |
| H(14A) | 5066 | 1758 | 6311 | 48 |
| H(14B) | 4238 | 1093 | 5738 | 48 |
| H(14C) | 3586 | 1505 | 6471 | 48 |
| H(22C) | 1219 | 1982 | 5644 | 50 |
| H(22B) | 1376 | 1507 | 4800 | 50 |
| H(22A) | 921 | 2385 | 4715 | 50 |
| H(16A) | 5718 | 1466 | 2387 | 55 |
| H(16B) | 4562 | 2035 | 1898 | 55 |

| | | | | |
|---|---|---|---|---|
| H(16C) | 4318 | 1130 | 1839 | 55 |
| H(19A) | 3696 | 476 | 4034 | 73 |
| H(19B) | 5181 | 479 | 3779 | 73 |
| H(19C) | 3863 | 226 | 3083 | 73 |
| H(17C) | 1927 | 1150 | 2232 | 64 |
| H(17B) | 1827 | 2054 | 2363 | 64 |
| H(17A) | 1508 | 1481 | 3092 | 64 |

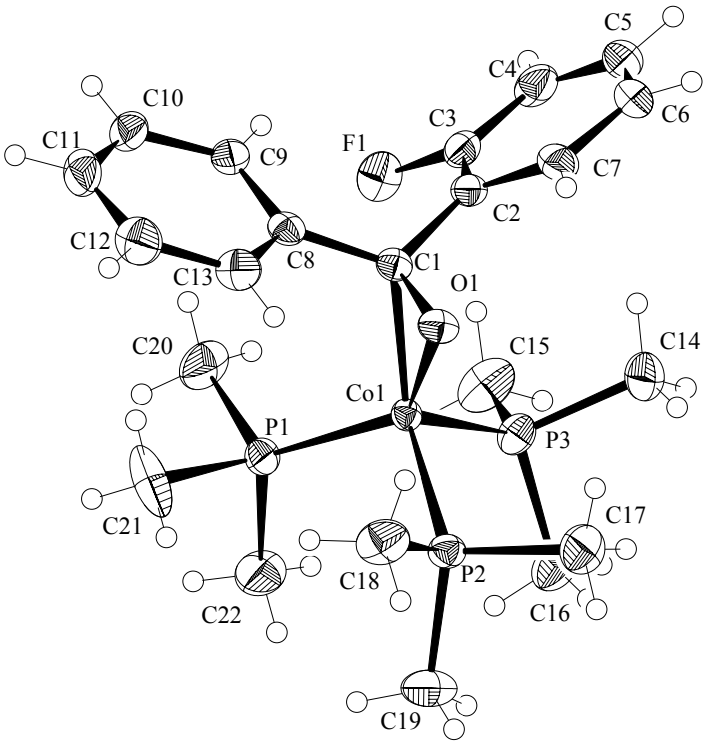
**Table 6.** Torsion angles [°] for **4**.

| | |
|---|---|
| O(1)-C(1)-C(2)-C(3) | -151.2(2) |
| C(8)-C(1)-C(2)-C(3) | 67.5(3) |
| Co(1)-C(1)-C(2)-C(3) | -78.7(3) |
| O(1)-C(1)-C(2)-C(7) | 25.4(3) |
| C(8)-C(1)-C(2)-C(7) | -115.9(2) |
| Co(1)-C(1)-C(2)-C(7) | 97.9(2) |
| C(7)-C(2)-C(3)-F(1) | -177.1(2) |
| C(1)-C(2)-C(3)-F(1) | -0.5(4) |
| C(7)-C(2)-C(3)-C(4) | -0.3(4) |
| C(1)-C(2)-C(3)-C(4) | 176.3(2) |
| F(1)-C(3)-C(4)-C(5) | 177.4(2) |
| C(2)-C(3)-C(4)-C(5) | 0.6(4) |
| C(3)-C(4)-C(5)-C(6) | -0.6(4) |
| C(4)-C(5)-C(6)-C(7) | 0.4(4) |
| C(5)-C(6)-C(7)-C(2) | -0.2(4) |
| C(3)-C(2)-C(7)-C(6) | 0.2(4) |
| C(1)-C(2)-C(7)-C(6) | -176.8(2) |
| O(1)-C(1)-C(8)-C(9) | -174.0(2) |
| C(2)-C(1)-C(8)-C(9) | -33.4(3) |
| Co(1)-C(1)-C(8)-C(9) | 113.2(2) |
| O(1)-C(1)-C(8)-C(13) | 5.9(3) |
| C(2)-C(1)-C(8)-C(13) | 146.5(2) |
| Co(1)-C(1)-C(8)-C(13) | -66.9(3) |
| C(13)-C(8)-C(9)-C(10) | 3.3(3) |
| C(1)-C(8)-C(9)-C(10) | -176.8(2) |
| C(8)-C(9)-C(10)-C(11) | -3.0(4) |
| C(9)-C(10)-C(11)-C(12) | 0.4(4) |
| C(10)-C(11)-C(12)-C(13) | 1.8(4) |
| C(11)-C(12)-C(13)-C(8) | -1.5(4) |
| C(9)-C(8)-C(13)-C(12) | -1.1(4) |
| C(1)-C(8)-C(13)-C(12) | 179.0(2) |
| C(8)-C(1)-Co(1)-O(1) | 107.7(2) |
| C(2)-C(1)-Co(1)-O(1) | -104.8(2) |

| | |
|---|---|
| O(1)-C(1)-Co(1)-P(1) | -139.76(10) |
| C(8)-C(1)-Co(1)-P(1) | -32.09(18) |
| C(2)-C(1)-Co(1)-P(1) | 115.46(16) |
| O(1)-C(1)-Co(1)-P(2) | -11.90(14) |
| C(8)-C(1)-Co(1)-P(2) | 95.77(17) |
| C(2)-C(1)-Co(1)-P(2) | -116.68(15) |
| O(1)-C(1)-Co(1)-P(3) | 113.61(10) |
| C(8)-C(1)-Co(1)-P(3) | -138.72(15) |
| C(2)-C(1)-Co(1)-P(3) | 8.83(18) |
| C(8)-C(1)-O(1)-Co(1) | -107.45(18) |
| C(2)-C(1)-O(1)-Co(1) | 109.66(18) |
| P(1)-Co(1)-O(1)-C(1) | 59.00(13) |
| P(2)-Co(1)-O(1)-C(1) | 170.83(11) |
| P(3)-Co(1)-O(1)-C(1) | -86.29(12) |
| O(1)-Co(1)-P(1)-C(20) | -76.02(15) |
| C(1)-Co(1)-P(1)-C(20) | -40.89(15) |
| P(2)-Co(1)-P(1)-C(20) | 178.42(13) |
| P(3)-Co(1)-P(1)-C(20) | 74.42(13) |
| O(1)-Co(1)-P(1)-C(21) | 42.90(18) |
| C(1)-Co(1)-P(1)-C(21) | 78.04(17) |
| P(2)-Co(1)-P(1)-C(21) | -62.65(16) |
| P(3)-Co(1)-P(1)-C(21) | -166.66(16) |
| O(1)-Co(1)-P(1)-C(22) | 162.91(17) |
| C(1)-Co(1)-P(1)-C(22) | -161.95(17) |
| P(2)-Co(1)-P(1)-C(22) | 57.36(15) |
| P(3)-Co(1)-P(1)-C(22) | -46.65(15) |
| O(1)-Co(1)-P(2)-C(18) | -48.67(12) |
| C(1)-Co(1)-P(2)-C(18) | -41.06(14) |
| P(1)-Co(1)-P(2)-C(18) | 87.38(12) |
| P(3)-Co(1)-P(2)-C(18) | -170.39(11) |
| O(1)-Co(1)-P(2)-C(19) | -171.81(15) |
| C(1)-Co(1)-P(2)-C(19) | -164.20(16) |
| P(1)-Co(1)-P(2)-C(19) | -35.76(14) |
| P(3)-Co(1)-P(2)-C(19) | 66.47(14) |
| O(1)-Co(1)-P(2)-C(17) | 61.75(12) |
| C(1)-Co(1)-P(2)-C(17) | 69.36(14) |

| | |
|---|---|
| P(1)-Co(1)-P(2)-C(17) | -162.20(11) |
| P(3)-Co(1)-P(2)-C(17) | -59.97(12) |
| O(1)-Co(1)-P(3)-C(14) | -9.60(13) |
| C(1)-Co(1)-P(3)-C(14) | -52.96(13) |
| P(1)-Co(1)-P(3)-C(14) | -165.08(11) |
| P(2)-Co(1)-P(3)-C(14) | 87.17(12) |
| O(1)-Co(1)-P(3)-C(16) | -126.66(12) |
| C(1)-Co(1)-P(3)-C(16) | -170.02(13) |
| P(1)-Co(1)-P(3)-C(16) | 77.86(11) |
| P(2)-Co(1)-P(3)-C(16) | -29.90(11) |
| O(1)-Co(1)-P(3)-C(15) | 111.59(15) |
| C(1)-Co(1)-P(3)-C(15) | 68.23(16) |
| P(1)-Co(1)-P(3)-C(15) | -43.89(14) |
| P(2)-Co(1)-P(3)-C(15) | -151.64(14) |

Symmetry transformations used to generate equivalent atoms:




Molecular structure of **4**.