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Regioselective *ortho*-Metallation of 2-Diphenylphosphanylpyridine and (2-(2-Diphenylphosphanyl)phenyl)-1-3-dioxalane with Methyltetrakis(trimethylphosphane)cobalt(I)

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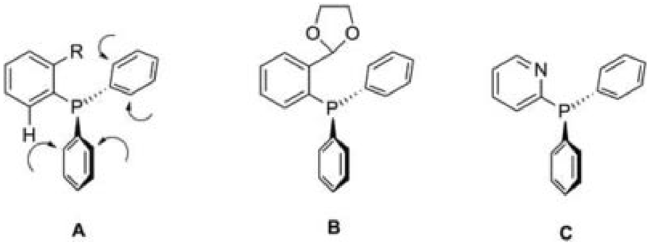
Keywords: C-H-Activation; Metallation (*ortho*); Cobalt; Insertion reactions; P ligands

Abstract. $Co(CH_3)(PMe_3)_4$ forms 100 % regioselectively with (2-(2-diphenylphosphanyl)phenyl)-1,3-dioxalane and 2-diphenylphosphanyl-pyridine, by elimination of methane, the four-membered metallacycles $Co\{(C_3O_2HC_6H_3)P(C_6H_5)_2\}(PMe_3)_3$ (**1**) and $Co\{(CNC_4H_3)P(C_6H_5)_2\}(PMe_3)_3$ (**4**). The regioselectivity is independent of the steric requirement of the *ortho* substituent in the 2-diphenylphosphanylaryl-ligands. Oxidative addition with iodomethane transforms **1** and **4** into octahedral, diamagnetic low-spin d^6 complexes $Co(CH_3)I\text{-}\{(C_3O_2HC_6H_3)P(C_6H_5)_2\}(PMe_3)_2$ (**2**) and $Co(CH_3)I\text{-}\{(CNC_4H_3)P(C_6H_5)_2\}(PMe_3)_2$ (**5**). Under an atmosphere of carbon monoxide, insertion into the Co-C bond results in ring expansion by forming the new assembled phosphanylbenzoyl complexes $Co\{(C_4O_3HC_6H_3)\text{-}P(C_6H_5)_2\}CO(PMe_3)_2$ (**3**) and $Co\{(OCNC_4H_3)P(C_6H_5)_2\}CO(PMe_3)_2$ (**6**). The three different types of cobaltacycles are supported by X-ray diffraction of **1**, **3**, **5** and **6**.

Introduction

C-H activation of various organic substrates and cyclometallation reactions have been extensively studied for more than five decades and found applications in industrial processes. These include activation of small molecules, which are important areas of research with respect to homogeneous catalysis. Most cyclometallation reactions require a pre-coordination of a heteroatom (N, P, S) when forming a metallacycle [1]. Among the oldest C-H activation processes are those involving phenylphosphanes with electron-rich complexes of the late transition metals. For most transition metals five-membered metallacycles have been described and some four- and six-membered ring systems were also found [2]. With electron-rich methyl cobalt compounds it was recently shown that *ortho* metallation proceeds under smooth conditions by release of methane via C-H activation of various *ortho* substituted 2-diphenylphosphanylaryl-ligands. The reaction occurred regioselectively and even heteroatoms, e.g. nitrogen in the substituents ($R = N(CH_3)_2$, CN) (**A**) were not engaged in metal coordination as long as no five membered metallacycle would be formed. An activation of other available C-H bonds (indicated by an arrow in Scheme A) was not observed [3]. In here we extend our investigation with a bulky oxygen carrying substituent in phenylphosphanes as 2-(2-diphenylphosphanyl)-phenyl)-1,3-dioxalane (**B**) and a less bulky substituent where the nitrogen donor atom is incorporated in the phenyl ring of 2-diphenylphosphanylpyridine (**C**).



Scheme A. *Ortho*-substituted pre-chelating 2-(diphenylphosphanyl)aryl ligands **A**, **B** and **C**

Results and Discussion

Reaction with (2-(2-Diphenylphosphanyl)phenyl)-1,3-dioxalane

After combining a THF solution of $CoCH_3(PMe_3)_4$ with (2-(2-diphenylphosphanyl)phenyl)-1,3-dioxalane at −70 °C, the mixture was warmed to 20 °C, to afford complete conversion after 16 h. Compound **1** (Scheme 1) was isolated in high yield, as dark red crystals that decompose around 111 °C. A pentacoordinated complex is formed, which is incorporated in a four-membered metallacycle, indicated by infrared absorptions of the Co-C-coordinated aryl group,

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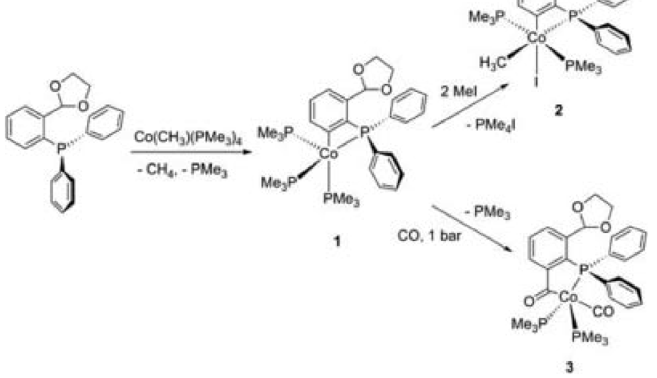
that shows the expected bathochromic shifts. The absorbances are shifted to lower energies than those of the free ligand, 1538 cm^{-1} (ν CoC=C; **1**). In the ^1H NMR spectrum, axial PMe_3 protons resonate at 0.88 ppm as a doublet ($^2J_{P,H} = 6.2$ Hz, 9H) and at 1.20 ppm as a virtual triplet (t′, $|^2J_{P,H} + {}^4J_{P,H}| = 4.4$ Hz, 18 H, PCH_3) for the two equatorial phosphane ligands. In the $^{31}P\{^1H\}$ NMR spectrum three different phosphorus nuclei resonate at −19.5 ppm, 2.4 ppm and 27.7 ppm with ($^2J_{P,P} = 86$, 71 and 44 Hz) with a high field shift for the PPh_2-donor group of about 15 ppm, indicating an incorporation in a four-membered metallacycle. The $^{13}C\{^1H\}$ NMR data confirms the cyclometallation, as a metallated carbon atom resonates at 171.1 ppm as multiplet (nuclear spin I(Co) = 7/2), while 10 carbon resonances are found in the aromatic region as required for the C_S-symmetry of **1**.



Scheme 1. Cyclometallation, oxidative addition and carbon monoxide insertion reaction pathway with (2-(2-diphenylphosphanyl)-phenyl)-1,3-dioxalane

The structural data for complex **1** (Figure 1) closely resemble those of the cyclometallated triphenylphosphane complexes [4]. The complex **1** adopts a trigonal bipyramidal geometry with the main axis along C1-Co1-P4 = 166.29°. The three equatorial positions are occupied by the PPh_2 anchoring group and two trimethylphosphane ligands. The Co-P and Co-C distances correspond with literature values. In the Co1-P4 distance (2.2073 Å) the *trans* influence of the carbon atom is noticed while the other two Co-*P*Me_3 distances are considerably shorter. The most striking feature in the structure of **1** is the narrow bite angle (C1-Co1-P1 = 70.90(8)°). Remarkably, a related reaction with rhodium [5] and platinum [6] complexes showed in both cases no *ortho*-metallation, instead the oxygen donor from the side chain is incorporated in the coordination sphere, when a six membered [P,O]-metallacycle is formed.

By an oxidative addition, complex **1** can be easily converted to low spin d^6-Co^{III} complex **2** (Scheme 1). From pentane solutions orange brown cubic crystals were isolated in 38 % yield, together with tetramethyl-phosphoniumiodide as a side product formed by quaternization of a trimethylphosphane ligand by iodomethane. The ^1H NMR spectrum of **2** exhibits the resonance of the methyl group at 0.49 ppm (3H) as a doublet of triplets with ($^3J_{P,H} = 9.1$ Hz and $^3J_{P,H} = 1.7$ Hz) and the two *trans* disposed trimethylphosphane ligands at 1.05 ppm ($|^2J_{P,H} + {}^4J_{P,H}| = 3.7$ Hz) as a virtual triplet. The unchanged ring size of the four-membered metallacycle after oxidative addition with iodomethane is indicated by the shift of the chelating PPh_2 group in the $^{31}P\{^1H\}$ NMR spectrum at −34.4 ppm, which is split into a triplet by coupling with two *trans* disposed trimethylphosphane groups (11.6 ppm, d, $^2J_{P,P} = 26.5$ Hz).

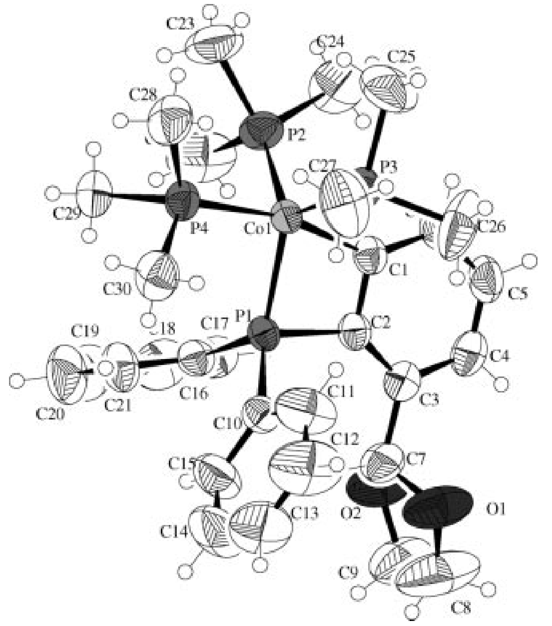


Figure 1. Molecular structure of **1**.

Selected distances/Å and angles/°: Co1-C1 1.993(3), Co1-P1 2.2130(9), Co1-P2 2.1782(10), Co1-P3 2.1777(9), Co1-P4 2.2073(9), C1-C2 1.416(4), C3-C4 1.394(4), O1-C7 1.403(4); C1-Co1-P1 70.90(8), C1-Co1-P4 166.29(8), C1-Co1-P3 90.74(8), C1-Co1-P2 91.73(9), P1-Co1-P2 119.01(3), P4-Co1-P1 95.40(3), P3-Co1-P1 121.23(4), P2-Co1-P4 97.05(3), P3-Co1-P2 116.78(4).

When complex **1** is stirred under an atmosphere of carbon monoxide (Scheme 1) it is smoothly transformed into the acyl complex **3**, by an insertion of CO into the Co-C bond followed by substitution of a trimethylphosphane ligand. From diethyl ether solutions red rhombic crystals of **3** were isolated, which melt with decomposition at 152 − 154 °C. From the IR spectra a very strong band for (νC≡O) 1854 cm^{-1} is observed, which is characteristic for terminal carbon monoxide ligands [7]. The ratio of resonances in the aromatic- and trimethylphosphane-region (1:2) derived by integration of the ^1H NMR spectrum, indicates a monosubstitution of one trimethylphosphane ligand by carbon monoxide.

The molecular structure of **3** (Figure 2) shows a cobalt atom centered in a trigonal bipyramid comprising three equatorial P-donor functions.

The axial positions are occupied by the carbon atoms (C1 and C11) of the acylgroup and the terminal carbonyl ligand respectively. Interestingly, the groups with the largest *trans* influence are almost perfectly aligned along an axis [C11-

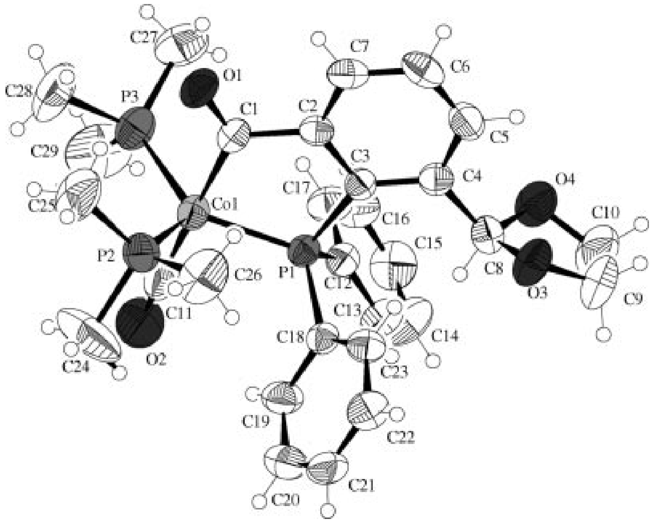


Figure 2. Molecular Structure of **3**.

Selected distances/Å and angles/°: Co1-C11 1.737(5), Co1-C1 1.932(4), Co1-P1 2.1553(12), Co1-P2 2.1804(14), Co1-P3 2.1819(14), O1-C1 1.233(4), O2-C11 1.161(4); C1-Co1-P1 86.19(12), C11-Co1-C1 175.23(19), C11-Co1-P1 91.85(14), C11-Co1-P2 97.35(16), C1-Co1-P2 87.42(12), P1-Co1-P2 112.17(5), C11-Co1-P3 91.18(15), C1-Co1-P3 86.80(12), P1-Co1-P3 130.36(5), P2-Co1-P3 116.51(5).

Co1-C1 = 175.23(2)°]. The presence of a five-membered cobaltacycle (low-field shift of PPh_2-group) for **3** derived from $^{31}P\{^{1}H\}$ NMR spectroscopy [(PPh_2) **1**: −19.5 ppm, **3**: 90.3 ppm] is confirmed by the molecular structure. The chelate bite angle with [C1-Co1-P1 = 86.19(12)°] as well as the sum of internal angles in the five-membered ring system (539.7°) indicates almost planarity in a sterically relaxed situation when compared with **1**. A related compound has been previously obtained by C-H activation of 2-diphenylphosphanyl-benzaldehyde [8].

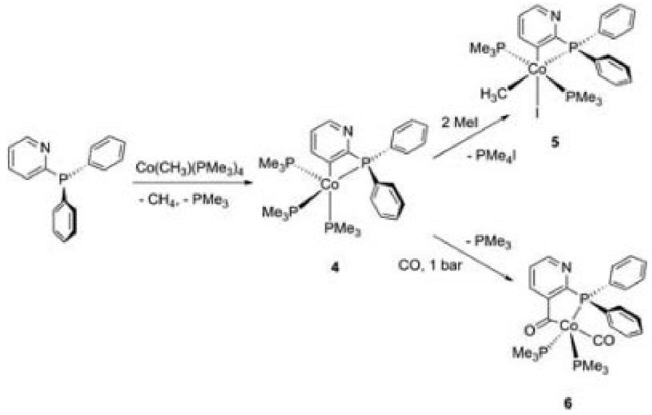
Reaction with 2-Diphenylphosphanylpyridine

Under similar reaction conditions as previously shown for (2-(2-diphenylphosphanyl)phenyl)-1,3-dioxalane, the reactions were carried out with 2-diphenylphosphanylpyridine (Scheme 2).

When solutions of $CoCH_3(PMe_3)_4$ and 2-diphenylphosphanyl-pyridine are combined in THF at −70 °C, the mixture darkens immediately and during warm up a gas evolution is detected (CH_4). Red, rhombic crystals of **4**, melting with decomposition above 98 °C, were obtained from diethyl ether solutions when cooling down to −27 °C.

In the $^{31}P\{^{1}H\}$ NMR spectrum of **4**, a pattern of three resonances is observed at [−10 (dt, $^{2}J_{P,P}$ = 42, 30 Hz, 1 P, PPh_2), 2.5 (dd, $^{2}J_{P,P}$ = 42, 12 Hz, 2 P, PCH_3) and 28 (dt, $^{2}J_{P,P}$ = 30, 12 Hz, 1 P, PCH_3) ppm], similar with **1**. The *Cs*-configuration of **4** was confirmed by the $^{13}C\{^{1}H\}$ NMR spectrum for 9 carbon resonances required in the aromatic region and the low-field shift for the metallated carbon atom at 168.0 ppm.

With 2-diphenylphosphanylpyridine it is the first example of an *ortho*-metallation (P,C-coordination) by a transition metal forming a four membered metallacycle, while in a more far related reaction of a pyridyldiphenylphosphanyloxide ligand with a platinum-methyl complex, a six-membered metallacycle (N,C-coordination) is observed [9].



Scheme 2. Cyclometallation, oxidative addition and carbon monoxide insertion reaction pathway with 2-diphenylphosphanylpyridine

Within 15 h, the appearance of a light-brown coloration and a white precipitate of tetramethylphosphonium iodide indicated an oxidative addition with iodomethane according to Scheme 2. Orange-brown crystals of **5** were obtained from either diethyl ether or pentane in moderate yields. With a tenfold excess iodomethane there was no higher yield than 28 %. ^{1}H NMR data are similar to those of **2** with a triplet ($^{3}J_{P,H}$ = 8.8 Hz) that arises from the $CoCH_3$ group and the two *trans* oriented trimethylphosphane ligands as virtual triplet ($|^{2}J_{P,H} + {}^{4}J_{P,H}|$ = 3.2 Hz).

The orange brown crystals of **5** were suitable for X-ray diffraction. Figure 3 shows the molecular structure of an *ortho*-metallated four-membered 2-diphenylphosphanylpyridine complex (metallation at the pyridine ring), the introduced CH_3-group, the iodo ligand and the three P-donor groups in *meridional* configuration. The both Co-C distances are similar with [1.934(3) Å] for sp^2-carbon and [2.028(3) Å] for sp^3-carbon. The Co1-P1 (PPh_2-donor) distance [2.309(3) Å] is slightly elongated compared with the two *trans* disposed trimethylphosphane ligands in similar distance with [Co1-P2 = 2.2443(8) and Co1-P3 = 2.2457(8) Å], while the Co1-I1 bond lengths (2.7003(6) Å) is close to the average values reported for related compounds [10]. The bond angles at cobalt deviate from ideal symmetry, because of steric repulsions. Those of the two *trans* coordinated phosphorus atoms appear to be augmented and the small bite angle [P1-Co1-C3 = 71.43(7)°] causes a bending of the three main axis towards the chelate ring. The main distortion in the octahedron can be found in the axis along the PPh_2-donor, cobalt and methyl group [P1-Co1-C1 = 159.89(7)°], due to the lower steric requirement of the methyl group. Similar angle distortions are described at Pt^{II}, Pt^{IV}, Rh^{III} und Ir^{III} when the metal is incorporated in four-membered metallacycles [11]. The main feature of regioselectivity is confirmed by the nitrogen position N1 (metallated ring).

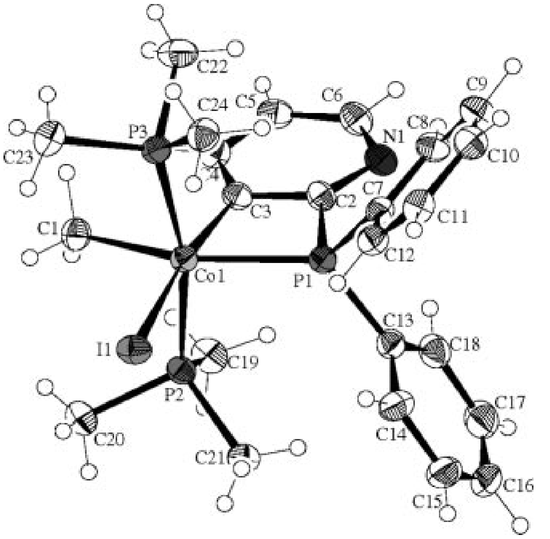


Figure 3. Molecular structure of **5**.

Selected distances/Å and angles/°: Co1-C1 2.028(3), Co1-C3 1.934(3), Co1-P1 2.309(3), Co1-P2 2.2443(8), Co1-P3 2.2457(8), Co1-I1 2.7003(6), C2-N1 1.338(3), N1-C6 1.346(3), C2-C3 1.403(3); P1-Co1-C3 71.43(7), P2-Co1-P3 167.09(3), C3-Co1-I1 170.83(7), C1-Co1-C3 88.46(10), P1-Co1-P2 96.47(5), P1-Co1-P3 96.24(4), P1-Co1-C1 159.89(7), I1-Co1-P1 99.40(3), I1-Co1-C1 100.71(7).

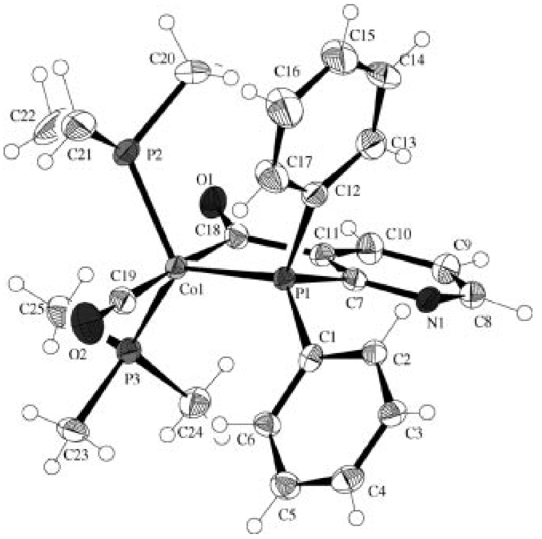


Figure 4. Molecular structure of **6**.

Selected distances/Å and angles/°: Co1-C18 1.943(3), Co1-C19 1.751(3), Co1-P1 2.1493(11), Co1-P2 2.1898(12), Co1-P3 2.1712(12), O1-C18 1.234(4), O2-C19 1.157(4), C7-C11 1.377(4), N1-C7 1.347(4); C18-Co1-P1 85.62(10), C19-Co1-C18 177.01(16), P1-Co1-P2 114.70(5), P1-Co1-P3 125.17(5), P3-Co1-P2 118.61(5), C19-Co1-P1 94.02(11), C19-Co1-P3 94.18(12), C19-Co1-P2 94.07(12).

The ring expansion (five-membered metallacycle) and subsequent mono substitution of an axial trimethylphosphane ligand (Scheme 2), is again observed when solutions of **4** are stirred under an atmosphere of carbon monoxide. In the IR spectrum of **6** the coordinated terminal CO ligand is detected at 1916 cm^{-1} (νC≡O), while the most striking feature is described by the $^{13}C\{^1H\}$ NMR spectrum for the resonance of the terminal carbonyl-group [221.0 ppm (m, CoC≡O)] and the acyl-function [259.5 ppm (m, CoC=O)] at low-field region, similar as found in **3**.

An X-ray diffraction from crystals of **6** was obtained, by cooling pentane solutions to −27 °C (Figure 4).

The cobalt atom resides in the center of a trigonal bipyramidal arrangement of two axial carbon donor atoms and three phosphorus nuclei in equatorial positions. The bite-angle of the chelating (2-diphenylphosphanyl)benzoyl-3-pyridyl ligand [C18-Co-P1 = 85.62(10)° is similar within experimental error to those of anionic phosphinophenolato (85.65(4)°) [12], or the acylphenolato (85.5(2)°) ligands [13].

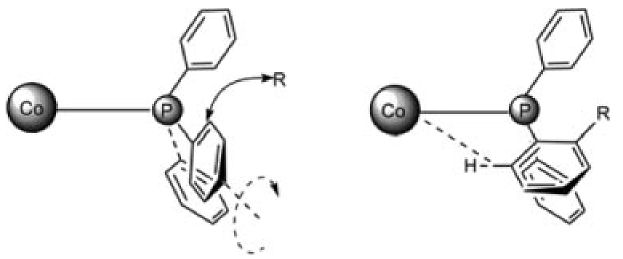
The coordination chemistry of 2-diphenylphosphanylpyridine is well established and the majority of these complexes describe a mononuclear P,N-coordination [14]. Other examples show a homonuclear [15], or heteronuclear [16], bridging of two metals with P,N-coordination. A cyclometallated 2-diphenylphosphanylpyridine (P,C-coordination) is not known up to today. The only related metallation is observed by a dinuclear rhenium complex where one phenyl ring is metallated [17]. It appears, that the preferred (P,N) coordination typically prevent an attack of the metal at the C-H bond and explains the scarcity of those types of complexes arising from C-H activation. Similar with the soft/hard (P,O)-chelating ligand (Scheme 1) the well balanced donor atom contributions from the more soft/soft (P,N) pre-chelating ligand is not suitable to facilitate such a coordination mode at a soft cobalt(I) atom.

Conclusion

Throughout C-H activation of monosubstituted 2-diphenylphosphanylaryl-ligands under mild conditions, four-membered cobaltacycles were synthesized. The reactions are 100 % regioselective. None of the reactions showed an incorporation of the heteroatoms (N, O) in a side reaction or C-H activation of other present *ortho* C-H bonds. These complexes easily react with carbon monoxide under ring expansion, when the novel five membered phosphinobenzoyl complexes are assembled and with iodomethane an oxidative addition is achieved forming stable low-spin d^6 cobalt complexes.

Independent of steric requirement in mono 2-substituted diphenylphosphanyl aryl ligands, the reaction pathway is always regioselective. The original notion of a steric hindered rotation caused by a substituent R (Scheme 3) for explaining regioselectivity that brings the C-H bond close to the metal is no longer supported, because cyclometallation of 2-diphenylphosphanylpyridine is believed to occur without hindered rotation.

It appears that the regioselectivity is influenced by the symmetry in the product complex (C_S−symmetry), which might be energetically favored. Alternatively, an activation of the phenylring caused by the substituents might be possible, but up today the regioselectivity also appears independent of electronic behavior of the substituents (electronic



Scheme 3. Sterically hindered rotation in regioselective *ortho*-metallation

donating or withdrawing substituents show the same regioselectivity).

We propose for every monosubstituted 2-diphenylphosphanylaryl-ligand a high regioselectivity, as long as a substituent is not incorporated in the coordination of the cobalt center. We suggest that these conclusions will prove general at least for $Co(CH_3)(PMe_3)_4$. Computational work is in progress to test this proposal.

Experimental Section

General Procedures and Materials: Standard vacuum techniques were used in manipulations of volatile and air-sensitive materials. Literature methods were used in the preparation of 2-diphenylphosphanylpyridine [18], and (2-(2-diphenylphosphanyl)phenyl)-1,3-dioxalane [19] and methyltetrakis-(trimethylphosphane)cobalt(I) [20]. The other chemicals were used as purchased. Infrared spectra (4000−400 cm^{-1}), as obtained from Nujol mulls between KBr disks, were recorded on a Nicolet 5700. ^{1}H, ^{13}C, and ^{31}P NMR (500, 300, 75, and 121 MHz, respectively) spectra were recorded on a Bruker DRX 500 and Avance 300 spectrometer. $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR resonances were obtained with broadband proton decoupling. Elemental analyses were carried out at Kolbe Microanalytical Laboratory, Mülheim/Ruhr (Germany) and on an Elementar Vario EL III. Melting points were measured in capillaries sealed under argon and are uncorrected. CCDC-678959 (for **1**), CCDC-686612 (for **3**), CCDC-678958 (for **5**) and CCDC-678957 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(2-Diphenylphosphanyl)-3-phenyl-(1,3-dioxalane-2-yl)-C,P)tris(trimethylphosphane)cobalt (1)

2-(2-Diphenylphosphanyl)phenyl-1,3-dioxalane (576 mg, 1.72 mmol) in 50 mL of diethyl ether was combined at −70 °C with $[CoCH_3(PMe_3)_4]$ (650 mg, 1.72 mmol) in 30 mL of diethyl ether. The reaction was accompanied by the evolution of a gas. After keeping the red-brown mixture at 20 °C for 16 h, the volatiles were removed in vacuo and the solid residue was extracted with two 70 mL portions of pentane. When the solution was kept at −27 °C, dark-red crystals of **1** were obtained. Yield 852 mg (81 %); m.p. 111−113 °C (dec.). − Anal calc. for $C_{30}H_{45}CoO_2P_4$ (620.5): calcd. C 58.07, H 7.31, P 19.97; found C 58.78, H 7.61, P 20.42 %.

IR (Nujol): $\tilde{\nu}$ = 3060 w, 3029 w, (C-H); 1581 w (C=C); 1538 m (CoC=C) cm^{-1}. − **^{1}H NMR** (500 MHz, $[D_8]$THF, 296 K): δ = 0.88 (d, $^{2}J_{P,H}$ = 6.2 Hz, 9 H, PCH_3), 1.20 (t′, $|^{2}J_{P,H} + {}^{4}J_{P,H}|$ = 4.4 Hz, 18 H, PCH_3), 3.20 (m, 2 H, OCH_2), 3.49 (m, 2 H, OCH_2), 5.72 (s, 1 H, CHO_2), 7.07 (d, $^{3}J_{H,H}$ = 7.4 Hz, 2 H, CH), 7.09−7.15 (m, 6 H, CH), 7.24 (t, $^{3}J_{H,H}$ = 7.0 Hz, 1 H, CH), 8.03 (t, $^{3}J_{H,H}$ = 7.5 Hz, 4 H, CH) ppm. − **^{13}C{^{1}H} NMR** (125.7 MHz, $[D_8]$THF, 296 K): δ = 23.5 − 23.8 (m, PCH_3(eq)), 23.9 − 24.1 (m, PCH_3(ax)), 64.9 (s, C-O), 101.1 (d, $^{4}J_{P,C}$ = 6.2 Hz, OCO), 118.6 (m, CH), 128.3 (d, $^{3}J_{P,C}$ = 7.8 Hz, CH), 128.8 (s, CH), 129.6 (d, $^{2}J_{P,C}$ = 12.9 Hz, CH), 130.8 (d, $^{4}J_{P,C}$ = 4.5 Hz, CH), 133.2 (d, $^{2}J_{P,C}$ = 13.5 Hz, CH), 139.2 (m, C), 139.8 (m, C), 153.7 (d, $^{1}J_{P,C}$ = 18.7 Hz, C), 171.1 (m, CoC) ppm. − **^{31}P{^{1}H} NMR** (202 MHz, $[D_8]$THF, 233 K): δ = −19.5 (dt, $^{2}J_{P,P}$ = 86 and 71 Hz, 1 P, PPh_2), 2.4 (dd, $^{2}J_{P,P}$ = 86 and 44 Hz, 2 P, PCH_3), 27.7 (dt, $^{2}J_{P,P}$ = 71 and 44 Hz, 1 P, PCH_3) ppm.

Iodo-methyl-(2-diphenylphosphanyl)-3-phenyl-(1,3-dioxalane-2-yl)-C,P)bis(trimethylphosphane)cobalt (2)

A solution of **1** (810 mg, 1.30 mmol) in 30 ml THF was combined with excess iodomethane (0.16 mL, 425 mg, 3.00 mmol) in THF (50 mL) at −70 °C. The solution was allowed to warm to ambient temperature and within 4 h the mixture took on a light-brown color and became turbid. After 15 h at 20 °C, the volatiles were removed in vacuo and the brown solid was extracted with a mixture of 80 mL diethyl ether / pentane (1:1). On storage of the extract at 4 °C, orange-brown crystals were obtained. Yield 340 mg (38 %); m.p. 123−125 °C. − (dec.). − Anal calc. for $C_{28}H_{39}CoIO_2P_3$ (686.38): calcd. C 49.00, H 5.73, P 13.54; found C 49.37, H 6.12, P 14.01 %.

IR (Nujol): $\tilde{\nu}$ = 3051 w, (C-H); 1581 w (C=C); 1535 m (CoC=C) 1157 m (δ $CoCH_3$) cm^{-1}. − **^{1}H NMR** (500 MHz, $[D_8]$THF): δ = 0.49 (dt, $^{3}J_{P,H}$ = 9.1 Hz, $^{3}J_{P,H}$ = 1.7 Hz, 3 H, $CoCH_3$), 1.05 (t′, $|^{2}J_{P,H} + {}^{4}J_{P,H}|$ = 3.7 Hz, 18 H, PCH_3), 3.18 (s(br), 2 H, OCH_2), 3.44 (s(br), 2 H, OCH_2), 5.64 (s, 1 H, CHO_2), 7.01 (d, $^{3}J_{H,H}$ = 7.5 Hz, 2 H, CH), 7.12−7.17 (m, 6 H, CH), 7.24 (dt, $^{3}J_{H,H}$ = 7.0 Hz, $^{4}J_{H,H}$ = 0.7 Hz, 1 H, CH), 8.03 (dt, $^{3}J_{H,H}$ = 7.5 Hz, $^{4}J_{H,H}$ = 0.6 Hz, 4 H, CH) ppm. − **^{13}C{^{1}H} NMR** (125.5 MHz, $[D_8]$THF): δ = 15.2 (t′, $|^{1}J_{P,C} + {}^{3}J_{P,C}|$ = 26.5 Hz, PCH_3), 63.7 (s, C-O), 98.9 (d, $^{4}J_{P,C}$ = 7.3 Hz, OCO), 118.4 (m, CH), 128.2 (d, $^{3}J_{P,C}$ = 8.0 Hz, CH), 128.8 (s, CH), 129.9 (d, $^{2}J_{P,C}$ = 11.9 Hz, CH), 130.8 (s, CH), 133.2 (d, $^{1}J_{P,C}$ = 13.5 Hz, CH), 138.2 (s, C), 139.8 (s, C), 151.5 (d, $^{1}J_{P,C}$ = 20.1 Hz, C), 169.1 (m, CoC) ppm. − **^{31}P{^{1}H} NMR** (202 MHz, $[D_8]$THF, 233 K): δ = 11.6 (d, $^{2}J_{P,P}$ = 26.5 Hz, 2 P, PMe_3), −34.4 (t, $^{2}J_{P,P}$ = 26.5 Hz, 1 P, PPh_2) ppm.

(2-Diphenylphosphanyl)-3-benzoyl-(1,3-dioxalane-2-yl)-C,P)(carbonyl)bis(trimethylphosphane)cobalt (3)

A sample of **1** (920 mg, 1.48 mmol) in 70 mL of pentane was kept stirring under 1 bar of carbon monoxide for 16 h during which time the color of the mixture turned from red to orange. The volatiles were removed in vacuo, and the solid residue was extracted with two 50 mL portions of diethyl ether. Crystallization at 4 °C furnishes orange-red rhombic crystals of **3**. Yield 658 mg (74 %); m.p. 152−154 °C (dec.). − Anal calc. for $C_{29}H_{36}CoO_4P_3$ (600.4): calcd. C 58.01, H 6.04, P 15.48; found C 57.88, H 5.56, P 15.71 %.

IR (Nujol): $\tilde{\nu}$ = 1854 vs (C≡O), 1582 m (C=C), 1538 w (CoC=C) cm^{-1}. − **^{1}H NMR** (500 MHz, $[D_8]$THF): δ = 1.15 (t′, $|^{2}J_{P,H} + {}^{4}J_{P,H}|$ = 7.2 Hz, 18 H, PCH_3), 3.12 (ddd, $^{3}J_{H,H}$ = 7.5 Hz, $^{3}J_{H,H}$ = 6.1 Hz, $^{2}J_{H,H}$ = 3.6 Hz, 2 H, OCH_2), 3.53 (ddd, $^{3}J_{H,H}$ = 7.5 Hz, $^{3}J_{H,H}$ = 6.1 Hz, $^{2}J_{H,H}$ = 3.6 Hz, 2 H, OCH_2), 5.94 (s, 1 H, CHO_2), 7.12 (dd, $^{3}J_{H,H}$ = 7.2 Hz, $^{3}J_{H,H}$ = 7.0 Hz, 2 H, CH), 7.17−7.21 (m, 4 H, CH), 7.41 (dt, $^{3}J_{H,H}$ = 7.5 Hz, $^{4}J_{H,H}$ = 2.7 Hz, 1 H, CH), 7.90 − 7.96 (m, 5 H, CH), 8.17 (dd, $^{3}J_{H,H}$ = 7.5 Hz, $^{4}J_{H,H}$ = 0.9 Hz, 1 H, CH) ppm. − **^{13}C{^{1}H} NMR** (125.4 MHz, $[D_8]$THF): δ = 18.3 (dt, $^{1}J_{P,C}$ = 12.8 Hz, $^{3}J_{P,C}$ = 4.5 Hz, PCH_3), 63.7 (s, C-O), 100.4 (d, $^{3}J_{P,C}$ = 1.5 Hz, OCO), 121.1 (d, $^{1}J_{P,C}$ = 20.3 Hz, CH), 127.06 (s, CH), 127.10 (s, CH), 128.6 (d, $^{4}J_{P,C}$ = 3.0 Hz, CH), 130.1 (d, $^{2}J_{P,C}$ = 12.8 Hz, CH), 130.3 (s, CH), 138.2 (td, $^{1}J_{P,C}$ = 27.9 Hz, $^{4}J_{P,C}$ = 3.7 Hz, C), 138.5 (s, C), 139.3 (s, C), 158.5 (s, C), 222.1 (m, C≡O), 260.2 (m, CoC=O) ppm. − **^{31}P{^{1}H} NMR** (202 MHz, $[D_8]$THF, 233 K): δ = 14.7 (d, $^{2}J_{P,P}$ = 72.2 Hz, 2 P, PMe_3), 90.3 (t, $^{2}J_{P,P}$ = 72.2 Hz, 1 P, PPh_2) ppm.

(2-Diphenylphosphanyl)-3-pyridyl-C,P)tris(trimethylphosphane)cobalt (4)

2-Diphenylphosphanylpyridine (548 mg, 2.08 mmol) in 50 mL of THF was combined at −70 °C with $[\mathrm{CoCH_3(PMe_3)_4}]$ (788 mg, 2.08 mmol) in 30 mL of THF. The reaction was accompanied by the evolution of a gas. After keeping the red-brown mixture at 20 °C for 16 h, the volatiles were removed in vacuo and the solid residue was extracted with two 70 mL portions of diethyl ether. When the solution was kept at −27 °C, red rhombic crystals of **4** were obtained. Yield 778 mg (68 %); m.p. 98−100 °C (dec.). − Anal calc. for $C_{26}H_{40}CoNP_4$ (549.44): calcd. C 56.84, H 7.34, N 2.55; found C 57.17, H 7.63, N 2.42 %.

IR (Nujol): $\tilde{\nu}$ = 1583 m (C=C), 1534 m (CoC=C) $\mathrm{cm^{-1}}$. − **^{1}H NMR** (300 MHz, [D$_6$]Benzene, 296 K): δ = 1.25 (s(br), 27 H, PCH$_3$), 6.53 (t, $^{3}J_{\mathrm{H,H}}$ = 7.5 Hz, 1 H, CH), 7.07 (t, $^{3}J_{\mathrm{H,H}}$ = 8.0 Hz, 1 H, CH), 7.24−7.29 (m, 6 H, CH), 7.66 (d, $^{3}J_{\mathrm{H,H}}$ = 7.3 Hz, 1 H, CH), 7.70 − 7.74 (m, 4 H, CH) ppm. − **^{13}C{^{1}H} NMR** (75.1 MHz, [D$_6$]Benzene, 296 K): δ = 21.7−22.9 (m, PCH$_3$), 115.4 (s, CH), 126.5 (d, $^{3}J_{\mathrm{P,C}}$ = 7.8 Hz, CH), 126.8 (s, CH), 127.5 (s, CH), 131.7 (d, $^{2}J_{\mathrm{P,C}}$ = 12.9 Hz, CH), 138.0 (s, C), 138.6 (s, C), 157.2 (d, $^{3}J_{\mathrm{P,C}}$ = 6.9 Hz, NC), 168.0 (m, CoC) ppm. − **^{31}P{^{1}H} NMR** (121.1 MHz, [D$_6$]Benzene, 296 K): δ = −10 (dt, $^{2}J_{\mathrm{P,P}}$ = 42 and 30 Hz, 1 P, PPh$_2$), 2.5 (dd, $^{2}J_{\mathrm{P,P}}$ = 42 and 12 Hz, 2 P, PCH$_3$), 28 (dt, $^{2}J_{\mathrm{P,P}}$ = 30 and 12 Hz, 1 P, PCH$_3$) ppm.

Iodo-methyl-(2-diphenylphosphanyl)-3-pyridyl-C,P)bis(trimethylphosphane)cobalt (5)

A solution of **4** (510 mg, 0.92 mmol) in 30 ml THF was combined with excess iodomethane (0.14 mL, 342 mg, 2.41 mmol) in THF (50 mL) at −70 °C. The solution was allowed to warm to ambient temperature and within 8 h the mixture took on orange-brown color. After 15 h at 20 °C, the volatiles were removed in vacuo and the brown solid was extracted with a mixture (80 mL) of pentane/THF 5:1. On storage of the extract at 4 °C, orange-brown crystals were obtained. Yield 159 mg (28 %); m.p. 126−128 °C. − Anal calc. for $C_{24}H_{34}CoINP_3$ (615.30): calcd. C 46.85, H 5.57, N 2.28; found C 47.48, H 5.80, N 2.20 %.

IR (Nujol): $\tilde{\nu}$ = 3049 w, (C-H); 1581 w (C=C); 1540 m (CoC=C) 1161 m (δ CoCH$_3$) $\mathrm{cm^{-1}}$. − **^{1}H NMR** (300 MHz, [D$_6$]Benzene, 296 K): δ = 0.73 (t, $^{3}J_{\mathrm{P,H}}$ = 8.8 Hz, 3 H, CoCH$_3$), 1.05 (t′, $|^{2}J_{\mathrm{P,H}} + {}^{4}J_{\mathrm{P,H}}|$ = 3.2 Hz, 18 H, PCH$_3$), 6.74 (t, $^{3}J_{\mathrm{H,H}}$ = 7.2 Hz, 1 H, CH), 6.87 (t, $^{3}J_{\mathrm{H,H}}$ = 7.5 Hz, 1 H, CH), 7.01−7.08 (m, 6 H, CH), 7.26 (m, 1 H, CH), 8.21 (m, 3 H, CH), 8.44 (s, 1 H, NCH) ppm. − **^{13}C{^{1}H} NMR** (75.5 MHz, [D$_6$]Benzene, 296 K): δ = 14.2 (s, CoCH$_3$), 14.9 (t, $^{1}J_{\mathrm{P,C}}$ = 15.1 Hz, PCH$_3$), 127.4 (d, $^{3}J_{\mathrm{P,C}}$ = 7.5 Hz, CH), 128.1 (s, CH), 131.2 (d, $^{3}J_{\mathrm{P,C}}$ = 8.3 Hz, CH), 133.7 (d, $^{1}J_{\mathrm{P,C}}$ = 20.3 Hz, C), 137.2 (d, $^{2}J_{\mathrm{P,C}}$ = 14.3 Hz, CH), 141.3 (d, $^{1}J_{\mathrm{P,C}}$ = 18.8 Hz, CH), 144.5 (d, $^{2}J_{\mathrm{P,C}}$ = 10.5 Hz, CH), 164.2 (m, NC), 195.2 (m, CoC) ppm. − **^{31}P{^{1}H} NMR** (121.5 MHz, [D$_6$]Benzene, 296 K): δ = 14.9 (s(br), 2 P, PMe$_3$), −23.1 (s(br), 1 P, PPh$_2$) ppm.

(2-Diphenylphosphanyl)benzoyl-3-pyridyl-C,P)(carbonyl)bis-(trimethylphosphane)cobalt (6)

A sample of **4** (750 mg, 1.36 mmol) in 70 mL of pentane was kept stirring under 1 bar of carbon monoxide for 3 h during which time the color of the mixture turned orange. The volatiles were removed in vacuum, and the solid residue was extracted with two 80 mL portions of diethyl ether. Crystallization at 4 °C affords red rhombic crystals of **6**. Yield 455 mg (63 %); m.p. 159−161 °C (dec.). − Anal calc. for $C_{25}H_{31}CoNO_2P_3$ (529.4): calcd. C 56.72, H 5.90, N 2.65; found C 57.22, H 6.14, N 2.58 %.

IR (Nujol): $\tilde{\nu}$ = 1916 vs (C≡O), 1568 m (C=C), 1537 w (C=O) $\mathrm{cm^{-1}}$. − **^{1}H NMR** (300 MHz, [D$_6$]Benzene, 296 K): δ = 1.22 (t′, $|^{2}J_{\mathrm{P,H}} + {}^{4}J_{\mathrm{P,H}}|$ = 7.2 Hz, 18 H, PCH$_3$), 6.68 (ddd, $^{3}J_{\mathrm{H,H}}$ = 7.8 Hz, $^{4}J_{\mathrm{H,H}}$ = 0.9 Hz, $^{3}J_{\mathrm{P,H}}$ = 4.5 Hz, 1 H, CH), 7.10 (dd, $^{3}J_{\mathrm{H,H}}$ = 7.2 Hz, $^{4}J_{\mathrm{H,H}}$ = 1.2 Hz, 2 H, CH), 7.13−7.20 (m, 4 H, CH), 7.93 (td, $^{3}J_{\mathrm{H,H}}$ = 7.5 Hz, $^{4}J_{\mathrm{H,H}}$ = 2.1 Hz, 1 H, CH), 8.11 (ddd, $^{3}J_{\mathrm{H,H}}$ = 7.8 Hz, $^{4}J_{\mathrm{P,H}}$ = 3.3 Hz, $^{5}J_{\mathrm{H,H}}$ = 0.9 Hz, 4 H, CH), 8.61 (dd, $^{4}J_{\mathrm{P,H}}$ = 4.5 Hz, $^{4}J_{\mathrm{H,H}}$ = 1.5 Hz, 1 H, CH) ppm. − **^{13}C{^{1}H} NMR** (75.5 MHz, [D$_6$]Benzene, 296 K): δ = 18.68 (dt, $^{2}J_{\mathrm{P,C}}$ = 12.8 Hz, $^{3}J_{\mathrm{P,C}}$ = 3.7 Hz, PCH$_3$), 125.8 (d, $^{1}J_{\mathrm{P,C}}$ = 18.8 Hz, CH), 126.7 (d, $^{3}J_{\mathrm{P,C}}$ = 9.1 Hz, CH), 127.7 (d, $^{4}J_{\mathrm{P,C}}$ = 1.5 Hz, CH), 131.7 (d, $^{2}J_{\mathrm{P,C}}$ = 12.8 Hz, CH), 137.9 (t, $^{4}J_{\mathrm{P,C}}$ = 3.1 Hz, C), 138.5 (t, $^{4}J_{\mathrm{P,C}}$ = 3.2 Hz, C), 148.4 (s, C), 149.9 (d, $^{3}J_{\mathrm{P,C}}$ = 7.5 Hz, C), 166.9 (d, $^{1}J_{\mathrm{P,C}}$ = 40.7 Hz, NC), 221.0 (m, CoC≡O), 259.5 (m, CoC=O) ppm. − (121.5 MHz, [D$_6$]Benzene, 296 K): δ = 15.8 (d, $^{2}J_{\mathrm{P,P}}$ = 65.3 Hz, 2 P, PMe$_3$), 80.5 (t, $^{2}J_{\mathrm{P,P}}$ = 65.3 Hz, 1 P, PPh$_2$) ppm.

Crystal Structure Analysis

Data collections were performed on a STOE IPDSII image plate detector and on a Bruker AXS SMART APEX diffractometer using Mo Kα radiation (λ = 0.71019 Å). Details of the crystal structure are given in Table 1 and Table 2. Data collection [21]: Stoe X-AREA, Bruker SMART. Data reduction [21]: Stoe X-RED, Bruker SAINT. The structures were solved by direct methods using SHELXS-97 [22] and anisotropic displacement parameters were applied to non-hydrogen atoms in a full-matrix least-squares refinement based on F^2 using SHELXL-97 [22]. Hydrogen atoms on C were placed at idealized positions (C-H = 0.93 Å, 0.96 Å for methyl groups) and were allowed to ride on the parent atom [U_{iso}(H) = 1.2U(C) for CH groups and U_{iso}(H) = 1.5U(C) for methyl groups].

Table 1. Crystal data for compounds **1** and **3**

	1	**3**
Empirical formula	$C_{30}H_{45}CoO_2P_4$	$C_{29}H_{36}CoO_4P_3$
Molecular mass	620.47	600.42
Crystal size /mm	0.12 × 0.17 × 0.3	0.08 × 0.10 × 0.15
Crystal system	monoclinic	monoclinic
Space group	*C*2/c	$P2_1$/n
a /Å	42.537(11)	12.245(3)
b /Å	9.435(3)	14.649(4)
c /Å	17.969(5)	16.768(4)
β /°	112.024(4)	92.514(5)
V /Å^3	6685.36(3)	3005.0(13)
Z	8	4
$D_{\mathrm{calcd.}}$ /(g/cm^3)	1.233	1.327
μ(Mo-Kα) /mm^{-1}	0.729	0.762
Temperature /K	293(2)	293(2)
Data coll. range /°	$2.1 \le 2° \le 50$	$3.6 \le 2° \le 51$
h	$-50 \le h \le 24$	$-14 \le h \le 14$
k	$-10 \le k \le 11$	$-14 \le k \le 17$
l	$-21 \le l \le 21$	$-19 \le l \le 18$
No. reflect. measured	16734	15696
No. unique data	5908[R_{int}=0.0260]	5325[R_{int}=0.0778]
Parameters	334	335
GoF on F^2	1.080	1.030
$R1$[I≥ 2σ(I)]	0.0358	0.0517
$wR2$(alldata)	0.0976	0.1163

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Table 2. Crystal data for compounds **5** and **6**

	5	**6**
Empirical formula	$C_{24}H_{34}CoINP_3$	$C_{25}H_{31}CoNO_2P_3$
Molecular mass	615.26	529.35
Crystal size /mm	0.11 × 0.34 × 0.46	0.08 × 0.10 × 0.12
Crystal system	orthorhombic	triclinic
Space group	*P*bca	$P\bar{1}$
a /Å	11.321(2)	9.883(2)
b /Å	14.072(3)	14.499(3)
c /Å	32.44(4)	18.931(4)
α /°		105.52(3)
β /°		96.64(3)
γ /°		90.18(3)
V /Å^3	5169(7)	2594.6(9)
Z	8	2
$D_{calcd.}$ /(g/cm^3)	1.581	1.355
μ(Mo-Kα) /mm^{-1}	2.056	0.868
Temperature /K	293(2)	293(2)
Data coll. range /°	4.2 ≤ 2° ≤ 54	3.1 ≤ 2° ≤ 52
h	$-14 \le h \le 14$	$-12 \le h \le 12$
k	$-17 \le k \le 17$	$-16 \le k \le 17$
l	$-41 \le l \le 41$	$-23 \le l \le 23$
No. reflect. measured	37919	18627
No. unique data	5582[R_{int}=0.0583]	9490[R_{int}=0.0474]
Parameters	407	804
GoF on F^2	1.103	1.033
$R1[I \ge 2\sigma(I)]$	0.0317	0.0464
$wR2$(alldata)	0.0913	0.1361

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