

Regiospecific Cyclometalation of Diphenyl(2-substituted phenyl)phosphane with Methyltetrakis(trimethylphosphane)cobalt(I)

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The pre-chelate molecules 2-(diphenylphosphanyl)-*N,N*-dimethylaniline, [2-(diphenylphosphanyl)benzyl]dimethylamine, 1-(diphenylphosphanyl)-2-ethylbenzene, 1-(diphenylphosphanyl)-2-isopropylbenzene, and 2-(diphenylphosphanyl)benzonitrile, in a reaction with [CoMe(PMe₃)₄], eliminate methane to afford the selectively 6-*ortho*-metalated complexes **1**–**5** that contain four-membered metallacycles. The molecular structure of **3** shows a *tbp*-coordinated cobalt atom, with axial C and PMe₃ donor groups. Metalation in the aliphatic side-chain occurs with 2-(diphenylphosphanyl)toluene, giving complex **6** that contains a five-membered metallacycle. Benzyldiphenylphosphane is selectively *ortho*-metalated in the benzyl group, affording **7**. As shown by the molecular structures, complex **7** is a true ligand isomer of **6**. Substitution of a trimethylphosphane group in compounds **4** and **6** by ethene gives the pentacoordinate complexes **8** and

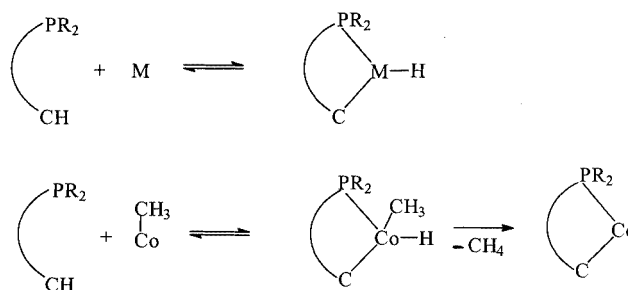
9, respectively. The ethene ligand is π -coordinated in the equatorial plane of a trigonal bipyramid. Under 1 bar of CO, complex **6** forms monocarbonyl complex **10**. Carbonylation of complexes **3** and **4** proceeds by insertion of CO into the Co–C bond under ring expansion, affording the aroylcobalt complexes **11** and **12**, respectively. Complex **6** reacts with iodomethane in an oxidative substitution reaction yielding a structurally characterized octahedral complex *mer*-**13**, which eliminates a methyl group in THF at 20 °C to form a penta-coordinate cobalt(II) complex **14**. Complex **3** oxidatively adds iodomethane in a stereoselective *cis* addition to give the cobalt(III) complex *mer*-**15**, which retains its four-membered metallacycle and the CoCH₃ group.

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Introduction

Cyclometalation reactions are among the oldest C–H-activation processes, and those involving phenylphosphanes are well known in electron-rich complexes of the late transition metals.^[1] In many cases cyclometalation has been shown to be a reversible reaction involving an oxidative-addition and a reductive-elimination step (Scheme 1).

A residual methylmetal function can utilize the new hydrido ligand in an alternative reductive elimination reaction and can also stabilize three-membered Zr–N–C rings.^[2] With [CoMe(PMe₃)₄], the subsequent elimination of methane, which proceeds at –70 °C, renders the formation of a metallacycle practically irreversible, since methane does not react in the same manner as dihydrogen at 20 °C in a hydrogenolytic cleavage reaction.^[3] Given a selective course of such cyclometalation reactions, we do not expect the kinetically favored product complex to undergo equilibration



Scheme 1. Reversible and irreversible cyclometalation reactions

of possible isomers. We have recently found an unusually high selectivity in the reaction of [CoMe(PMe₃)₄] with 2-(diphenylphosphanyl)-*N,N*-dimethylaniline,^[4] and report here on our investigation of substituent effects on the selectivity of cyclometalation reactions. Our strategy was firstly to generate gradual steric and electronic changes in the vicinity of the anchoring PPh₂ group in order to favor attack at the available four sites in the unsubstituted phenyl groups, and secondly to provide 2-substituents that would favor an attack at the side-chain. Investigation of molecular structures with respect to ring size and bite-angle of chelating ligands are warranted because these parameters have

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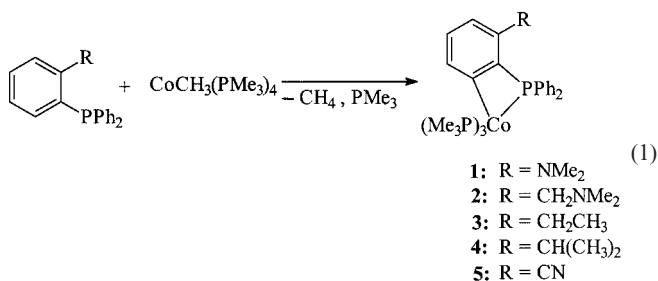
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been shown in homogeneous catalysis to be among the most sensitive steering devices within the metal coordination sphere.^[5]

Results and Discussion

a) The $\text{ArNMe}_2 \rightarrow \text{ArCH}_2\text{NMe}_2 \rightarrow \text{ArCH}_2\text{Me} \rightarrow \text{ArCHMe}_2$ Line

A side-chain in one of the six *ortho* positions of triphenylphosphane containing an N-donor function and activated aliphatic C–H bonds was provided in the pre-chelate molecules 2-(diphenylphosphanyl)-*N,N*-dimethylaniline, [2-(diphenylphosphanyl)benzyl]dimethylamine, 1-(diphenylphosphanyl)-2-ethylbenzene, and 1-(diphenylphosphanyl)-2-isopropylbenzene. Reactions with $[\text{CoMe}(\text{PMe}_3)_4]$ proceeded at -70°C in THF [Equation (1)], and afforded the selectively *ortho*-metalated complexes **1**,^[4] and **2–4**.



The ^{31}P NMR spectra at 233 K most clearly show three resonances with chemical shifts and a coupling pattern which are characteristic of an *ortho*-metalated tris(trimethylphosphane)cobalt complex.^[3] As no other signals are detected, the absence of possible isomers in solution (< ca. 2%) is demonstrated in all four compounds.

The dominant feature in the molecular structure of **3** is a four-membered cobaltacycle (Figure 1), in which the chelating ligand spans the C-axial and P-equatorial positions of a trigonal bipyramid. The small bite-angle $[\text{C}12\text{--Co--P}1 = 71.02(15)^\circ]$, which falls just outside the range of Rh and Ir complexes ($67\text{--}69^\circ$),^[6] causes bending between the axial positions $[\text{C}12\text{--Co--P}4 = 166.25(15)^\circ]$. Bond lengths and angles do not substantially deviate from those in the unsubstituted molecule.^[3]

b) The $\text{ArNMe}_2 \rightarrow \text{ArCH}_2\text{Me} \rightarrow \text{ArCN}$ Line

Electron-donating dimethylamino and ethyl groups were replaced by the strong electron-accepting cyano group. However, reaction of $[\text{CoMe}(\text{PMe}_3)_4]$ with 2-(diphenylphosphanyl)benzonitrile followed the same route as in Equation (1), affording **5** as a single *ortho*-metalated isomer. The ^{31}P NMR spectrum at 233 K closely resembles those of **1–4**. Thus, there is little chance for the electronic steering of the *ortho*-metalation reaction.

c) The $\text{ArOH} \rightarrow \text{ArNH}_2 \rightarrow \text{ArCH}_3$ Line

The isoelectronic donor functions of the pre-chelate systems in 2-(diphenylphosphanyl)phenol or 2-(diphenylphos-

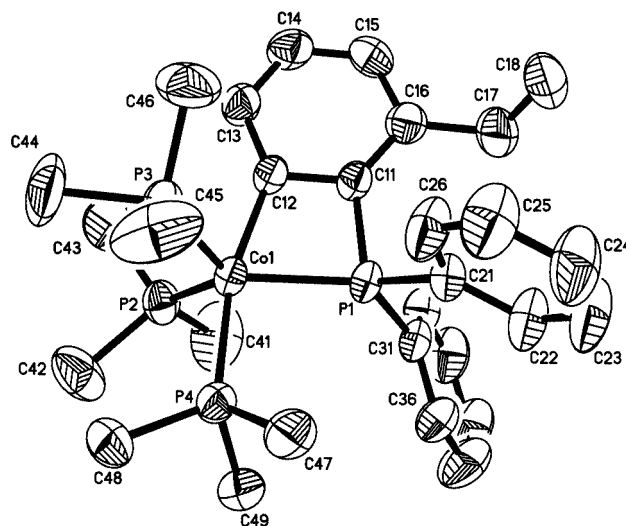
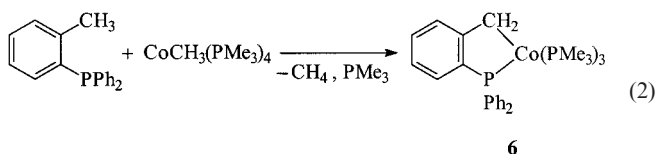


Figure 1. Molecular structure of **3** (ORTEP plot with hydrogen atoms omitted); selected bond lengths [Å] and angles $^\circ$: Co–C12 1.984(5), Co–P1 2.2103(14), Co–P2 2.1639(17), Co–P3 2.1691(17), Co–P4 2.1857(17), P1–C11 1.796(6), C11–C12 1.401(7); C12–Co–P1 71.02(15), C12–Co–P2 90.96(16), C12–Co–P3 90.89(15), C12–Co–P4 166.25(15), P1–Co–P2 119.25(7), P1–Co–P3 121.97(7), P1–Co–P4 95.23(6), P2–Co–P3 115.56(7), P2–Co–P4 95.79(7), P3–Co–P4 96.95(7)

phanyl)aniline were compared with the P,C-donor group in 2-(diphenylphosphanyl)toluene. Reaction of this type of weak C–H acid with $[\text{CoMe}(\text{PMe}_3)_4]$ at -70°C produces methane [Equation (2)].



From a red-brown solution in pentane, complex **6** is obtained as black prismatic crystals. In the ^1H NMR spectrum at 296 K, a broad resonance at $\delta = 1.80$ ppm (2 H) containing multiple phosphorus coupling is assigned to a CoCH_2 group. Doublet and pseudotriplet PCH₃ resonances with intensity ratios of 1:2 also indicate little ligand mobility. Complex **6** remains pentacoordinate, which differs from the rapidly exchanging trimethylphosphane from [P,O]-chelate and [P,N]-chelate systems on the NMR time scale. However, the ^{31}P NMR chemical shifts at 233 K are found in similar positions to those of the [P,N] and [P,O] complexes, and are in no way related to those in complexes **1–4**.

Therefore, a selective attack appears to be directed at the *ortho*-methyl group to form a five-membered metallacycle, which is known to form with platinum.^[7] The molecular structure (Figure 2) is entirely consistent with the configuration of **6** derived from the solution data. A cobalt atom is centered in a trigonal bipyramid with axial CH₂ and PMe₃ groups and a five-membered metallacycle occupying C-axial and P-equatorial positions with a narrow bite-angle $[\text{C}10\text{--Co--P}1 = 77.77(17)^\circ]$ and considerable ring bending

(sum of internal angles = 518.8°). The Co–C10 distance [2.080(5) Å] is within the range of Co–C(sp³) bonds (2.03–2.15 Å),^[8] and Co–P distances are typical and appear unaffected by the *trans* influence of the distant CH₂ group. We note here an unexpected and complete switching of the cyclometalation reaction on changing from a 2-methyl to a 2-ethyl group.

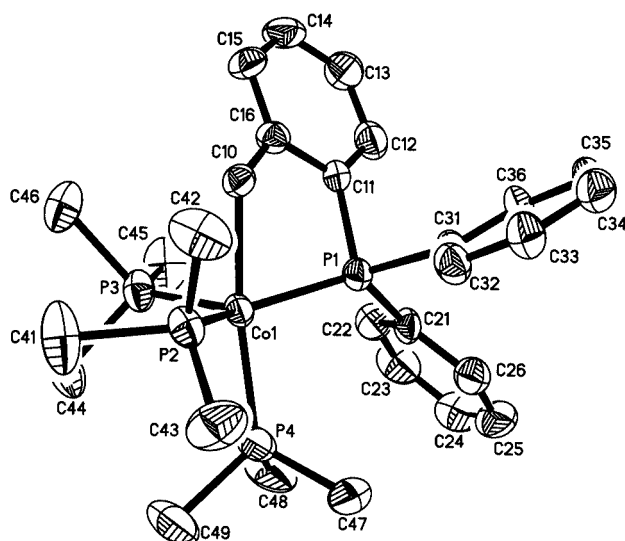
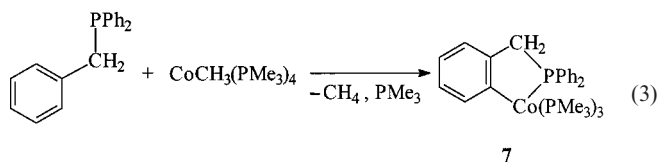


Figure 2. Molecular structure of **6** (ORTEP plot with hydrogen atoms omitted); selected bond lengths [Å] and angles [°]: Co–C10 2.080(5), Co–P1 2.1646(18), Co–P2 2.206(2), Co–P3 2.186(2), Co–P4 2.180(2), P1–C11 1.827(7), C10–C16 1.494(8), C11–C16 1.399(8); C10–Co–P1 77.77(17), C10–Co–P2 87.15(17), C10–Co–P3 88.10(18), C10–Co–P4 172.48(18), P1–Co–P2 132.14(8), P1–Co–P3 114.22(8), P1–Co–P4 95.86(7), P2–Co–P3 110.29(7), P2–Co–P4 94.36(8), P3–Co–P4 98.26(8)

Formation of a five-membered cobaltacycle with reversed ring positions of Co(PMe₃)₃ and PPh₂ groups can be expected from a reaction of [CoMe(PMe₃)₄] with benzyldiphenylphosphane [Equation (3)].



When the reactants are combined at –70 °C, the color changes to red-brown and the evolution of gas commences. Eventually, red crystals of **7**, which are air-sensitive and decompose under argon above 75 °C, were obtained from pentane. The ³¹P NMR spectrum contains a doublet of triplets (δ = 63 ppm, PPh₂) and two doublets of doublets (δ = –4 and 22 ppm, PMe₃), with couplings that suggest a five-membered cobaltacycle in the C(axial)/P(equatorial) positions of a trigonal bipyramid. The expected configuration is observed in the molecular structure of **7** (Figure 3).

All bond lengths in **7** are similar to those in the ligand isomer **6** (Figure 2). In particular, the distance [Co–C11 = 2.011(4) Å] falls in the range reported for Co–C(sp²) bonds

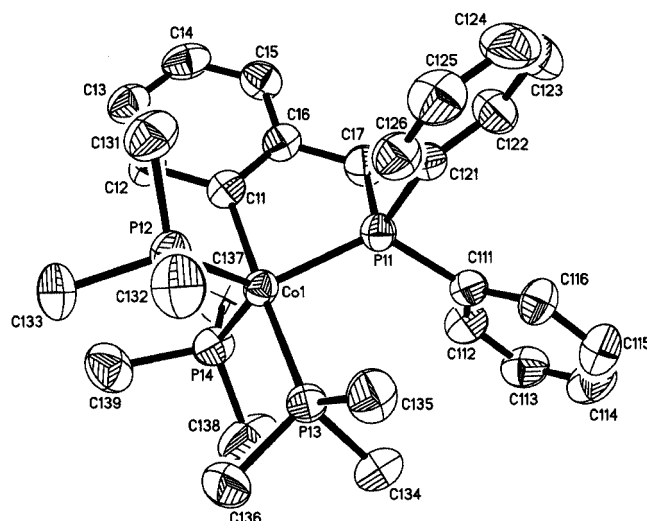
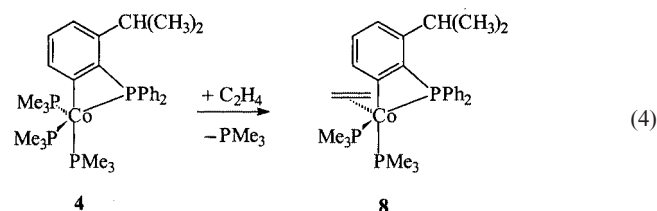


Figure 3. Molecular structure of **7** (molecule A) (ORTEP plot with hydrogen atoms omitted); selected bond lengths [Å] and angles [°]: Co–C11 2.011(4), Co–P11 2.1625(12), Co–P12 2.2197(13), Co–P13 2.1994(12), Co–P14 2.1833(13), P11–C17 1.830(4), C16–C17 1.501(5), C11–C16 1.415(6); C11–Co–P11 83.08(12), C11–Co–P12 88.51(12), C11–Co–P13 177.17(12), C11–Co–P14 84.22(12), P11–Co–P12 120.47(5), P11–Co–P13 94.83(5), P11–Co–P14 119.37(5), P12–Co–P13 94.21(5), P12–Co–P14 118.13(5), P13–Co–P14 95.19(5), Co–C11–C16 120.6(3), C11–C16–C17 118.0(4), C16–C17–P11 106.2(3)

(1.97–2.01 Å).^[8,9] The approximation to an ideal tbp geometry is better in **7**, and the sum of the internal angles in the cobaltacycle (532.7°) is closer to planarity (540°) than in **6** (518.8°).

d) Reactions with Ethene

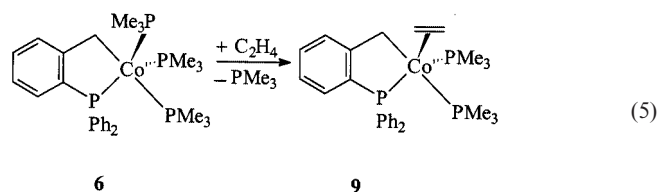
π-Olefin coordination in aryl(trimethylphosphane)cobalt(i) complexes is an expected phenomenon.^[4] The steric limitations of pentacoordination will be modified by the angular strain of the four- and five-membered metallacycles on the preferred equatorial binding site. A spontaneous substitution reaction is not feasible with complex **4**. When complex **4** is kept at 100 °C for 3 h under vacuum, a vacant coordination site is formed by dissociation of 1 mol-equiv. of trimethylphosphane that is necessary for subsequent coordination of olefin to occur [Equation (4)].



On dissolution of **4** in diethyl ether under 1 bar of ethene, complex **8** is obtained as orange crystals. In the ³¹P NMR spectrum of **8**, three doublets of doublets are seen at δ = –12, 9, and 17 ppm. These signals are in the same region as those of a four-membered cobaltacycle, as expected from the data of compounds **1–5**.

When heated under argon, decomposition of **8** occurs with the release of ethene, and no alteration of the four-membered metallacycle is indicated (IR) prior to the deposition of cobalt.

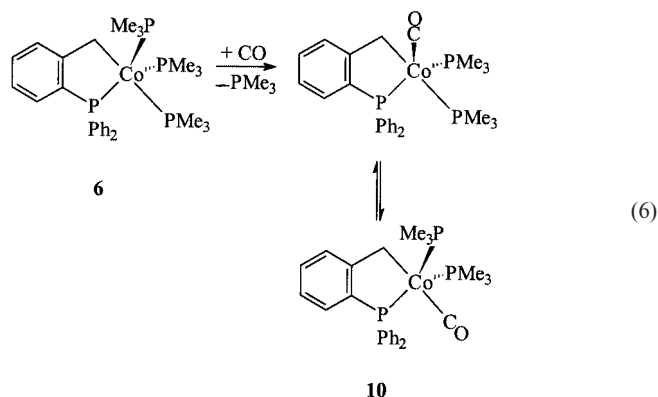
Without thermal pretreatment of complex **6**, which contains a five-membered cobaltacycle, substitution of trimethylphosphane by ethene occurs [Equation (5)].



The orange-yellow needles of **9** (from pentane, decomp. > 87 °C) exhibit a better thermal stability than π -ethene complexes containing five-membered cobaltacycles with (P,N) and (P,O) ligands,^[4,10] which are isoelectronic. From the ³¹P NMR spectrum, the doublet of doublets pattern, with characteristic shifts at $\delta = 66, 18$, and 11 ppm, indicates that the π -ethene ligand occupies an equatorial position.

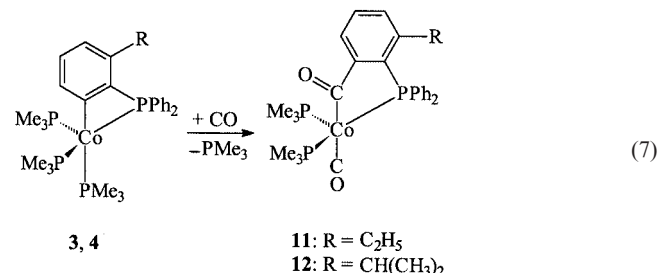
e) Reactions with Carbon Monoxide

Carbonylated methylcobalt(I) compounds, [CoCH₃(CO)(PMe₃)₃] or [Co(CH₃CO)(CO)₂(PMe₃)₂],^[11] are unreactive towards diphenyl(2-substituted phenyl)phosphanes and do not undergo a cyclometalation reaction of the proscribed type. However, CO ligands are smoothly introduced into metallacyclic product complexes. In solution under 1 bar of CO at 20 °C, **6** forms the monocarbonyl complex **10** [Equation (6)].



The dark-red crystals of **10** are thermally more stable (by 30 K) and less air-sensitive than those of complexes containing five-membered cobaltacycles with (P,N) and (P,O) ligands.^[4,10] The ³¹P NMR spectra in THF solutions show mixtures of isomers, with couplings consistent with a *tbp* configuration where a terminal carbonyl ligand resides either in an axial or in an equatorial position. In toluene solutions, only the isomer with the CO ligand in the axial position is observed.

When carbonylation reactions of complexes **3** and **4**, which contain four-membered cobaltacycles, take place under the same conditions, monosubstitution is accompanied by insertion of CO into the Co–C bond under ring expansion [Equation (7)], thus affording the acylcobalt complexes **11** and **12**, respectively.

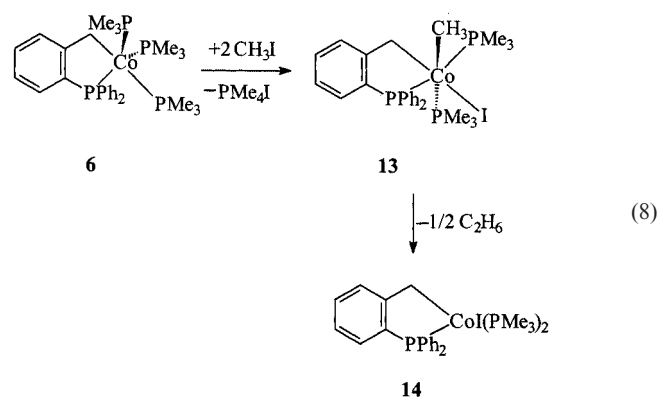


The lustrous red crystals of **11** and **12** have narrow melting ranges (**11**: 152–153 °C; **12**: 161–162 °C) and melt without decomposing. The IR spectra contain two conspicuous new bands which are assigned to the terminal carbonyl ligand and to the benzoylcobalt group [**11**: $\tilde{\nu} = 1913$ (C≡O), 1542 cm^{−1} (C=O); **12**: $\tilde{\nu} = 1906$ (C≡O), 1513 cm^{−1} (C=O)].

In the ³¹P NMR spectra, the ring expansion causes a low-field shift of the chelating phosphorus resonance by 85 ppm, which appears as a triplet by coupling to two equatorial trimethylphosphane groups. The observed doublet and triplet pattern is only compatible with the acyl and carbonyl ligands arranged in the axial positions.

f) Reactions with Iodomethane

Complex **6** reacts with excess iodomethane in diethyl ether by dissociation and quaternization of a trimethylphosphane [Equation (8)], thus undergoing an oxidative substitution reaction.



All volatile materials were removed in vacuo as soon as the precipitation of white tetramethylphosphonium iodide began. Extraction of the remaining solid with diethyl ether at 20 °C and cooling of the red-brown solution gave a moderate yield of short orange rods. Complex **13** is air-stable, but decomposes above 82 °C. In tetrahydrofuran at 20 °C,

spontaneous evolution of ethane transforms hexacoordinate **13** into the pentacoordinate cobalt(II) complex **14** [Equation (8)]. More conveniently, **14** is obtained by performing the synthesis in THF.

A $^3\text{P}\{^1\text{H}\}$ NMR spectrum of **13** in $[\text{D}_8]\text{THF}$ at 213 K shows three multiplet signals, suggesting three P-donor functions in an octahedral coordination geometry, but allows no clear distinction between the *mer* and *fac* configurations. The molecular structure of *mer*-**13** was revealed by a single-crystal X-ray diffraction analysis (Figure 4).

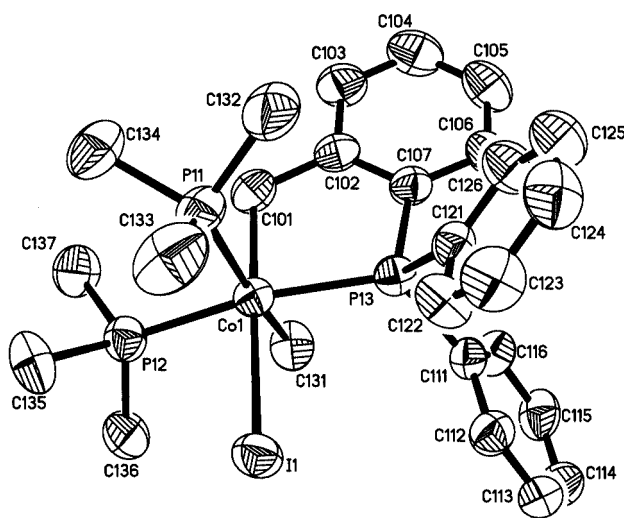
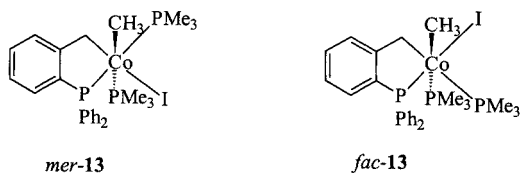


Figure 4. Molecular structure of *mer*-**13** (ORTEP plot with hydrogen atoms omitted); selected bond lengths [Å] and angles [°]: Co–C101 2.016(5), Co–C131 2.053(5), Co–I 2.7250(9), Co–P11 2.2749(17), Co–P12 2.2581(19), Co–P13 2.2301(18), C101–C102 1.515(8), C102–C107 1.386(8), P13–C107 1.818(5); C101–Co–P13 86.89(18), C101–Co–I 178.47(17), C101–Co–P12 94.70(18), P11–Co–P12 95.82(7), P11–Co–P13 98.31(6), P12–Co–P13 165.85(6), C107–P13–Co 102.8(2), P13–C107–C102 112.4(4), C101–C102–C107 122.3(5), Co–C101–C102 114.9(4).

The iodide ion and one of the trimethylphosphane ligands are coplanar with the cobaltacycle, while the other trimethylphosphane ligand and the CoCH_3 group are below and above the plane. While the Co–P and Co–C bond lengths are as expected, the Co–I bond is slightly elongated by the benzylic CH_2 –Co interaction in *trans* position.

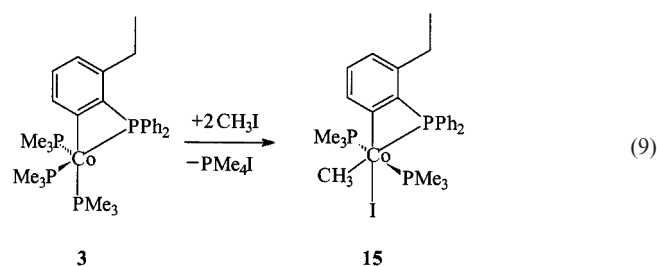


As the *trans* influences along Me_3P –Co– CH_3 would be very similar to that of Me_3P –Co– CH_3 in the *fac* configuration, *mer*-**13** would appear to be the product of a *cis* addition under kinetic control. However, when compared with **6**, the chelate bite angle $[\text{C101}–\text{Co}–\text{P13} = 86.89(13)^\circ]$ is augmented by 10° , while the Co–C bond is shortened by 6.5 pm. The sum of the internal angles is 539.3° , indicating considerable relaxation of the metallacycle towards

planarity. These differences could make *mer*-**13** the thermodynamically most stable isomer. Eventually, *mer*-**13** is metastable with respect to a C–C-coupling reaction forming **14**.

Although the molecular geometry of **14** has not been clarified due to poor crystal quality and broad and overlapping NMR signals, the magnetic moment ($\mu_{\text{eff}}/\mu_{\text{B}} = 1.93$) is as expected for a *tbp* configuration of cobalt (d^7).^[13–15]

Under the same conditions, **3** oxidatively adds iodomethane after substitution and quaternization of a trimethylphosphane group [Equation (9)].



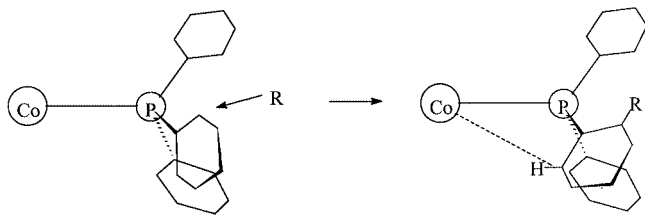
The dark-red crystals of **15** melt at 115 – 116°C under argon, and are stable for more than 1 d in air at 20°C . The IR spectrum resembles that of **3**, except for an additional band $[\tilde{\nu} = 1165\text{ cm}^{-1} (\text{CoCH}_3)]$. The ^3P NMR spectrum at 213 K shows a triplet resonance at $\delta = -32$ ppm, characteristic of a PPh_2 group in a four-membered cobaltacycle, and a doublet at $\delta = 10$ ppm containing a typical *cis* coupling ($^2J = 23\text{ Hz}$). The observed pattern is consistent with two isochronic trimethylphosphane ^3P nuclei in *trans* positions, and a meridional arrangement of the three P-donor atoms which appears to result from a regioselective *cis* addition of iodomethane.^[3] At variance with the spontaneous transformation of *mer*-**13** [Equation (8)], solutions of **15** in THF at 20°C remain stable for at least 1 d.

While cobalt(I) compounds containing five-membered metallacycles in a reaction with iodomethane undergo oxidative substitution, followed by reductive elimination of ethane, those containing four-membered cobaltacycles attain the cobalt(III) state without a subsequent C–C-coupling reaction. In both transformations the endocyclic Co–C bonds remain unaffected.

Conclusion

The reactivity in irreversible cyclometalation processes with $[\text{CoMe}(\text{PMe}_3)_4]$ appears to be controlled by a high electron density on the metal atom, and is lost in the presence of a single strongly π -accepting ligand, e.g. in $\text{CoMe}(\text{CO})(\text{PMe}_3)_3$. The observed selectivity, which is based on the orientation of the C–H bonds that are in the proximity of the metal atom, is sterically controlled by the preferred substrate conformation. The usual fan-type conformation of a triphenylphosphane ligand is most effectively distorted by a 2-substituent, whereby the substituted phenyl group is rotated in such a way that only this particular *ortho*-CH group closes in on the metal atom (Scheme 2) and the four-

membered cobaltacycle is formed. Thus, a sterically hindered rotation of an aryl group renders the cyclo-metalation reaction regioselective.



Scheme 2. Sterically controlled proximity conformation

A five-membered cobaltacycle is formed as the preferred ring size, by activation of a benzylic C–H bond only in the absence of steric strain. In a monosubstituted triphenylphosphane steric crowding is significant as the substituents are changed from 2-methyl to the 2-ethyl substituents. Once formed, the five-membered cobaltacycle does not insert a CO ligand in a process that accompanies carbonylation of complexes with four-membered cobaltacycles. Neither metallacycle shows insertion of a π -ethene ligand.

While cobalt(I) compounds containing five-membered metallacycles in a reaction with iodomethane undergo oxidative substitution, followed by reductive elimination of ethane, those containing four-membered cobaltacycles attain the cobalt(III) state without a subsequent C–C-coupling reaction. In both transformations the endocyclic Co–C bonds remain unaffected.

Experimental Section

General Procedures and Materials: All air-sensitive and volatile materials were handled using standard vacuum techniques and were kept under argon. Microanalyses: Kolbe Microanalytical Laboratory, Mülheim/Ruhr, FRG. Melting points/decomposition temperatures: Sealed capillaries, uncorrected values. Chemicals (Merck/Schuchardt) were used as purchased. Literature methods were applied for the preparation of 2-(diphenylphosphanyl)-*N,N*-dimethylaniline,^[16] [2-(diphenylphosphanyl)benzyl]dimethylamine,^[17] 1-(diphenylphosphanyl)-2-ethylbenzene, 1-(diphenylphosphanyl)-2-isopropylbenzene,^[18] 2-(diphenylphosphanyl)benzonitrile,^[19] 2-(diphenylphosphanyl)toluene,^[20] benzylidenediphenylphosphane,^[21] and [CoMe(PMe₃)₄].^[11] IR: Nujol mulls between KBr discs, Bruker spectrophotometer type FRA 106. ¹H and ¹³C NMR spectra (300 MHz and 75 MHz, respectively) were recorded with a Bruker ARX-300 spectrometer, ³¹P NMR spectra (81 MHz) with a Bruker AM-200 instrument. ¹³C and ³¹P resonances were obtained with proton decoupling. Magnetic susceptibility data were obtained by the Faraday method using a Cahn D 200 torsion balance (Bruker) at 1.5 Tesla.

[3-(Dimethylamino)-2-(diphenylphosphanyl)phenyl-*C'*,*P*]tris(trimethylphosphane)cobalt (1): 2-(Diphenylphosphanyl)-*N,N*-dimethylaniline (549 mg, 1.79 mmol) in 50 mL of diethyl ether was combined at –70 °C with [CoMe(PMe₃)₄] (680 mg, 1.79 mmol) in 30 mL of diethyl ether. The reaction was accompanied by the evolution of a gas. After the solution had warmed up, the red-brown mixture was kept at 20 °C for 16 h. The volatiles were removed in vacuo, the solid residue was extracted with 80 mL of pentane, and

the solution cooled to 4 °C, affording dark-red rectangular crystals of **1**. Yield 270 mg (85%); m.p. 112–114 °C (dec.). ¹H NMR (300 MHz, [D₈]THF, 296 K): δ = 1.02 [d, ²*J*(PH) = 5.6 Hz, 9 H, PCH₃], 1.23 [s (br), 18 H, PCH₃], 2.13 (s, 6 H, NCH₃), 5.90–6.23 (m, 3 H, CH), 7.22–7.24 (m, 6 H, CH), 7.75–7.79 (m, 4 H, CH) ppm. ¹³C NMR (75.4 MHz, [D₈]THF, 296 K): δ = 22.2–22.7 (m, PCH₃), 23.3 (m, PCH₃), 43.3 (s, NCH₃), 109.3 (s, CH), 125.9 [d, ³*J*(PC) = 3.1 Hz, CH], 126.0 (s, CH), 126.3 [d, ³*J*(PC) = 5.6 Hz, CH], 126.9 (s, CH), 133.2 [d, ²*J*(PC) = 7.6 Hz, CH], 133.3 [d, ²*J*(PC) = 7.6 Hz, CH], 139.1 [d, ²*J*(PC) = 9.2 Hz, CH], 171.3 (m, CoC) ppm. ³¹P NMR (81 MHz, [D₈]THF, 233 K): δ = –24 [dt, ²*J*(PP) = 89 and 68 Hz, 1 P, PPh₂], –4 [dd, ²*J*(PP) = 89 and 68 Hz, 2 P, PCH₃], 22 [dt, ²*J*(PP) = 68 and 47 Hz, 1 P, PCH₃] ppm. C₂₉H₄₆CoNP₄ (591.5): calcd. C 58.89, H 7.84, N 2.37, P 20.95; found C 58.92, H 7.82, N 2.27, P 20.83.

{3-[(Dimethylamino)methyl]-2-(diphenylphosphanyl)phenyl-*C'*,*P*}-tris(trimethylphosphane)cobalt (2): [2-(Diphenylphosphanyl)benzyl]dimethylamine (608 mg, 1.90 mmol) in 50 mL of diethyl ether was combined at –70 °C with [CoMe(PMe₃)₄] (720 mg, 1.90 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 **2** were obtained. Yield 967 mg (84%); m.p. 107–109 °C (dec.). ¹H NMR (300 MHz, [D₈]THF, 296 K): δ = 0.90 [d, ²*J*(PH) = 6.2 Hz, 9 H, PCH₃], 1.28 [s (br), 18 H, PCH₃], 1.73 (s, 6 H, NCH₃), 2.78 (s, 2 H, NCH₂), 6.68–6.77 (m, 3 H, CH), 7.24–7.26 (m, 6 H, CH), 7.72–7.78 (m, 4 H, CH) ppm. ¹³C NMR (75.4 MHz, [D₈]THF, 296 K): δ = 22.1–22.5 (m, PCH₃), 23.3 [d, ¹*J*(PC) = 20.1 Hz, PCH₃], 27.3 (s, NCH₃), 58.1 (s, NCH₂), 118.5 [d, ³*J*(PC) = 3.1 Hz, CH], 126.4 (s, CH), 126.5 [d, ³*J*(PC) = 5.6 Hz, CH], 126.9 (s, CH), 134.8 (s, CH), 135.6 [d, ²*J*(PC) = 7.6 Hz, CH], 135.7 [d, ²*J*(PC) = 7.6 Hz, CH], 138.1 [d, ²*J*(PC) = 9.2 Hz, C], 151.1 [d, ²*J*(PC) = 10.7 Hz, C], 1511.5 [d, ²*J*(PC) = 10.7 Hz, C], 169.9 (m, CoC) ppm. ³¹P NMR (81 MHz, [D₈]THF, 233 K): δ = –26 [dt, ²*J*(PP) = 89 and 70 Hz, 1 P, PPh₂], –4 [dd, ²*J*(PP) = 89 and 48 Hz, 2 P, PCH₃], 21 [dt, ²*J*(PP) = 70 and 48 Hz, 1 P, PCH₃] ppm. C₃₀H₄₈CoNP₄ (605.5): calcd. C 59.50, H 7.99, N 2.31, P 20.46; found C 59.36, H 8.10, N 2.18, P 20.38.

[2-(Diphenylphosphanyl)-3-ethylphenyl-*C'*,*P*]tris(trimethylphosphane)cobalt (3): 1-(Diphenylphosphanyl)-2-ethylbenzene (590 mg, 2.03 mmol) in 50 mL of THF was combined at –70 °C with [CoMe(PMe₃)₄] (770 mg, 2.03 mmol) in 30 mL of THF. As the solution warmed up, the slow evolution of a gas was observed. After keeping the dark-red mixture at 20 °C for 16 h, the volatiles were removed in vacuo and the solid residue was extracted with two 50-mL portions of pentane. Reduction of the volume to 60 mL and keeping of the red solution at 4 °C afforded dark-red rectangular crystals of **3**, which were suitable for X-ray diffraction. Yield 809 mg (69%); m.p. 120–121 °C. ¹H NMR (300 MHz, [D₈]THF, 296 K): δ = 0.53 (t, ³*J* = 7.5 Hz, 3 H, CCH₃), 1.09 [d, ²*J*(PH) = 6.3 Hz, 9 H, PCH₃], 1.25 [t', ²*J*(PH) + ⁴*J*(PH)] = 4.5 Hz, 18 H, PCH₃], 2.43 (q, ³*J* = 7.5 Hz, 2 H, CH₂), 6.29 (d, ³*J* = 6.4 Hz, 1 H, CH), 6.67 (t, ³*J* = 7.1 Hz, 1 H, CH), 6.73 (m, 1 H, CH), 7.21–7.27 (m, 6 H, CH), 7.72–7.80 (m, 4 H, CH) ppm. ¹³C NMR (75.4 MHz, [D₈]THF, 296 K): δ = 22.1 (s, CH₃), 22.1–22.9 (m, PCH₃), 23.7 (s, CH₂), 117.9 [d, ²*J*(PC) = 11.5 Hz, CH], 126.9 (s, CH), 128.6 [d, ³*J*(PC) = 9.0 Hz, CH], 129.3 [d, ⁴*J*(PC) = 3.1 Hz, CH], 130.1 [d, ¹*J*(PC) = 15.1 Hz, CH], 131.5 [d, ²*J*(PC) = 12.3 Hz, CH], 137.9 [d, ²*J*(PC) = 10.5 Hz, CH], 138.2 (s, C), 145.5 (m, C), 171.5 (m, CoC) ppm. ³¹P NMR (81 MHz, [D₈]THF, 233 K): δ = –26 [dt, ²*J*(PP) =

87 and 69 Hz, 1 P, PPh₂], -4 [dd, ²J(PP) = 87 and 47 Hz, 2 P, PCH₃], 21 [dt, ²J(PP) = 69 and 47 Hz, 1 P, PCH₃] ppm. C₂₉H₄₅CoP₄ (576.5): calcd. C 60.42, H 7.87, P 21.49; found C 60.51, H 8.13, P 21.19.

[2-(Diphenylphosphanyl)-3-isopropylphenyl-C',P]tris(trimethylphosphane)cobalt (4): 1-(Diphenylphosphanyl)-2-isopropylbenzene (732 mg, 2.40 mmol) in 50 mL of THF was combined at -70 °C with [CoMe(PMe₃)₄] (910 mg, 2.40 mmol) in 50 mL of THF. After the solution had warmed up, the dark-red mixture was kept at 20 °C for 16 h. The volatiles were removed in vacuo and the solid residue was extracted with two 80-mL portions of pentane. When the solution was kept at 4 °C, dark-red rectangular crystals of **4** were obtained. Yield 1040 mg (73%); m.p. 95–98 °C. ¹H NMR (300 MHz, [D₈]THF, 296 K): δ = 0.61 [d, ³J = 6.8 Hz, 6 H, C(CH₃)₂], 1.08 [d, ²J(PH) = 6.3 Hz, 9 H, PCH₃], 1.25 [t', ²J(PH) + ⁴J(PH)] = 4.4 Hz, 18 H, PCH₃], 2.52 (sept, ³J = 6.8 Hz, 1 H, CH), 6.34 (d, ³J = 7.2 Hz, 1 H, CH), 6.66 (t, ³J = 7.2 Hz, 1 H, CH), 6.72 (m, 1 H, CH), 7.24–7.26 (m, 6 H, CH), 7.75–7.82 (m, 4 H, CH) ppm. ¹³C NMR (75.4 MHz, [D₈]THF, 296 K): δ = 21.2 (s, CH₃), 22.5–22.6 (m, PCH₃), 27.9 (s, CH), 114.8 (s, CH), 126.5 [d, ²J(PC) = 8.5 Hz, CH], 126.9 (s, CH), 131.7 [d, ³J(PC) = 13.2 Hz, CH], 135.2 (s, CH), 135.4 [d, ¹J(PC) = 16.6 Hz, CH], 138.2 (m, C), 138.4 (s, CH), 140.4 (s, C), 171.2 (m, CoC) ppm. ³¹P NMR (81 MHz, [D₈]THF, 233 K): δ = -26 [dt, ²J(PP) = 87 and 71 Hz, 1 P, PPh₂], -4 [dd, ²J(PP) = 87 and 47 Hz, 2 P, PCH₃], 21 [dt, ²J(PP) = 71 and 47 Hz, 1 P, PCH₃] ppm. C₃₀H₄₇CoP₄ (590.5): calcd. C 61.02, H 8.02, P 20.98; found C 61.35, H 8.37, P 20.54.

[3-Cyano-2-(diphenylphosphanyl)phenyl-C',P]tris(trimethylphosphane)cobalt (5): 2-(Diphenylphosphanyl)benzonitrile (486 mg, 1.69 mmol) in 50 mL of THF was combined with [CoMe(PMe₃)₄] (640 mg, 1.69 mmol) in 50 mL of THF, at -70 °C. After the solution had warmed up, the dark-brown mixture was stirred at 20 °C for 16 h. The volatiles were then removed in vacuo. The solid residue was extracted with two 80-mL portions of pentane. At 4 °C, black needles of **5** were obtained. Yield 408 mg (42%); m.p. 114–116 °C (dec.). IR (Nujol): ν̃ = 2209 cm⁻¹ (C≡N). ¹H NMR (300 MHz, [D₈]THF, 296 K): δ = 1.11 [d, ²J(PH) = 6.6 Hz, 9 H, PCH₃], 1.30 [t', ²J(PH) + ⁴J(PH)] = 4.5 Hz, 18 H, PCH₃], 6.66 (d, ³J = 4.7 Hz, 1 H, CH), 6.68 (d, ³J = 8.2 Hz, 1 H, CH), 7.01 (m, 1 H, CH), 7.24–7.30 (m, 6 H, CH), 7.80–7.86 (m, 4 H, CH) ppm. ¹³C NMR (75.4 MHz, [D₈]THF, 296 K): δ = 21.8 (m, PCH₃), 22.3 (m, PCH₃), 119.3 [m, C(CN)], 121.7, 125.5 (s, CH), 126.4 [d, ²J(PC) = 7.7 Hz, CH], 127.4 (s, CH), 132.4 [d, ²J(PC) = 13.5 Hz, CH], 134.2, 136.5 (s, CH), 138.8 (s, C), 139.6 (m, C), 169.9 (m, CoC) ppm. ³¹P NMR (81 MHz, [D₈]THF, 233 K): δ = -26 [dt, ²J(PP) = 89 and 73 Hz, 1 P, PPh₂], -4 [dd, ²J(PP) = 89 and 50 Hz, 2 P, PCH₃], 21 [dt, ²J(PP) = 73 and 50 Hz, 1 P, PCH₃] ppm. C₂₈H₄₁CoNP₄ (574.5): calcd. C 58.54, H 7.19, N 2.44, P 21.57; found C 58.41, H 7.48, N 2.41, P 21.51.

[2-(Diphenylphosphanyl)tolyl-C,P]tris(trimethylphosphane)cobalt (6). **Method a):** 2-(Diphenylphosphanyl)toluene (616 mg, 2.23 mmol) and CoCl(PMe₃)₃ (720 mg, 2.23 mmol) in 40 mL of THF were combined at -70 °C with 1.6 M MeLi in diethyl ether (1.4 mL, 2.23 mmol), whilst stirring. The dark-green mixture turned red-brown. After the solution had warmed up, and after stirring at 20 °C for 30 min, the volatiles were removed in vacuo and the solid residue was extracted with two 80-mL portions of diethyl ether. Removal of the solvent afforded a dark-brown solid of **6**. Raw yield 928 mg (74%). **Method b):** 2-(Diphenylphosphanyl)toluene (489 mg, 1.77 mmol) in 50 mL of THF was combined with [CoMe(PMe₃)₄] (670 mg, 1.77 mmol) in 50 mL of THF, at -70 °C. As the solution warmed up, the mixture turned red-brown and was

stirred at 20 °C for 16 h. The volatiles were removed in vacuo, and the solid residue was extracted with three 80-mL portions of pentane. At 4 °C, black crystals of **6**, which were suitable for X-ray diffraction, were obtained. Yield 806 mg (81%); m.p. 124–126 °C (dec.). ¹H NMR (300 MHz, [D₈]THF, 296 K): δ = 0.93 [d, ²J(PH) = 6.5 Hz, 9 H, PCH₃], 1.19 [t', ²J(PH) + ⁴J(PH)] = 4.3 Hz, 18 H, PCH₃], 1.80 [m (br), 2 H, CoCH₂], 6.71 (t, ³J = 7.2 Hz, 1 H, CH), 6.80 (tt, ³J = 7.2, ⁴J = 1.4 Hz, 1 H, CH), 6.92 (d, ³J = 7.2 Hz, 1 H, CH), 7.08 (t, ³J = 6.3 Hz, 1 H, CH), 7.22–7.24 (m, 6 H, CH), 7.56–7.65 (m, 4 H, CH) ppm. ¹³C NMR (75.4 MHz, [D₈]THF, 296 K): δ = 21.1–22.9 (m, PCH₃), 24.8 (m, CoCH₂), 108.2 (m, C), 117.3 (m, CH), 120.4 (s, CH), 122.9 [d, ²J(PC) = 13.0 Hz, CH], 125.1 (s, CH), 125.9 [d, ⁴J(PC) = 3.1 Hz, CH], 130.1 [d, ¹J(PC) = 15.1 Hz, CH], 131.5 [d, ²J(PC) = 12.3 Hz, CH], 137.9 [d, ²J(PC) = 13.1 Hz, CH], 126.4 [d, ¹J(PC) = 22.4 Hz, C], 130.2 (s, CH), 132.6 [d, ²J(PC) = 12.3 Hz, C], 141.2 (m, C) ppm. ³¹P NMR (81 MHz, [D₈]THF, 233 K): δ = -4 [dd, ²J(PP) = 94 and 44 Hz, 2 P, PCH₃], 22 [dd, ²J(PP) = 50 and 44 Hz, 1 P, PCH₃], 58 [dt, ²J(PP) = 94 and 50 Hz, 1 P, PPh₂] ppm. C₂₈H₄₃CoP₄ (562.5): calcd. C 59.79, H 7.71, P 22.03; found C 59.97, H 7.30, P 22.08.

[2-(Diphenylphosphanyl)benzyl-C',P]tris(trimethylphosphane)cobalt (7): Benzylidiphenylphosphane (679 mg, 2.45 mmol) in 50 mL of THF was combined with [CoMe(PMe₃)₄] (930 mg, 2.45 mmol) in 50 mL of THF, at -70 °C. The color of the solution changed from brown to deep-red. After the solution had warmed up, the mixture was stirred at 20 °C for 4 h. The volatiles were then removed in vacuo to give a light-red solid. This was dissolved in 50 mL of diethyl ether and crystallized at 4 °C to give red cubes of **7**, which were suitable for X-ray diffraction. Yield 856 mg (62%); m.p. 75–77 °C (dec.). ¹H NMR (300 MHz, [D₈]THF, 296 K): δ = 0.97 [d, ²J(PH) = 6.3 Hz, 9 H, PCH₃], 1.16 [t', ²J(PH) + ⁴J(PH)] = 4.6 Hz, 18 H, PCH₃], 1.80 [d, ²J(PH) = 8.2 Hz, 2 H, PCH₂], 6.49 (m, 2 H, CH), 6.70 (m, 1 H, CH), 7.19–7.25 (m, 6 H, CH), 7.42 (m, 1 H, CH), 7.56–7.62 (m, 4 H, CH) ppm. ¹³C NMR (75.4 MHz, [D₈]THF, 296 K): δ = 23.4 [d, ¹J(PC) = 20.8 Hz, PCH₃], 23.9 [dd, ¹J(PC) = 12.6, ³J(PC) = 6.4 Hz, PCH₃], 50.4 [d, ¹J(PC) = 27.1, ³J(PC) = 8.7 Hz, PCH₂], 119.9 (s, CH), 121.6 (s, CH), 121.9 (s, CH), 127.5 [d, ³J(PC) = 8.0 Hz, CH], 127.6 (s, CH), 132.8 [d, ²J(PC) = 11.6 Hz, CH], 141.6 (m, C), 143.6 (m, C), 144.6 (s, CH), 171.6 (m, CoC) ppm. ³¹P NMR (81 MHz, [D₈]THF, 233 K): δ = -4 [dd, ²J(PP) = 104 and 54 Hz, 2 P, PCH₃], 22 [dd, ²J(PP) = 54 and 51 Hz, 1 P, PCH₃], 63 [dt, ²J(PP) = 104 and 51 Hz, 1 P, PPh₂] ppm. C₂₈H₄₃CoP₄ (562.5): calcd. C 59.79, H 7.71, P 22.03; found C 59.63, H 7.79, P 22.12.

[2-(Diphenylphosphanyl)-3-isopropylphenyl-C',P](ethene)bis(trimethylphosphane)cobalt (8): A sample of **4** (610 mg, 1.03 mmol) was heated in vacuo at 100 °C for 3 h. It was then dissolved in 70 mL of diethyl ether at 20 °C, and was stirred under 1 bar of ethene for 3 h. The volatiles were removed in vacuo and the solid residue was extracted with two 50-mL portions of pentane. Crystallization at 4 °C afforded orange crystals of **8**, together with the dark crystals of **4**. After mechanical separation the yield was 185 mg (33%); m.p. 105–107 °C (dec.). ¹H NMR (300 MHz, [D₈]THF, 296 K): δ = 0.85 [d, ²J(PH) = 5.8 Hz, 9 H, PCH₃], 0.97 (d, ³J = 6.9 Hz, 6 H, CCH₃), 1.01 [d, ²J(PH) = 5.9 Hz, 9 H, PCH₃], 1.51 (m, 1 H, =CH₂), 1.88 (m, 2 H, =CH₂), 2.35 (m, 1 H, =CH₂), 2.46 (sept, ³J = 6.9 Hz, 1 H, CHCH₃), 6.42 (t, ⁴J = 2.4 Hz, CH), 6.45 (t, ⁴J = 2.2 Hz, CH), 6.72 (dt, ³J = 7.5, ⁴J = 1.8 Hz, 1 H, CH), 7.26–7.28 (m, 3 H, CH), 7.38–7.41 (m, 3 H, CH), 7.64–7.70 (m, 2 H, CH), 7.94–8.00 (m, 2 H, CH) ppm. ¹³C NMR (75.4 MHz, [D₈]THF, 296 K): δ = 16.4 [d, ¹J(PC) = 22.7 Hz, PCH₃], 18.9 [d, ¹J(PC) = 18.4 Hz, PCH₃], 20.9 (s, CHCH₃), 28.5 [d, ³J(PC) =

4.5 Hz, CHCH₃], 31.4 [d, ²J(PC) = 16.1 Hz, =CH₂], 37.1 [d, ²J(PC) = 15.5 Hz, =CH₂], 116.2 [d, ³J(PC) = 6.1 Hz, CH], 126.6 [d, ³J(PC) = 8.2 Hz, CH], 127.4 [d, ²J(PC) = 12.6 Hz, C], 128.9 (s, CH), 131.4 [d, ²J(PC) = 11.1 Hz, CH], 132.1 [d, ²J(PC) = 11.2 Hz, CH], 136.1 [d, ¹J(PC) = 15.9 Hz, C], 138.2 (s, C), 141.7 (s, C) ppm. ³¹P NMR (81 MHz, [D₈]THF, 193 K): δ = -21 [dd, ²J(PP) = 49 and 56 Hz, 1 P, PPh₂], 9 [dd, ²J(PP) = 49 and 33 Hz, 1 P, PCH₃], 17 [dd, ²J(PP) = 33 and 56 Hz, 1 P, PCH₃] ppm. C₂₉H₄₂CoP₃ (542.5): calcd. C 64.21, H 7.80, P 17.13; found C 63.85, H 7.90, P 17.15.

[2-(Diphenylphosphanyl)tolyl-C,P](ethene)bis(trimethylphosphane)cobalt (9): A sample of **6** (820 mg, 1.45 mmol) in 50 mL of diethyl ether was stirred under 1 bar of ethene for 1 h. A light-red solution formed. The volatiles were removed in vacuo and the solid residue was extracted with three 50-mL portions of pentane. Crystallization at 4 °C afforded orange needles of **9**. Yield 584 mg (78%); m.p. 87–89 °C (dec.). ¹H NMR (300 MHz, [D₈]THF, 296 K): δ = 0.71 [d, ²J(PH) = 6.1 Hz, 9 H, PCH₃], 1.21 [d, ²J(PH) = 5.4 Hz, 9 H, PCH₃], 1.65 (m, 2 H, =CH₂), 1.97 (m, 2 H, =CH₂), 6.82 (m, 1 H, CH), 6.90 (m, 2 H, CH), 7.14 (t, ³J = 6.5 Hz, 1 H, CH), 7.32–7.36 (m, 6 H, CH), 7.45 (m, 2 H, CH), 8.02–8.04 (m, 2 H, CH) ppm. ¹³C NMR (75.4 MHz, [D₈]THF, 296 K): δ = 16.9 [d, ¹J(PC) = 18.4 Hz, PCH₃], 19.7 [d, ¹J(PC) = 16.6 Hz, PCH₃], 31.7 (m, CoCH₂), 38.7 [d, ²J(PC) = 16.5 Hz, =CH₂], 39.8 [d, ²J(PC) = 20.5 Hz, =CH₂], 121.9 [d, ⁴J(PC) = 4.9 Hz, CH], 124.9 [d, ²J(PC) = 11.0 Hz, CH], 127.3 [d, ³J(PC) = 8.4 Hz, CH], 127.5 [d, ³J(PC) = 8.3 Hz, CH], 127.6 [d, ³J(PC) = 7.2 Hz, CH], 128.2 [d, ¹J(PC) = 22.0 Hz, CH], 133.2 [d, ²J(PC) = 10.5 Hz, CH], 134.1 [d, ²J(PC) = 11.6 Hz, CH], 141.1 [d, ¹J(PC) = 20.9 Hz, C], 162.1 (s, C) ppm. ³¹P NMR (81 MHz, [D₈]THF, 233 K): δ = 11 [dd, ²J(PP) = 40 and 25 Hz, 1 P, PCH₃], 18 [dd, ²J(PP) = 25 and 38 Hz, 1 P, PCH₃], 66 [dd, ²J(PP) = 40 and 38 Hz, 1 P, PPh₂] ppm. C₂₇H₃₈CoP₃ (514.5): calcd. C 63.04, H 7.45, P 18.06; found C 63.12, H 7.07, P 18.72.

(Carbonyl)[2-(diphenylphosphanyl)tolyl-C,P]bis(trimethylphosphane)cobalt (10): A sample of **6** (590 mg, 1.05 mmol) in 30 mL of THF was stirred under 1 bar of CO for 30 min. A light-red solution formed. The volatiles were removed in vacuo and the solid residue was extracted with 50 mL of pentane. Crystallization at 4 °C afforded red crystals of **10**, which were suitable for X-ray diffraction. Yield 410 mg (76%); m.p. 132–135 °C (dec.). IR (Nujol): ν̃ = 1894 cm⁻¹ (C=O_{ax}), 1850 cm⁻¹ (C=O_{eq}). ¹H NMR (300 MHz, [D₈]THF, 296 K): C=O_{ax} isomer (88%): δ = 1.00 [t', ²J(PH) + ⁴J(PH)] = 6.2 Hz, 18 H, PCH₃], 2.09 (m, 2 H, CoCH₂), 6.84 (t, ³J = 7.3 Hz, 1 H, CH), 7.02 (m, 2 H, CH), 7.18 (d, ³J = 6.9 Hz, 1 H, CH), 7.26–7.31 (m, 6 H, CH), 7.43–7.47 (m, 4 H, CH); C=O_{eq} isomer (12%): δ = 0.86 [d, ²J(PH) = 7.3 Hz, 18 H, PCH₃], 1.29 [d, ²J(PH) = 7.5 Hz, 18 H, PCH₃], 2.35 (m, 2 H, CoCH₂), 6.95–7.62 (m, 14 H, CH) ppm. ¹³C NMR (75.4 MHz, [D₈]THF, 296 K): C=O_{ax} isomer (88%): δ = 20.1 (s, PCH₃), 24.0 (m, CoCH₂), 124.1 [d, ³J(PC) = 4.6 Hz, CH], 127.4 (s, CH), 127.4 [d, ¹J(PC) = 16.4 Hz, CH], 128.5 [d, ²J(PC) = 8.3 Hz, CH], 128.8 (s, CH), 129.9 (s, CH), 133.1 [d, ²J(PC) = 12.3 Hz, CH], 140.1 (s, C) ppm. ³¹P NMR (81 MHz, [D₈]THF, 233 K): CO_{ax} isomer (88%): δ = 6 [d, ²J(PP) = 98 Hz, 2 P, PCH₃], 73 [t, ²J(PP) = 98 Hz, 1 P, PPh₂]; CO_{eq} isomer (12%): δ = -1 [dd, ²J(PP) = 82 and 38 Hz, 1 P, PCH₃], 25 [dd, ²J(PP) = 38 and 51 Hz, 1 P, PCH₃], 67 [dd, ²J(PP) = 82 and 51 Hz, PPh₂] ppm. C₂₆H₃₄CoOP₃ (514.4): calcd. C 60.71, H 6.66, P 18.06; found C 60.94, H 7.45, P 17.62.

(Carbonyl)[2-(diphenylphosphanyl)-3-ethylbenzoyl-C,P]bis(trimethylphosphane)cobalt (11): A sample of **3** (580 mg, 1.01 mmol) in 50 mL of THF was stirred under 1 bar of CO for 30 min. A light-

red solution formed. The volatiles were removed in vacuo and the solid residue was extracted with two 50-mL portions of pentane. Crystallization at 4 °C afforded dark red plates of **11**. Yield 475 mg (85%); m.p. 152–153 °C. IR (Nujol): ν̃ = 1913 cm⁻¹ (C=O). ¹H NMR (300 MHz, [D₈]THF, 296 K): δ = 0.52 (t, ³J = 7.5 Hz, 3 H, CH₃), 1.09 [t', ²J(PH) + ⁴J(PH)] = 7.2 Hz, 18 H, PCH₃], 2.43 (q, ³J = 7.5 Hz, 2 H, CH₂), 7.26–7.40 (m, 9 H, CH), 7.54–7.61 (m, 4 H, CH) ppm. ¹³C NMR (75.4 MHz, [D₈]THF, 296 K): δ = 17.2 (s, PCH₃), 18.2 (m, PCH₃), 19.9 (s, CH₃), 26.7 (s, CH₂), 47.5 (s, CH), 55.9 (s, CH₂), 117.6 [d, ¹J(PC) = 21.2 Hz, CH], 126.9 (s, CH), 128.6 [d, ²J(PC) = 9.0 Hz, CH], 129.3 [d, ³J(PC) = 3.1 Hz, CH], 128.8 (s, CH), 130.1 [d, ¹J(PC) = 15.1 Hz, CH], 130.4 (s, CH), 137.8 (s, C), 138.2 (s, C), 145.5 (s, C), 157.7 (s, C) ppm. ³¹P NMR (81 MHz, [D₈]THF, 193 K): δ = 9 [d, ²J(PP) = 81 Hz, 2 P, PCH₃], 84 [t, ²J(PP) = 81 Hz, 1 P, PPh₂] ppm. C₂₈H₃₆CoO₂P₃ (556.4): calcd. C 60.44, H 6.52, P 16.70; found C 60.40, H 6.72, P 16.53.

(Carbonyl)[2-(diphenylphosphanyl)-3-isopropylbenzoyl-C,P]bis(trimethylphosphane)cobalt (12): A sample of **4** (750 mg, 1.27 mmol) in 50 mL of THF was stirred under 1 bar of CO for 3 h. A light-red solution formed. The volatiles were removed in vacuo and the solid residue was extracted with two 50-mL portions of pentane. Crystallization at 4 °C afforded dark-red crystals of **12**. Yield 572 mg (79%); m.p. 161–162 °C. IR (Nujol): ν̃ = 1906 cm⁻¹ (C=O). ¹H NMR (300 MHz, [D₈]THF, 296 K): δ = 0.65 [d, ³J = 6.7 Hz, 6 H, C(CH₃)₂], 1.05 [t', ²J(PH) + ⁴J(PH)] = 7.3 Hz, 18 H, PCH₃], 3.04 (sept, ³J = 6.7 Hz, 1 H, CH), 7.30–7.39 (m, 9 H, CH), 7.58–7.65 (m, 4 H, CH) ppm. ¹³C NMR (75.4 MHz, [D₈]THF, 296 K): δ = 21.7 (s, CH₃), 18.2 [dt, ¹J(PC) = 12.6, ³J(PC) = 4.2 Hz, PCH₃], 30.9 (s, CH), 117.6 (s, CH), 117.9 (s, CH), 126.9 [d, ²J(PC) = 8.9 Hz, CH], 127.2 (s, CH), 130.2 (s, CH), 130.5 [d, ³J(PC) = 12.2 Hz, CH], 137.6 (s, C), 137.9 (s, C), 138.3 (m, C), 150.3 (s, C) ppm. ³¹P NMR (81 MHz, [D₈]THF, 233 K): δ = 8 [d, ²J(PP) = 79 Hz, 2 P, PCH₃], 85 [t, ²J(PP) = 79 Hz, 1 P, PPh₂] ppm. C₂₉H₃₈CoO₂P₃ (570.5): calcd. C 61.06, H 6.71, P 16.29; found C 61.05, H 6.86, P 16.21.

mer-cis-[2-(Diphenylphosphanyl)tolyl-C,P](iodo)(methyl)bis(trimethylphosphane)cobalt (13): A sample of **6** (810 mg, 1.44 mmol) in 50 mL of diethyl ether at -70 °C was combined with a slight excess of iodomethane (552 mg, 3.89 mmol). The mixture was allowed to warm to 20 °C, after which it turned brown and deposited an off-white solid of tetramethylphosphonium iodide (IR). After 4 h, the solid was removed by filtering. Crystallization at 4 °C afforded orange crystals of **13**·0.50Et₂, which were suitable for X-ray diffraction. Yield 440 mg (46%); m.p. 82–84 °C (dec.). ¹H NMR (300 MHz, [D₈]THF, 296 K): δ = 0.53 (m, 3 H, CoCH₃), 0.95 [s (br), 18 H, PCH₃], 1.12 (m, 2 H, CoCH₂), 6.56 (m, 1 H, CH), 7.05 (m, 2 H, CH), 7.31–7.74 (m, 11 H, CH) ppm. ³¹P NMR (81 MHz, [D₈]THF, 213 K): δ = -11 (m, 1 P, PCH₃), -1 (m, 1 P, PCH₃), 10 (m, 1 P, PPh₂) ppm. C₂₈H₄₂CoIO_{0.5}P₃ (665.4): calcd. C 50.54, H 6.36, P 13.96; found C 50.40, H 6.64, P 14.21.

[2-(Diphenylphosphanyl)tolyl-C,P](iodo)bis(trimethylphosphane)cobalt (14): A sample of **6** (760 mg, 1.35 mmol) in 60 mL of THF was combined with iodomethane (192 mg, 1.35 mmol). After 4 h, a slight precipitate of tetramethylphosphonium iodide formed, which was filtered off. The filtrate was concentrated to dryness. Extraction with three 80-mL portions of diethyl ether and cooling to 4 °C afforded black crystals of **14**. Yield 780 mg (94%); m.p. 157–159 °C (dec.). Magnetic moment: μ_{eff} = 1.93 μ_B. C₂₅H₃₄CoIP₃ (613.3): calcd. C 48.96, H 5.59, P 15.15; found C 48.62, H 5.88, P 15.25.

mer-trans-[2-(Diphenylphosphanyl)-3-ethylphenyl-C',P](iodo)(methyl)bis(trimethylphosphane)cobalt (15): A sample of **3** (870 mg,

Table 1. Crystal data for compounds **3**, **6**, **7**, and **13**

	3	6	7	13
Empirical formula	C ₂₉ H ₄₅ CoP ₄	C ₂₈ H ₄₃ CoP ₄	C ₂₈ H ₄₃ CoP ₄	C ₂₆ H ₃₇ CoIOP ₃ 0.5 Et ₂ O
Formula mass	576.5	562.4	562.4	665.4
Crystal size [mm]	0.38 × 0.25 × 0.16	0.38 × 0.25 × 0.12	0.50 × 0.40 × 0.22	0.44 × 0.20 × 0.19
Crystal system	orthorhombic	orthorhombic	monoclinic	triclinic
Space group	<i>Pbca</i>	<i>Pbca</i>	<i>P2₁/n</i>	<i>P</i> $\bar{1}$
<i>a</i> [Å]	9.060(1)	9.8127(16)	15.231(2)	10.492(2)
<i>b</i> [Å]	18.069(2)	18.7719(19)	24.516(4)	14.450(2)
<i>c</i> [Å]	38.641(6)	32.408(7)	16.201(3)	20.882(3)
α [°]	90	90	90	87.92(1)
β [°]	90	90	101.38(1)	75.56(1)
γ [°]	90	90	90	87.99(1)
<i>V</i> [Å ³]	6325.7(14)	5969.6(17)	5930.6(17)	3062.8(8)
<i>Z</i>	8	8	8	4
<i>D</i> _{calcd.} [g/cm ³]	1.211	1.252	1.260	1.443
μ (Mo- <i>K</i> α) [mm ⁻¹]	0.760	0.804	0.809	1.741
Temperature [K]	293(2)	293(2)	293(2)	293(2)
Data coll. range [°]	4.2 ≤ 2 θ ≤ 54	4.5 ≤ 2 θ ≤ 55	5.1 ≤ 2 θ ≤ 54	4.8 ≤ 2 θ ≤ 55
<i>h</i>	−1 ≤ <i>h</i> ≤ 11	0 ≤ <i>h</i> ≤ 12	−1 ≤ <i>h</i> ≤ 19	−1 ≤ <i>h</i> ≤ 13
<i>k</i>	−23 ≤ <i>k</i> ≤ 1	−1 ≤ <i>k</i> ≤ 24	−31 ≤ <i>k</i> ≤ 1	−18 ≤ <i>k</i> ≤ 18
<i>l</i>	−1 ≤ <i>l</i> ≤ 49	−42 ≤ <i>l</i> ≤ 1	−20 ≤ <i>l</i> ≤ 20	−26 ≤ <i>l</i> ≤ 27
No. reflect. measured	8431	7506	15074	16375
No. unique data	6891 [<i>R</i> _{int} = 0.0587]	6859 [<i>R</i> _{int} = 0.0667]	12931 [<i>R</i> _{int} = 0.0441]	14074 [<i>R</i> _{int} = 0.030]
Parameters	318	307	569	605
<i>GoF</i> on <i>F</i> ²	1.017	0.937	1.003	0.978
<i>R</i> 1 [<i>I</i> ≥ 2 σ (<i>I</i>)]	0.0573	0.0586	0.0555	0.0459
<i>wR</i> 2 (all data)	0.1754	0.1735	0.1307	0.1182

1.51 mmol) in 50 mL of diethyl ether at −70 °C was combined with iodomethane (514 mg, 3.62 mmol). The mixture was allowed to warm to 20 °C, after which it turned red and deposited solid tetramethylphosphonium iodide. After 3 h, the solid was removed by filtering. From the filtrate, dark-red crystals of **15** were obtained at −27 °C. Yield 504 mg (52%); m.p. 115–116 °C. ¹H NMR (300 MHz, [D₈]THF, 296 K): δ = 0.52 (t, ³*J* = 7.5 Hz, 3 H, CH₃), 0.54 (m, 3 H, CoCH₃), 1.03 [s (br), 18 H, PCH₃], 2.43 (q, ³*J* = 7.5 Hz, 2 H, CH₂), 5.81–7.77 (m, 13 H, CH) ppm. ³¹P NMR (81 MHz, [D₈]THF, 213 K): δ = −32 [t, ²*J*(PP) = 23 Hz, 1 P, PPh₂], 10 [d, ²*J*(PP) = 23 Hz, 2 P, PCH₃] ppm. C₂₇H₃₉CoIP₃ (642.4); calcd. C 50.48, H 6.12, P 14.47; found C 50.24, H 5.72, P 14.54.

Crystal Structure Analyses: Crystal data are presented in Table 1. Data collection: **3**: A crystal was sealed under argon in a glass capillary and mounted on a Bruker AXS P4 diffractometer. Intensities were collected (ω -scans) using graphite-monochromated Mo-*K* α radiation; *Lp* correction and absorption correction based on ψ -scans were applied. The structure was solved by direct and conventional Fourier methods. All non-hydrogen atoms were treated anisotropically, hydrogen atoms were treated with a riding model in idealized positions. **6**: Crystal mounting, data collection, structure solution, and refinement as for **3**. **7**: Crystal mounting, data collection, structure solution, and refinement as for **3**. Two independent molecules per asymmetric unit. **13**·0.50Et₂O: Crystal mounting, data collection, structure solution, and refinement as for **3**. Two independent molecules per asymmetric unit. CCDC-184438 (**3**), -184439 (**6**), -184440 (**7**), and -184441 (**13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/contents/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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