Five- and Six-Membered Cobaltocycles with C,P-Chelating Ligands through Regiospecific Cyclometalation of Mono(2-Substituted) Triphenylphosphane

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Keywords: Chelates / Cobalt / Metalation / Metallacycles / Structure elucidation

Cyclometalation in the aliphatic ring occurs in the reaction between [$CoCH_3(PMe_3)_4$] and 5-(diphenylphosphanyl)-1,2,3,4-tetrahydronaphthalene to give [{8-(diphenylphosphanyl)-1,2,3,4-tetrahydronaphthyl-(C^1,*P*)}tris(trimethylphosphane)cobalt] (**1**), containing a five-membered metallacycle as shown in the molecular structure. While 1-(diphenylphosphanyl)naphthalene reacts accordingly, affording [{8-(diphenylphosphanyl)naphthyl-(C^1,*P*)}tris(trimethylphosphane)cobalt] (**2**), 2-(diphenylphosphanyl)biphenyl yields *ortho*-metalated [{2-(diphenylphosphanyl)-3-phenylphenyl-(C^1,*P*)}tris(trimethylphosphane)cobalt] (**3**), containing a four-membered metallacycle. 1-(Diphenylphosphanyl)-8-methylnaphthalene is metalated in the aliphatic substituent to form [{[8-(diphenylphosphanyl)naphth-1-yl]methyl-(*C*,*P*)}tris(trimethylphosphane)cobalt] (**4**). The molecular structure shows a trigonal-bipyramidal configuration of the cobalt atom accommodating a six-membered metallacycle. 2-(Diphenylphosphanyl)styrene replaces two trimethylphosphane ligands to give [{2-(diphenylphosphanyl)styrene-(*C*,*C*-η^2,*P*)}methylbis(trimethylphosphane)cobalt] (**5**), avoiding metalation. Replacement of equatorial trimethylphosphane in compounds **1**–**3** by ethene gives π-ethene complexes **6**–**8**. In the molecular structure of **7** the C–C vector of the π-ethene ligand is arranged in the equatorial plane of a trigonal bipyramid. Under 1 bar of CO, compound **2** forms a monocarbonyl complex **9**, in which an equatorial carbonyl ligand is found in the molecular structure. Iodomethane transforms **2** into pentacoordinate [{2-(diphenylphosphanyl)naphthyl-(C^1,*P*)}iodobis(trimethylphosphane)cobalt] (**10**) with retention of the metallacycle.
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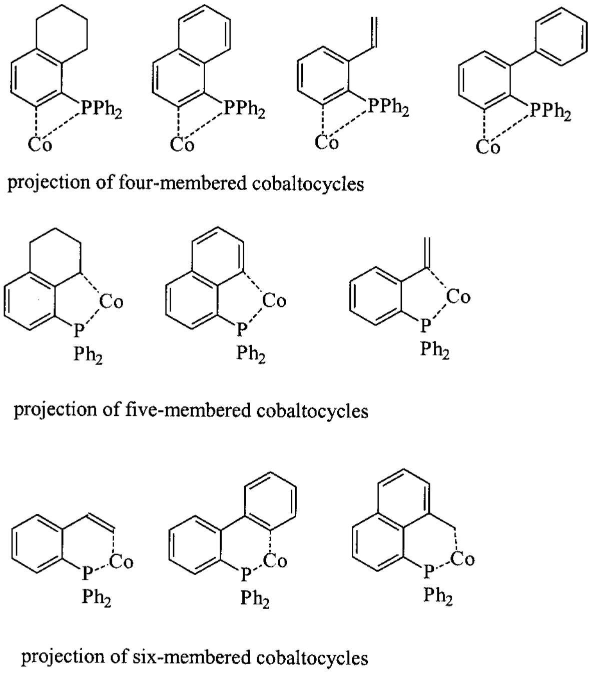
Introduction

Cyclometalation reactions with mono(2-substituted) triphenylphosphanes and [$CoCH_3(PMe_3)_4$] proceed with elimination of methane, whereby the selective product formation is rendered irreversible.[1] The observed regiospecificity, based on the orientation of C−H bonds situated in the vicinity of the metal atom, is sterically controlled by the preferred substrate conformation. Four-membered cobaltocycles have been found to originate from an *ortho*-metalation process, while in exceptional cases five-membered rings arise from attack in the side chain, although on the basis of C−H and C−Co bond energies the balance is believed to be less favorable for C(sp^3)−H bonds.[2] With the aim of selectively generating larger metallacycles we have metalated some pre-chelate phosphane ligands capable of forming five- and six-membered cobaltocycles (Scheme 1). An optional *ortho*-metalation route, disregarding the *ortho*-CH groups in the phenyl substituents, is also indicated for all four pre-chelate systems under investigation.



Scheme 1. Projection of cyclometalation reactions

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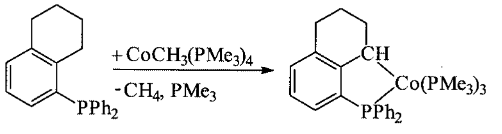
Results and Discussion

The $ArCH_3 \rightarrow ArCH_2 \rightarrow ArCH$ Line

Proximity of a C−H bond to the metal atom and a perpendicular orientation are believed to be necessary prerequisites for a cyclometalation reaction to occur. The unusual switching of selectivities from side-chain attack (2-methyl substituent) to *ortho*-metalation (2-ethyl substituent), which is steric in origin, prompted us to clarify the cyclometalation process further by restricting the proximity conformations. Rotational orientations of C−H bonds will be restricted in an aliphatic ring when 5-(diphenylphosphanyl)-1,2,3,4-tetrahydronaphthalene is chosen as a prechelate reactant. Reaction with $[CoCH_3(PMe_3)_4]$ proceeds below 20 °C [Equation (1)].



(1)

1

Red-brown crystals of **1**, melting with decomposition above 121 °C, were obtained from pentane. In the ^{31}P NMR spectrum, the observed coordination chemical shift of $\delta \approx 80$ ppm is only compatible with the PPh_2 group ($\delta = 64$ ppm) as part of a five-membered cobaltocycle. This configuration was confirmed in the molecular structure of **1** (Figure 1).

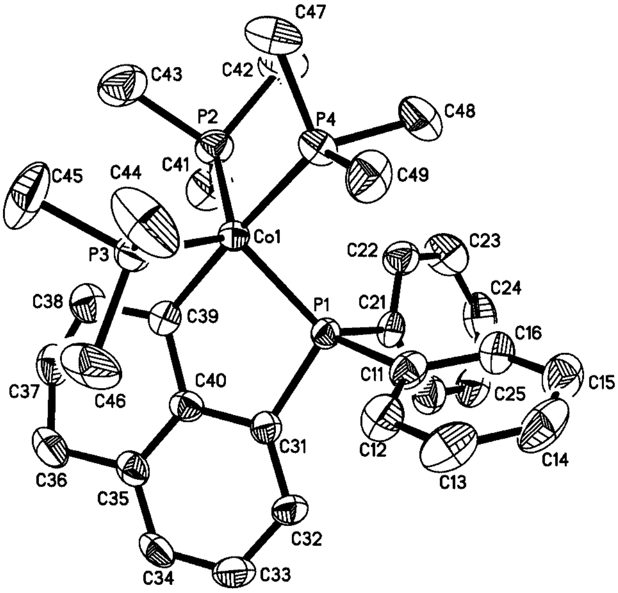
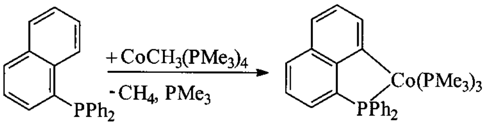


Figure 1. Molecular structure of **1** (ORTEP plot with hydrogen atoms omitted); selected bond lengths [Å] and angles [°]: Co−C39 2.082(6), Co−P1 2.1612(17), Co−P2 2.2189(17), Co−P3 2.1911(18), Co−P4 2.223(2), P1−C31 1.837(6), C31−C40 1.401(8), C39−C40 1.487(8); C39−Co−P1 81.18(17), C39−Co−P2 88.12(18), C39−Co−P3 85.34(19), C39−Co−P4 176.58(18), P1−Co−P2 120.50(7), P1−Co−P3 117.05(7), P1−Co−P4 95.56(6), P2−Co−P3 120.11(7), P2−Co−P4 94.45(7), P3−Co−P4 95.29(7), Co−P1−C31 105.26(19), P1−C31−C40 110.3(4), C31−C40−C39 117.8(5), Co−C39−C40 116.5(4)

The cobalt atom is centered in a trigonal bipyramid with axial CH and PMe_3 groups and a five-membered metallacycle spanning C-axial and P-equatorial positions with a C39−Co−P1 bite angle of 81.18(17)°. The Co−C bond is unusually long [Co−C39 = 2.082(6) Å], and while the adjacent distance $C(sp^3)-C(sp^3)$ is shortened [C39−C38 = 1.422(8) Å] the $C(sp^3)-C(sp^2)$ distance is normal [C39−C40 = 1.487(8) Å]. A multiplet arising from multiple phosphorus coupling at $\delta = 1.08$ ppm (1 H) in the ^1H NMR spectrum at 296 K is attributable to the CoCH group, and there is nothing remarkable in the remaining cycloaliphatic proton signals ($\delta = 2.20-2.63$ ppm, 6 H). As there are no unusual anisotropic properties of the carbon atoms, and as split models for the atomic positions of C39 and C38 were found insufficient, the structural irregularity in the cycloaliphatic ring is attributed to packing forces.

Incorporation of the CH_2 group in a cyclohexenyl ring switches the cyclometalation reaction from *ortho*-metalation of a $C(sp^2)-H$ bond to side-chain attack at a $C(sp^3)-H$ bond.

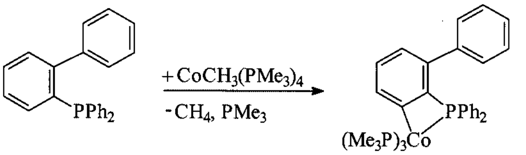
1-(Diphenylphosphanyl)naphthalene, providing two in-plane *ortho*-$C(sp^2)-H$ bonds, reacts with $[CoCH_3(PMe_3)_4]$ at −70 °C [Equation (2)] to afford **2** exclusively, isolated in 85% yield. The ^{31}P NMR chemical shifts and coupling constants at 193 K are found in positions and of an order expected for a five-membered cobaltocycle. The configuration of **2** was confirmed by monosubstitution with carbon monoxide to afford **9** (see below). Formation of a similar metallacycle starting from iridium(III) chloride was reported to require reflux conditions in 2-methoxyethanol.[3]



(2)

2

In order to address the matter of preference of six- or four-membered cobaltocycles, 2-(diphenylphosphanyl)biphenyl was treated with $[CoCH_3(PMe_3)_4]$ [Equation (3)].



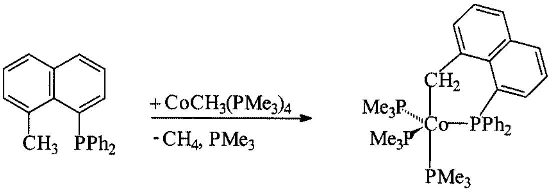
(3)

3

After evolution of gas, the mixture became red-brown in color and afforded **3** as a waxy solid, which was characterized by spectroscopy but gave no satisfactory elemental analysis. Evidence for the presence of a four-membered cobaltocycle was substantiated by its π-ethene derivative **8** (see below).

Metalation of the congested methyl group in 1-(diphenylphosphanyl)-8-methylnaphthalene should provide a six-membered cobaltocycle, if not dominated by *ortho*-metalation (Scheme 1). The relative proximity effects at the cobalt center upon coordination of the anchoring PPh_2 group allow reaction with $[CoCH_3(PMe_3)_4]$ at −70 °C and evolution of methane to proceed within 5 min.

Metalation occurs specifically at the naphthylmethyl group, forming the six-membered metallacycle [Equation (4)]. Compound **4** was crystallized from pentane as short, dark brown rods. The ^{31}P NMR spectrum shows two doublets of triplets and a doublet of doublets, as in the five-membered cobaltocycles of **1** or **2**. The observed pattern is in agreement with axial CH_2 and PMe_3 groups and three P donor functions in equatorial positions. A six-membered chelate ring spanning axial C and equatorial P sites of a trigonal bipyramid is shown in the molecular structure of **4** (Figure 2).



(4)

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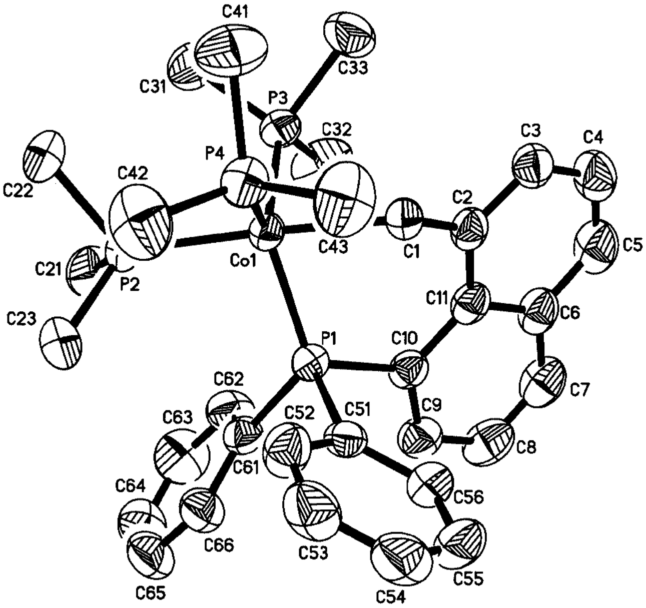
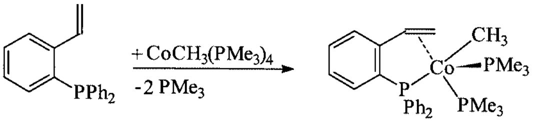


Figure 2. Molecular structure of **4** (ORTEP plot with hydrogen atoms omitted); selected bond lengths [Å] and angles [°]: Co−C1 2.090 (3), Co−P1 2.1438(9), Co−P2 2.1904(12), Co−P3 2.1932(10), Co−P4 2.2180(11), P1−C10 1.859(3), C10−C11 1.421(4), C2−C11 1.420(4), C1−C2 1.484(4); C1−Co−P1 79.72(9), C1−Co−P2 176.61(10), C1−Co−P3 88.32(10), C1−Co−P4 85.25(9), P1−Co−P2 98.60(4), P1−Co−P3 120.87(4), P1−Co−P4 121.21(4), P2−Co−P3 95.06(4), P2−Co−P4 93.18(4), P3−Co−P4 115.02(4), Co−P1−C10 117.05(10), P1−C10−C11 120.4(2), C2−C11−C10 123.5(2), C11−C2−C1 121.7(3), Co−C1−C2 123.4(2)

The cobalt atom is situated 109.5(1) pm above the best plane in the chelate ring. Bond lengths and angles show only minor deviations from the molecular structure of **1** (Figure 1).

Formation of all three ring sizes can be envisaged in 2-(diphenylphosphanyl)styrene (Scheme 1). However, treatment with $[CoCH_3(PMe_3)_4]$ failed to show evolution of gas, proceeding instead by substitution of two trimethylphosphane ligands [Equation (5)].



(5)

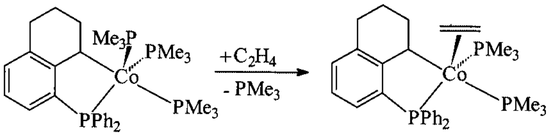
5

Compound **5** was obtained as an orange solid, decomposing above 152 °C under argon and stable in air under ambient conditions for at least 2 h. In the ^{1}H NMR spectrum at 296 K, a doublet of triplets at δ = −0.85 ppm (3 H) represents the $CoCH_3$ group, while in the ^{31}P NMR spectrum at 233 K, two doublets of doublets for an axial and two anisochronic equatorial P-donor atoms indicate a tbp-coordinated cobalt atom with local C_s symmetry caused by an equatorial π-vinyl ligand. 2-(Diphenylphosphanyl)styrene appears to be trapped as a neutral chelating ligand[4] that does not undergo a metalation reaction.

Reactions with Ethene

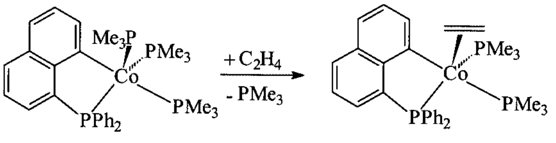
π-Olefin coordination in aryl(trimethylphosphane)cobalt(I) complexes is usually achieved through a smooth substitution reaction.[1a,5] Complex **6** was observed to crystallize much better under 1 bar of ethene than under argon.

The underlying replacement of dissociated trimethylphosphane by ethene [Equations (6) and (7)] converts **1** and **2** into π-ethene compounds that form orange plates (**6**) and short orange rods (**7**) from pentane solutions.



(6)

1 **6**



(7)

2 **7**

When the complexes are heated under argon, decomposition (**6**: > 101 °C; **7**: > 105 °C) proceeds with release of ethene, and no alteration in the five-membered metallacycle was indicated (IR) prior to deposition of cobalt. The expected tbp configuration was confirmed in the molecular structure of **7** (Figure 3).

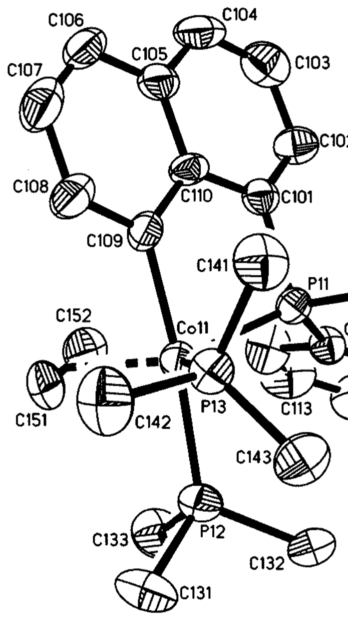
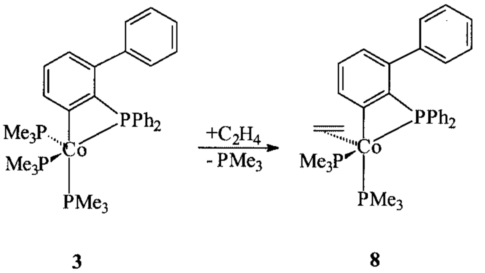


Figure 3. Molecular structure of **7** (molecule A) (ORTEP plot with hydrogen atoms omitted); selected bond lengths [Å] and angles [°]: Co−C109 2.001(5), Co−C151 2.026(6), Co−C152 2.045(7), Co−P11 2.1830(16), Co−P12 2.2413(18), Co−P13 2.2097(17), P11−C101 1.821(6), C101−C110 1.409(7), C109−C110 1.432(7); C109−Co−P11 83.82(16), C109−Co−P12 174.07(16), C109−Co−P13 88.06(17), P11−Co−P12 99.20(6), P11−Co−P13 105.74(6), P12−Co−P13 95.98(7), Co−P11−C101 102.55(18), P11−C101−C110 111.0(4), C101−C110−C109 119.0(5), Co−C109−C110 118.5(4)

A cobalt atom is found in the central position of a trigonal bipyramid with axial C and PMe_3 donor groups and a side-on coordinated ethene ligand with its C−C vector arranged in the equatorial plane, although crowded by PPh_2 and PMe_3 groups. The chelate bite angle [C109−Co−P = 83.82(16)°] is only 2° larger than in **1**, and the axial P−Co distance [Co−P12 = 2.2413(18) Å] is again the longest in the molecule, due to the *trans* influence of the naphthyl ligand.

Irrespective of the ring size or the heteroatom in P,C-, P,N-, and P,O-cobaltocycles, coordination of ethene in tbp complex molecules is regioselective, due to a better overlap with the strongest π-acceptor ligand in an equatorial position.[6]

A smooth replacement of trimethylphosphane by ethene also proceeds [Equation (8)] with complex **3**, which contains a four-membered cobaltocycle.

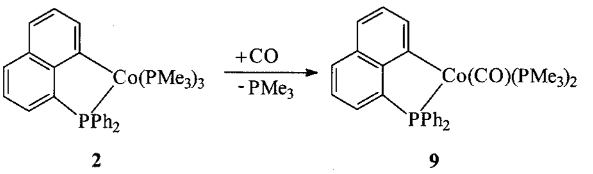


(8)

Three doublets of doublets in the ^{31}P NMR spectrum of **8**, at δ = −11, 9, and 21 ppm, fall in the positions corresponding to a four-membered cobaltocycle expected from data for *ortho*-metalated compounds[1] and indicate an equatorial position of the π-ethene ligand.

Reaction with Carbon Monoxide

In solution under 1 bar of CO at 20 °C, **2** forms a monocarbonyl complexe **9** [Equation (9)].



(9)

The dark red crystals of **9** are thermally about 30 K more stable than their parent trimethylphosphane compound and are less air-sensitive. ^{31}P NMR spectra obtained from THF solutions show a mixture of isomers with $J_{P,P}$ coupling constants consistent with tbp configurations in which a terminal carbonyl ligand resides either in an axial or in an equatorial position. In toluene solution, only the isomer with axial CO is observed.

The molecular structure of **9** (Figure 4) shows the tbp configuration of the isomer containing an equatorial carbonyl ligand and, in view of the otherwise similar infrared spectra, confirms the presence of a five-membered cobaltocycle in **2**. The chelate bite angle in **9** [C38−Co−P1 = 83.97(12)°] is as in **7**, and the sum of internal angles (534.7°) indicates little deviation from planarity. The Co−CO dis-

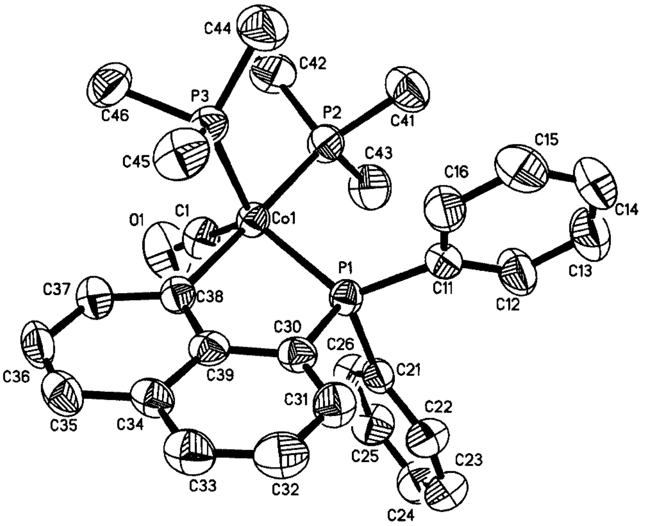
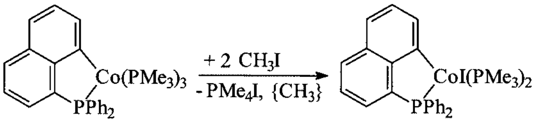


Figure 4. Molecular structure of **9** (ORTEP plot with hydrogen atoms omitted); selected bond lengths [Å] and angles [°]: Co−C38 1.996(4), Co−C1 1.720(5), Co−P1 2.1753(12), Co−P2 2.1935(13), Co−P3 2.2213(13), P1−C30 1.824(4), C30−C39 1.410(6), C38−C39 1.445(5); C38−Co−P1 83.97(12), C38−Co−P2 176.71(13), C38−Co−P3 85.07(12), P1−Co−P2 98.10(5), P1−Co−P3 113.16(5), P2−Co−P3 96.41(5), Co−P1−C30 103.09(14), P1−C30−C39 110.1(3), C30−C39−C38 119.6(4), Co−C38−C39 118.0(3)

tance [Co−C1 = 1.720(5) Å] is at the short end of the range for monocarbonylcobalt(I) complexes although in most cases the CO ligand occupies an axial position.[7]

Reactions with Iodomethane

Iodomethane oxidizes **2** [Equation (10)] to form a cobalt(II) complex **10** without there being evidence of a cobalt(III) intermediate.[1a] Although the molecular geometry of **10** has not been clarified, the magnetic moment of 1.91 is as would be expected for a tbp configuration at the cobalt atom (d^7).[1a,8]



(10)

2 **10**

Conclusion

The irreversible cyclometalation processes with $[CoCH_3(PMe_3)_4]$ appear to depend on the conformation of the 2-substituent when accommodated within the first coordination sphere of the metal atom. As soon as proximity to the electron-rich metal center is optimized, the product is formed by a sequence of fast steps involving oxidative addition of an aliphatic or an aromatic CH group, followed by elimination of methane. The ring size of the C,P-cobaltocycles in the product complex may be four, five, or six and does not dictate the regiospecificity of the cyclometalation reaction. Neither cobaltocycle inserts a π-coordinated ethene ligand into the Co−C bond and neither is expanded by CO uptake as with four-membered cobaltocycles.[1]

Experimental Section

General Procedures and Materials: All air-sensitive and volatile materials were handled by use of 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 in the preparation of 1-iodo-8-methylnaphthalene,[9] 5-(diphenylphosphanyl)-1,2,3,4-tetrahydronaphthalene,[10] 2-(diphenylphosphanyl)biphenyl,[11] 2-(diphenylphosphanyl)stryrene,[12] and $[CoCH_3(PMe_3)_4]$.[13] IR: Nujol mulls between KBr discs, Bruker spectrophotometer type FRA 106. ^1H and ^{13}C NMR spectra (300 MHz and 75 MHz, respectively) were recorded with a Bruker ARX 300 spectrometer, ^{31}P NMR spectra (81 MHz) with a Bruker AM 200 instrument. ^{13}C and ^{31}P resonances were obtained with broad-band proton decoupling. Magnetic susceptibility data were obtained by the Faraday method with a Cahn D 200 torsion balance (Bruker) at 1.5 Tesla.

1-(Diphenylphosphanyl)-8-methylnaphthalene: *n*BuLi (9.7 mL 1.6 N in hexane, 15.7 mmol) was added slowly at −70 °C to 1-iodo-8-methylnaphthalene (4.20 g, 15.7 mmol) in 50 mL of diethyl ether, and the mixture was allowed to warm to −30 °C. After 2 h, chlorodiphenylphosphane (3.45 g, 15.7 mmol) was added, and the resulting suspension was stirred at 20 °C for 4 h. The volatiles were then removed in vacuo and the residue was extracted with two portions of methylcyclohexane (each 50 mL). On cooling of the combined extracts to 4 °C, white cubic crystals (1.89 g, 37%) were formed; m.p. 131−132 °C. ^1H NMR (300 MHz, CD_2Cl_2, 296 K): $\delta = 3.08$ (d, $J_{P,H} = 4.2$ Hz, 3 H, CH_3), 7.12 (ddd, $^3J = 6.5$, $^4J_{P,H} = 5.0$, $^4J = 1.5$ Hz, 1 H, CH), 7.21−7.28 (m, 6 H, CH), 7.31−7.32 (m, 1 H, CH), 7.34 −7.38 (m, 6 H, CH), 7.73 (d, $^3J = 7.9$ Hz, 1 H, CH), 7.85 (dd, $^3J = 8.1$, $^4J = 1.4$ Hz, 1 H, CH) ppm. ^{13}C NMR (75.4 MHz, CD_2Cl_2, 296 K): $\delta = 27.5$ (d, $^1J_{P,C} = 32.0$ Hz, CH_3), 125.2 (s, CH), 125.9 (s, CH), 126.6 (d, $^2J_{P,C} = 16.3$ Hz, C), 128.5 (s, CH), 129.2 (d, $^2J_{P,C} = 16.5$ Hz, CH), 131.3 (s, CH), 131.9 (s, CH), 132.2 (m, CH), 134.6 (d, $^3J_{P,C} = 20.4$ Hz, CH), 135.5 (d, $^3J_{P,C} = 29.3$ Hz, C), 135.9 (s, CH), 136.0 (s, C), 136.7 (s, C), 139.1 (d, $^2J_{P,C} = 14.0$ Hz, C) ppm. ^{31}P NMR (81 MHz, CD_2Cl_2, 296 K): $\delta = -0.5$ ppm. $C_{23}H_{19}P$ (326.2): calcd. C 84.64, H 5.87; found C 84.17, H 5.98.

[{8-(Diphenylphosphanyl)-1,2,3,4-tetrahydronaphthyl-(*C¹*,*P*)}tris(trimethylphosphane)cobalt(I)] (1): 5-(Diphenylphosphanyl)-1,2,3,4-tetrahydronaphthalene (685 mg, 2.16 mmol) in THF (50 mL) was mixed at −70 °C with $[CoCH_3(PMe_3)_4]$ (820 mg, 2.16 mmol) in THF (50 mL). On warming, the mixture turned red-brown and was stirred at 20 °C for 16 h. The volatiles were then removed in vacuo, and the waxy residue was extracted with pentane (two 50-mL portions). At 4 °C, the solution afforded deep-red octahedral crystals of **1**, suitable for X-ray diffraction. Yield 535 mg (41%); m.p. 121−123 °C. ^1H NMR (300 MHz, [D₈]THF, 296 K): $\delta = 0.98$ (d, $^2J_{P,H} = 6.3$ Hz, 9 H, PCH_3), 1.08 (m, 1 H, CoCH), 1.25 (m, 18 H, PCH_3), 2.20 (m, 2 H, CH_2), 2.48 (m, 2 H, CH_2), 2.63 (dd, $^2J_{P,H} = 8.2$, 7.6 Hz, 2 H, CH_2), 5.89 (m, 1 H, CH), 6.75−6.79 (m, 2 H, CH), 7.09−7.12 (m, 6 H, CH), 7.52−7.55 (m, 4 H, CH) ppm. ^{13}C NMR (75.4 MHz, [D₈]THF, 296 K): $\delta = 21.7$ (m, PCH_3), 23.1 (m, CoCH), 23.9 (m, CH_2), 25.6 (m, CH_2), 27.4 (m, CH_2), 123.1(d, $^3J_{P,C} = 4.3$ Hz, CH), 125.4 (s, CH), 126.1 (d, $^3J_{P,C} = 7.6$ Hz, CH), 126.2 (s, CH), 126.5 (s, CH), 131.9 (d, $^2J_{P,C} = 13.0$ Hz, CH), 133.6 (s, C) ppm. ^{31}P NMR (81 MHz, [D₈]THF, 233 K): $\delta = -3$ (dd, $^2J_{Peq,Peq} = 97$, $^2J_{Peq,Pax} = 53$ Hz, 2 P, PCH_3), 24 (dt, $^2J_{Pax,Peq} = 53$, $^2J_{Pax,Peq} = 53$ Hz, 1 P, PCH_3), 64 (dt, $^2J_{Peq,Peq} = 97$, $^2J_{Peq,Pax} = 53$ Hz, 1 P, PPh_2) ppm. $C_{31}H_{47}CoP_4$ (602.5): calcd. C 61.79, H 7.86, P 20.56; found C 61.47, H 7.47, P 21.05.

[{8-(Diphenylphosphanyl)naphthyl-(*C¹*,*P*)}tris(trimethylphosphane)cobalt(I)] (2): 1-(Diphenylphosphanyl)naphthalene (710 mg, 2.27 mmol) in THF (50 mL) was mixed at −70 °C with $[CoCH_3(PMe_3)_4]$ (860 mg, 2.27 mmol) in THF (50 mL). On warming, the mixture turned red-brown and was stirred at 20 °C for 16 h. The volatiles were then removed in vacuo, and the waxy residue was extracted with diethyl ether (three 80-mL portions). At −27 °C, the solution afforded black rhombuses of **2**. Yield 1150 mg (85%); m.p. 107−109 °C (dec.). ^1H NMR (300 MHz, [D₈]THF, 296 K): $\delta = 1.01$ (d, $^2J_{P,H} = 6.4$ Hz, 9 H, PCH_3), 1.09 (m, 18 H, PCH_3), 6.88 (t, $^3J = 7.6$ Hz, 1 H, CH), 7.12 (m, 2 H, CH), 7.19−7.21 (m, 2 H, CH), 7.39−7.47 (m, 7 H, CH), 7.61−7.69 (m, 4 H, CH) ppm. ^{13}C NMR (75.4 MHz, [D₈]THF, 296 K): $\delta = 21.9$ (dd, $^1J_{P,C} = 14.2$, $^3J_{P,C} = 7.6$ Hz, PCH_3), 22.5 (m, PCH_3), 117.6 (s, CH), 122.6 (s, CH), 122.8 (d, $^3J_{P,C} = 6.1$ Hz, CH), 124.6 (s, CH), 126.2 (d, $^3J_{P,C} = 7.6$ Hz, CH), 126.4 (s, CH), 127.2 (s, CH), 131.6 (d, $^1J_{P,C} = 15.2$ Hz, C), 132.2 (d, $^2J_{P,C} = 12.2$ Hz, CH), 139.8 (d, $^2J_{P,C} = 12.2$ Hz, C), 142.3 (m, C) ppm. ^{31}P NMR (81 MHz, [D₈]THF, 233 K): $\delta = -3$ (dd, $^2J_{Peq,Peq} = 100$, $^2J_{Peq,Pax} = 54$ Hz, 2 P, PCH_3), 24 (dt, $^2J_{\rm Pax,Peq} = 54$, $^2J_{\rm Pax,Peq} = 54$ Hz, 1 P, PCH$_3$), 64 (dt, $^2J_{\rm Peq,Peq} = 100$, $^2J_{\rm Peq,Pax} = 54$ Hz, 1 P, PPh$_2$) ppm. $C_{31}H_{43}CoP_4$ (598.5): calcd. C 62.21, H 7.24, P 20.70; found C 61.43, H 7.36, P 21.11.

[{2-(Diphenylphosphanyl)-3-phenylphenyl-(C^1,P)}tris(trimethylphosphane)cobalt(I)] (3): 2-(Diphenylphosphanyl)biphenyl (608 mg, 1.79 mmol) in THF (50 mL) was mixed at −70 °C with [CoCH$_3$(PMe$_3$)$_4$] (680 mg, 1.79 mmol) in THF (30 mL). After warming, the dark red mixture was stirred at 20 °C for 5 h, and the volatiles were then removed in vacuo. The solid residue was extracted with pentane (80 mL). No crystallization was achieved either at 4 or at −27 °C from pentane, diethyl ether, THF, or mixtures of these solvents. Evaporation of solvent afforded **3** as a dark-red, waxy solid. Crude yield 940 mg. ^{1}H NMR (300 MHz, [D$_8$]THF, 296 K): δ = 1.05 (d, $^2J_{\rm P,H} = 6.4$ Hz, 9 H, PCH$_3$), 1.30 (t′, $|^2J_{\rm P,H} + {}^4J_{\rm P,H}| = 4.6$ Hz, 18 H, PCH$_3$), 5.40−7.70 (m, 18 H, CH) ppm. ^{31}P NMR (81 MHz, [D$_8$]THF, 233 K): δ = −21 (dt, $^2J_{\rm Peq,Peq} = 90$, $^2J_{\rm Peq,Pax} = 71$ Hz, 1 P, PPh$_2$), −4 (dd, $^2J_{\rm Peq,Peq} = 90$, $^2J_{\rm Peq,Pax} = 48$ Hz, 2 P, PCH$_3$), 21 (dt, $^2J_{\rm Pax,Peq} = 71$, $^2J_{\rm Pax,Peq} = 48$ Hz, 1 P, PCH$_3$) ppm.

[{[8-(Diphenylphosphanyl)naphth-1-yl]methyl-(C,P)}tris(trimethylphosphane)cobalt(I)] (4): 1-(Diphenylphosphanyl)-8-methylnaphthalene (740 mg, 2.26 mmol) in THF (50 mL) was added at −78 °C to a solution of [CoCH$_3$(PMe$_3$)$_4$] (857 mg, 2.26 mmol) in THF (50 mL). A rapid change of color from dark red to brown was observed as the solution warmed up. After 5 h, the solvent was removed in vacuo and the residue was extracted with pentane (two portions of 50 mL). Crystallization at 4 °C afforded dark brown cubes of **4**, suitable for X-ray diffraction. Yield 625 mg (45%); m.p. 146−148 °C (dec.). ^{1}H NMR (300 MHz, [D$_8$]THF, 296 K): δ = 1.02 (s, 27 H, PCH$_3$), 1.92 (q, $^3J_{\rm P,H} = 11.7$ Hz, 2 H, CoCH$_2$), 6.72 (dt, $^3J = 7.5$, $^4J = 0.8$ Hz, 1 H, CH), 7.03 (dt, $^3J = 7.8$, $^4J = 2.5$ Hz, 2 H, CH), 7.16−7.21 (m, 6 H, CH), 7.31−7.33 (m, 2 H, CH), 7.42−7.47 (m, 4 H, CH), 7.67 (d, $^3J = 8.0$ Hz, 1 H, CH) ppm. ^{13}C NMR (75.4 MHz, [D$_8$]THF, 296 K): δ = 11.6 (m, CoCH$_2$), 19.8 (m, PCH$_3$), 122.0 (d, $^3J_{\rm P,C} = 4.3$ Hz, CH), 125.4 (s, CH), 126.1 (d, $^3J_{\rm P,C} = 7.6$ Hz, CH), 126.2 (s, CH), 126.5 (s, CH), 131.9 (d, $^2J_{\rm P,C} = 13.0$ Hz, CH), 133.6 (s, C) ppm. ^{31}P NMR (81 MHz, [D$_8$]THF, 203 K): δ = −3 (dd, $^2J_{\rm Peq,Peq} = 102$, $^2J_{\rm Peq,Pax} = 40$ Hz, 2 P, PCH$_3$), 20 (dt, $^2J_{\rm Pax,Peq} = 46$, $^2J_{\rm Pax,Peq} = 40$ Hz, 1 P, PCH$_3$), 48 (dt, $^2J_{\rm Peq,Peq} = 102$, $^2J_{\rm Peq,Pax} = 46$ Hz, 1 P, PPh$_2$) ppm. $C_{32}H_{45}CoP_4$ (612.5): calcd. C 62.75, H 7.40, P 20.23; found C 62.72, H 7.38, P 20.39.

[{2-(Diphenylphosphanyl)styrene-(C,C-η^2,P)}methylbis(trimethylphosphane)cobalt(I)] (5): 2-(Diphenylphosphanyl)stryrene (571 mg, 1.98 mmol) in diethyl ether (40 mL) was mixed at −70 °C with [CoCH$_3$(PMe$_3$)$_4$] (750 mg, 1.98 mmol) in diethyl ether (40 mL). After warming, the orange mixture was stirred at 20 °C for 3 h, and the volume was then reduced to 40 mL. Pentane (50 mL) was added with vigorous stirring to precipitate **5** as a light brown solid. This was isolated by filtration and washing with pentane. Yield 652 mg (64%); m.p. 152−154 °C (dec.). ^{1}H NMR (300 MHz, [D$_8$]THF, 296 K): δ = −0.85 (dt, $^3J_{\rm P,H} = 8.1$, 1.8 Hz, CoCH$_3$), 0.78 (d, $^2J_{\rm P,H} = 5.6$ Hz, 9 H, PCH$_3$), 1.30 (d, $^2J_{\rm P,H} = 5.5$ Hz, 9 H, PCH$_3$), 1.80 (m, 2 H, =CH$_2$), 2.64 (m, 1 H, =CH), 6.86 (t, $^3J = 7.3$ Hz, CH), 7.01 (dt, $^3J = 6.3$, $^4J = 1.3$ Hz, 1 H, CH), 7.18 (t, $^3J = 6.7$ Hz, 1 H, CH), 7.26−7.31 (m, 6 H, CH), 7.31−7.33 (m, 1 H, CH), 7.38−7.41 (m, 2 H, CH), 7.77−7.83 (m, 2 H, CH) ppm. ^{13}C NMR (75.4 MHz, [D$_8$]THF, 296 K): δ = 17.6 (d, $^1J_{\rm P,C} = 14.7$ Hz, PCH$_3$), 18.9 (d, $^1J_{\rm P,C} = 16.7$ Hz, PCH$_3$), 50.8 (s, =CH$_2$), 62.1 (d, $^2J_{\rm P,C} = 18.2$ Hz, =CH), 121.7 (d, $^4J_{\rm P,C} = 4.1$ Hz, CH), 123.4 (d, $^2J_{\rm P,C} = 112.6$ Hz, CH), 126.4 (d, $^3J_{\rm P,C} = 7.9$ Hz, CH), 126.7 (d, $^3J_{\rm P,C} = 7.7$ Hz, CH), 127.3 (s, CH), 127.8 (s, CH), 130 (s, CH), 132.8 (d, $^2J_{\rm P,C} = 10.5$ Hz, C), 133.2 (d, $^2J_{\rm P,C} = 9.8$ Hz, CH), 137.8 (s, C), 138.4 (s, C) ppm. ^{31}P NMR (81 MHz, [D$_8$]THF, 233 K): δ = 9 (dd, $^2J_{\rm Peq,Pax} = 44$, $^2J_{\rm Peq,Pax} = 26$ Hz, 2 P, PCH$_3$), 71 (dd, $^2J_{\rm Pax,Peq} = 26$, $^2J_{\rm Pax,Peq} = 44$ Hz, 1 P, PPh$_2$) ppm. $C_{27}H_{38}CoP_3$ (514.2): calcd. C 63.04, H 7.45, P 18.06; found C 63.44, H 6.79, P 18.18.

[{8-(Diphenylphosphanyl)-1,2,3,4-tetrahydronaphthyl-(C^1,P)}-(ethene)bis(trimethylphosphane)cobalt(I)] (6): A sample of **3** (620 mg, 1.03 mmol) in diethyl ether (30 mL) was stirred under 1 bar of ethene for 1 h to provide an orange-red solution. The volatiles were removed in vacuo and the solid residue was extracted with pentane (40 mL). Crystallization at 4 °C afforded orange, hexagonal plates of **6**. Yield 490 mg (86%); m.p. 101−103 °C (dec.). ^{1}H NMR (300 MHz, [D$_8$]THF, 296 K): δ = 0.98 (d, $^2J_{\rm P,H} = 6.3$ Hz, 9 H, PCH$_3$), 1.08 (m, 1 H, CoCH), 1.25 (br. s, 9 H, PCH$_3$), 2.19−2.21 (m, 2 H, CH$_2$), 2.48 (m, 2 H, CH$_2$), 2.63 (dd, $^3J = 8.2$, $^3J = 7.6$ Hz, 2 H, CH$_2$), 5.89 (m, 1 H, CH), 6.75−6.79 (m, 2 H, CH), 7.09−7.12 (m, 2 H, CH), 7.52−7.55 (m, 4 H, CH) ppm. ^{1}H NMR (300 MHz, [D$_8$]toluene, 296 K): δ = 0.53 (d, $^2J_{\rm P,H} = 6.4$ Hz, 9 H, PCH$_3$), 0.86 (m, 1 H, CoCH), 1.05 (d, $^2J_{\rm P,H} = 5.0$ Hz, 9 H, PCH$_3$), 1.88−2.54 (m, 6 H, CH$_2$), 1.90 (m, 2 H, =CH$_2$), 2.29 (m, 2 H, =CH$_2$), 5.35 (m, 1 H, CH), 6.42−6.59 (m, 2 H, CH), 6.92−7.03 (m, 2 H, CH), 7.61−7.84 (m, 4 H, CH) ppm. ^{13}C NMR (75.4 MHz, [D$_8$]THF, 296 K): δ = 16.3 (d, $^1J_{\rm P,C} = 19.5$ Hz, PCH$_3$), 19.1 (d, $^1J_{\rm P,C} = 19.5$ Hz, PCH$_3$), 23.4 (m, CoCH), 25.4 (m, CH$_2$), 27.6 (s, CH$_2$), 29.1 (s, CH$_2$), 39.2 (m, =CH$_2$), 40.9 (m, =CH$_2$), 121.1 (s, CH), 123.2 (d, $^3J_{\rm P,C} = 5.2$ Hz, CH), 124.7 (s, CH), 126.1 (d, $^2J_{\rm P,C} = 12.3$ Hz, C), 126.2 (d, $^1J_{\rm P,C} = 15.1$ Hz, C), 126.9 (d, $^2J_{\rm P,C} = 12.7$ Hz, CH), 127.2 (d, $^1J_{\rm P,C} = 20.5$ Hz, CH), 131.8 (d, $^1J_{\rm P,C} = 16.3$ Hz, C), 132. 4 (d, $^2J_{\rm P,C} = 11.8$ Hz, CH), 140.2 (s, C) ppm. ^{13}C NMR (75.4 MHz, [D$_8$]toluene, 296 K): δ = 18.1 (d, $^1J_{\rm P,C} = 18.4$ Hz, PCH$_3$), 21.8 (d, $^1J_{\rm P,C} = 19.3$ Hz, PCH$_3$), 23.3 (m, CoCH), 26.8 (m, CH$_2$), 29.0 (s, CH$_2$), 30.5 (s, CH$_2$), 41.1 (d, $^2J_{\rm P,C} = 18.2$ Hz, =CH$_2$), 42.4 (d, $^2J_{\rm P,C} = 16.4$ Hz, =CH$_2$), 122.8 (s, CH), 124.7 (d, $^2J_{\rm P,C} = 14.2$ Hz, CH), 124.8 (s, CH), 127.6 (d, $^2J_{\rm P,C} = 11.2$ Hz, CH), 128.4 (s, C), 133.2 (d, $^3J_{\rm P,C} = 10.5$ Hz, CH), 133.5 (d, $^3J_{\rm P,C} = 9.5$ Hz, CH), 134.4 (d, $^2J_{\rm P,C} = 16.1$ Hz, C), 141.7 (d, $^2J_{\rm P,C} = 22.6$ Hz, CH), 155.0 (d, $^1J_{\rm P,C} = 43.7$ Hz, C) ppm. ^{31}P NMR (81 MHz, [D$_8$]THF, 213 K): δ = 5 (dd, $^2J_{\rm Peq,Pax} = 46$, $^2J_{\rm Peq,Peq} = 38$ Hz, 1 P, PCH$_3$), 17 (dd, $^2J_{\rm Pax,Peq} = 32$, $^2J_{\rm Pax,Peq} = 46$ Hz, 1 P, PCH$_3$), 75 (dd, $^2J_{\rm Peq,Pax} = 32$, $^2J_{\rm Peq,Peq} = 38$ Hz, 1 P, PPh$_2$) ppm. $C_{30}H_{42}CoP_3$ (554.5): calcd. C 64.98, H 7.63, P 16.76; found C 65.36, H 7.82, P 16.39.

[{2-(Diphenylphosphanyl)naphthyl-(C^1,P)}(ethene)bis(trimethylphosphane)cobalt(I)] (7): A sample of **2** (680 mg, 1.13 mmol) in diethyl ether (50 mL) was stirred under 1 bar of ethene for 1 h to provide a light red solution. The volatiles were removed in vacuo, and the solid residue was extracted with pentane (three 50-mL portions). Crystallization at 4 °C afforded short orange rods of **7**, suitable for X-ray diffraction. Yield 506 mg (81%); m.p. 105−107 °C (dec.). ^{1}H NMR (300 MHz, [D$_8$]THF, 296 K): δ = 0.90 (d, $^2J_{\rm P,H} = 6.5$ Hz, 9 H, PCH$_3$), 1.05 (d, $^2J_{\rm P,H} = 6.0$ Hz, 9 H, PCH$_3$), 1.49 (m, 2 H, =CH$_2$), 2.47 (m, 2 H, =CH$_2$), 6.95 (t, $^3J = 7.5$ Hz, 2 H, CH), 7.15 (dd, $^3J = 6.8$, $^4J = 1.6$ Hz, 1 H, CH), 7.17 (dd, $^3J = 8.3$, $^4J = 1.3$ Hz, 1 H, CH), 7.21 (dd, $^3J = 4.4$, $^4J = 1.8$ Hz, 1 H, CH), 7.26−7.33 (m, 7 H, CH), 7.46 (m, 2 H, CH), 7.54 (dd, $^3J = 7.6$, $^4J = 1.8$ Hz, 1 H, CH), 7.67−7.71 (m, 2 H, CH) ppm. ^{13}C NMR (75.4 MHz, [D$_8$]THF, 296 K): δ = 17.6 (d, $^1J_{\rm P,C} = 11.3$ Hz, PCH$_3$), 20.3 (d, $^1J_{\rm P,C} = 18.8$ Hz, PCH$_3$), 25.4 (m, CH$_2$), 40.1 (d, $^2J_{\rm P,C} = 16.9$ Hz, =CH$_2$), 42.1 (d, $^2J_{\rm P,C} = 15.9$ Hz, =CH$_2$), 119.8 (s, CH), 124.4 (d, $^3J_{\rm P,C} = 5.4$ Hz, CH), 125.9 (s, CH), 127.4 (s, CH), 127.6

(d, $^{1}J_{P,C}$ = 14.0 Hz, C), 127.9 (s, CH), 128.9 (d, $^{1}J_{P,C}$ = 23.9 Hz, CH), 132.6 (d, $^{2}J_{P,C}$ = 10.7 Hz, CH), 133.1 (d, $^{3}J_{P,C}$ = 7.3 Hz, CH), 133.7 (d, $^{3}J_{P,C}$ = 12.3 Hz, C), 141.2 (d, $^{3}J_{P,C}$ = 6.4 Hz, CH), 145.8 (m, C), 149.4 (s, C), 150.1 (s, C) ppm. ^{31}P NMR (81 MHz, [D$_8$]THF, 213 K): δ = 4 (dd, $^{2}J_{Peq,Pax}$ = 45, $^{2}J_{Peq,Peq}$ = 36 Hz, 1 P, PCH$_3$), 17 (dd, $^{2}J_{Pax,Peq}$ = 33, $^{2}J_{Pax,Peq}$ = 45 Hz, 1 P, PCH$_3$), 75 (dd, $^{2}J_{Peq,Pax}$ = 33, $^{2}J_{Peq,Peq}$ = 36 Hz, 1 P, PPh$_2$) ppm. $C_{30}H_{38}CoP_3$ (550.4): calcd. C 65.46, H 6.96, P 16.88; found C 64.81, H 6.71, P 17.27.

[{2-(Diphenylphosphanyl)-3-phenylphenyl-(*C*^{1},*P*)}(ethene)bis(trimethylphosphane)cobalt(I)] (8): A sample of **3** (940 mg, ca. 1.5 mmol) in THF (40 mL) was stirred under 1 bar of ethene for 3 h. The volatiles were removed in vacuo, and the oily residue was extracted with pentane (50 mL). Crystallization at 4 °C afforded short, orange rods of **8.** Yield 503 mg (58%); m.p. 95−97 °C (dec.). ^{1}H NMR (300 MHz, [D$_8$]THF, 296 K): δ = 0.82 (d, $^{2}J_{P,H}$ = 6.3 Hz, 9 H, PCH$_3$), 1.10 (d, $^{2}J_{P,H}$ = 5.9 Hz, 9 H, PCH$_3$), 1.66 (m, 1 H, =CH), 1.91 (m, 2 H, =CH$_2$), 2.31 (m, 1 H, =CH), 6.51 (m, 1 H, CH), 6.72 (dd, ^{3}J = 5.0, ^{4}J = 1.5 Hz, 2 H, CH), 7.15 (dd, ^{3}J = 6.8, ^{4}J = 1.6 Hz, 1 H, CH), 7.17 (dd, ^{3}J = 8.3, ^{4}J = 1.3 Hz, 1 H, CH), 6.85 (m, 3 H, CH), 6.95 (dd, ^{3}J = 7.3, ^{4}J = 1.4 Hz, 1 H, CH), 7.16 (dd, ^{3}J = 7.2, ^{4}J = 1.5 Hz, 1 H, CH), 7.21 (m, 6 H, CH), 7.41(dd, ^{3}J = 9.4, ^{4}J = 1.5 Hz, 1 H, CH), 7.42 (m, 2 H, CH), 7.68 (dd, ^{3}J = 9.4, ^{4}J = 1.9 Hz, 1 H, CH), 7.70 (dd, ^{3}J = 5.8, ^{4}J = 2.6 Hz, 1 H, CH) ppm. ^{13}C NMR (75.4 MHz, [D$_8$]THF, 296 K): δ = 16.5 (d, $^{1}J_{P,C}$ = 18.1 Hz, PCH$_3$), 20.3 (d, $^{1}J_{P,C}$ = 18.4 Hz, PCH$_3$), 32.5 (d, $^{2}J_{P,C}$ = 10.4 Hz, =CH$_2$), 38.8 (d, $^{2}J_{P,C}$ = 18.1 Hz, =CH$_2$), 121.5 (s, CH), 124.7 (s, CH), 125.9 (s, CH), 126.6 (d, $^{2}J_{P,C}$ = 8.8 Hz, CH), 127.1 (s, CH), 127.8 (s, CH), 128.2 (s, CH), 128.6 (d, $^{1}J_{P,C}$ = 15.2 Hz, C), 131.9 (d, $^{2}J_{P,C}$ = 12.1 Hz, CH), 132.2 (d, $^{2}J_{P,C}$ = 12.2 Hz, CH), 135.6 (d, $^{1}J_{P,C}$ = 16.4 Hz, CH), 136.9 (s, C), 139.1 (d, $^{1}J_{P,C}$ = 17.5 Hz, C), 140.7 (d, $^{3}J_{P,C}$ = 4.3 Hz, C), 146.4 (s, C), 153.0 (m, CoC) ppm. ^{31}P NMR (81 MHz, [D$_8$]THF, 233 K): δ = −11 (dd, $^{2}J_{Peq,Pax}$ = 47, $^{2}J_{Peq,Peq}$ = 51 Hz, 1 P, PPh$_2$), 9 (dd, $^{2}J_{Pax,Peq}$ = 31, $^{2}J_{Pax,Peq}$ = 47 Hz, 1 P, PCH$_3$), 21 (dd, $^{2}J_{Peq,Pax}$ = 31, $^{2}J_{Peq,Peq}$ = 51 Hz, 1 P, PCH$_3$) ppm. $C_{32}H_{40}CoP_3$ (576.2): calcd. C 66.67, H 6.99, P 16.22; found C 66.45, H 7.41, P 16.14.

[(Carbonyl){2-(diphenylphosphanyl)naphthyl-(*C*^{1},*P*)}bis(trimethylphosphane)cobalt(I)] (9): A sample of **2** (770 mg, 1.28 mmol) in THF (40 mL) was stirred under 1 bar of CO for 1 h to provide a light red solution. The volatiles were removed in vacuo, and the solid residue was extracted with pentane (three 70-mL portions). Crystallization at −27 °C afforded short, orange rods of **9** suitable for X-ray diffraction. Yield 616 mg (87%); m.p. 112−114 °C (dec.). IR (Nujol): $\tilde{\nu}$ = 1905 cm^{-1} (C≡O). ^{1}H NMR (300 MHz, [D$_8$]THF, 296 K): CO-eq isomer (12%): δ = 0.68 (d, $^{2}J_{P,H}$ = 6.3 Hz, 18 H, PCH$_3$), 1.12 (d, $^{2}J_{P,H}$ = 7.9 Hz, 18 H, PCH$_3$), 7.01−8.02 (m, 16 H, CH) ppm; CO-ax isomer (88%): δ = 0.69 (d, $^{2}J_{P,H}$ = 6.3 Hz, 9 H, PCH$_3$), 1.00 (t′, $|^{2}J_{P,H} + {}^{4}J_{P,H}|$ = 6.8 Hz, 18 H, PCH$_3$), 1.19 (d, $^{2}J_{P,H}$ = 7.9 Hz, 9 H, PCH$_3$), 7.08 (d, ^{3}J = 6.6 Hz, 1 H, CH), 7.10 (t, ^{3}J = 7.4 Hz, 1 H, CH), 7.26−7.29 (m, 8 H, CH), 7.43−7.49 (m, 4 H, CH), 7.61 (d, ^{3}J = 6.9 Hz, 1 H, CH), 7.70 (d, ^{3}J = 6.9 Hz, 1 H, CH), 7.84 (d, ^{3}J = 7.0 Hz, 1 H, CH), 7.97 (d, ^{3}J = 8.2 Hz, 1 H, CH) ppm. ^{13}C NMR (75.4 MHz, [D$_8$]THF, 296 K) CO-ax isomer (88%): δ = 19.8 (m, PCH$_3$), 120.5 (s, C), 125.5 (d, $^{3}J_{P,C}$ = 5.4 Hz, CH), 125.8 (s, CH), 126.5 (s, C), 128.6 (d, $^{1}J_{P,C}$ = 15.5 Hz, C), 128.8 (d, $^{2}J_{P,C}$ = 8.4 Hz, CH), 129.4 (s, CH), 130.4 (s, CH), 132.6 (d, $^{2}J_{P,C}$ = 12.7 Hz, CH), 133.3 (s, C), 134.7 (d, $^{1}J_{P,C}$ = 14.3 Hz, C), 138.9 (m, CH), 141.6 (s, C), 142.0 (s, C), 203.2 (s, CO) ppm. ^{31}P NMR (81 MHz, [D$_8$]THF, 233 K) CO$_{ax}$ isomer (12%): δ = 5 (d, $^{2}J_{Peq,Peq}$ = 96 Hz, 2 P, PCH$_3$), 63 (t, $^{2}J_{Peq,Peq}$ = 96 Hz, 1 P, PPh$_2$) ppm; CO$_{eq}$ isomer (88%): δ = −1 (dd, $^{2}J_{Peq,Peq}$ = 81, $^{2}J_{Peq,Pax}$ = 48 Hz, 1 P, PCH$_3$), 23 (dd, $^{2}J_{Pax,Peq}$ = 48, $^{2}J_{Pax,Peq}$ = 48 Hz, 1 P, PCH$_3$), 70 (dd, $^{2}J_{Peq,Peq}$ = 81, $^{2}J_{Peq,Pax}$ = 48 Hz, PPh$_2$) ppm. $C_{29}H_{34}CoOP_3$ (550.4): calcd. C 63.28, H 6.23, P 16.88; found C 62.67, H 5.78, P 17.30.

[{2-(Diphenylphosphanyl)naphthyl-(*C*^{1},*P*)}iodobis(trimethylphosphane)cobalt(II)] (10): A sample of **2** (670 mg, 1.12 mmol) in diethyl ether (50 mL) was mixed at −70 °C with iodomethane (365 mg, 2.57 mmol, slight excess). After 1 h at 20 °C, the mixture was filtered and the solution was kept at 4 °C to afford dark-brown crystals of **10**. The solid was extracted with diethyl ether (two 80-mL portions) to give a second fraction of **10**, which was combined with the first. Yield 421 mg (58%); m.p. 158−160 °C (dec.). Magnetic moment: μ_{eff} = 1.91 μ_B. $C_{28}H_{34}CoIP_3$ (649.3): calcd. C 51.79, H 5.28, P 14.31; found C 51.78, H 5.41, P 14.26.

Crystal Structure Analyses: Crystal data are presented in Tables 1 and 2. Complex **1**: A crystal was sealed under argon in a glass capillary and mounted on a Bruker AXS P4 diffractometer. Reflections were collected (ω-scans) by use of graphite-monochromated Mo-K_α radiation; a Lorentz polarization correction and an 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. Complex **4**: Crystal mounting, data collection, structure solution, and refinement as for **1**. Complex **7**: Crystal mounting, data collection, structure solution, and refinement as for **1**. Two independent molecules per asymmetric unit. Complex **9**: Crystal mounting, data collection, structure solution, and refinement as for **1**. CCDC-184425 (**1**), -184426 (**4**), -184427 (**7**), and -184428 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystal data for compounds **1** and **4**

	1	**4**
Empirical formula	$C_{31}H_{47}CoP_4$	$C_{32}H_{45}CoP_4$
Molecular mass	602.5	612.5
Crystal size [mm]	0.50 × 0.45 × 0.45	0.44 × 0.40 × 0.40
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_1/c$
a [Å]	10.929(3)	9.096(3)
b[Å]	16.544(3)	35.594(3)
c [Å]	17.501(9)	9.913(2)
β [°]	90	98.79(2)
V [Å^3]	3164.3(19)	3171.8(13)
Z	4	4
$D_{calcd.}$ [g/cm^3]	1.265	1.283
μ (Mo-K_α) [mm^{-1}]	0.763	0.762
Temperature [K]	203(2)	293(2)
Data coll. range [°]	$4.7 \le 2\theta \le 55$	$4.6 \le 2\theta \le 55$
h	$-1 \le h \le 14$	$-1 \le h \le 11$
k	$-1 \le k \le 21$	$-1 \le k \le 46$
l	$-1 \le l \le 22$	$-12 \le l \le 12$
No. reflect. measured	4975	8877
No. unique data	4759 (R_{int} = 0.0323)	7266 (R_{int} = 0.0310)
Parameters	335	334
GoF on F^2	1.010	0.968
$R1$ [$I \ge 2\sigma(I)$]	0.0578	0.0484
$wR2$ (all data)	0.1243	0.1051

Table 2. Crystal data for compounds **7** and **9**

	7	**9**
Empirical formula	$C_{30}H_{38}CoP_3$	$C_{29}H_{34}CoOP_3$
Molecular mass	550.4	550.4
Crystal size [mm]	0.40 × 0.35 × 0.30	0.38 × 0.15 × 0.06
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a [Å]	9.697(2)	18.242(2)
b [Å]	16.411(2)	9.016(1)
c [Å]	35.970(6)	18.301(2)
β [°]	97.36(2)	111.94(1)
V [Å^3]	5677.0(17)	2792.0(5)
Z	8	4
$D_{calcd.}$ [g/cm^3]	1.288	1.309
μ (Mo-K_α) [mm^{-1}]	0.790	0.806
Temperature [K]	293(2)	293(2)
Data coll. range [°]	$4.2 \leq 2\theta \leq 54$	$4.5 \leq 2\theta \leq 50$
h	$-12 \leq h \leq 1$	$-1 \leq h \leq 21$
k	$-1 \leq k \leq 20$	$-1 \leq k \leq 10$
l	$-45 \leq l \leq 45$	$-21 \leq l \leq 20$
No. reflect. measured	15436	6135
No. unique data	12400 (R_{int} = 0.0584)	4910 (R_{int} = 0.0378)
Parameters	638	313
GoF on F^2	0.977	0.984
$R1$ [$I \geq 2\sigma(I)$]	0.0665	0.0469
$wR2$ (all data)	0.1677	0.1304

Acknowledgments

Financial support of this work by Fonds der Chemischen Industrie is gratefully acknowledged.

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Received September 20, 2002
[I02520]