# Improved Access to {[ω-(Phosphanyl)alkyl]cyclopentadienyl}cobalt(I) Complexes: Decomplexation of the Phosphane Arm; Alkyne Complexes; Synthesis of Mononuclear Vinylidenecobalt(I) Complexes

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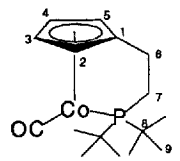
An improved synthesis of [(2-phosphanylethyl)cyclopentadienyl]cobalt(I) chelate complexes is presented, in which the paramagnetic chloride **3** is a precursor of the ethene complex **4**. The latter readily undergoes ligand exchange reactions which in the case of bidendate reagents (1,5-cyclooctadiene, 1,2-bis(diisopropylphosphanyl)ethane, 2,2'-bipyridine, norbornadiene) cause a decomplexation of the phosphane arm at room temperature with formation of **7**, **5**, **6**, **8**. The ethene ligand in **4** can be replaced by alkynes under equally mild reaction conditions (formation of **9**, **11**–**16**). The reaction with ethyne results in the formation of vinylidene complex **10**. The yields of the reactions with nonaromatic alkynes could be improved by treating **3** with the alkyne in the presence of sodium amalgam. The unsubstituted vinylidene complex **10** and its *tert*-butyl derivative **17** were obtained by this route in 88 and 40% yield, respectively.

Following extensive research into the chemistry of cyclopentadienyl complexes of many transition metals bearing the unsubstituted ligand[1,2], interest has now turned to substituted cyclopentadienyl ligands[3,4]. Functionally substituted cyclopentadienyl ligands can also fundamentally change the coordination properties of the ligands when the substituent can itself coordinate to the metal[3,5]. Ligands of this kind are di- or even multidendate, and their specific properties are determined by all the participating ligand moieties. Bidendate ligands are particularly interesting when the participating ligand moieties are of different nature, since each ligand exerts a different influence on reactivity. The cyclopentadienyl ligand and phosphane ligands are among the most used ligands in organometallic chemistry, and they are quite different. Whereas the cyclopentadienyl ligand is a negatively charged π ligand, phosphanes are electroneutral σ donor ligands, of which a large number of substituent patterns have been investigated[6]. Heterobidendate ligands include, among others, phosphanylcyclopentadienyl systems, in which a phosphane functionality is directly connected to a cyclopentadienyl system[7,8]. A direct bond between the cyclopentadienyl and the phosphane part of such ligands may result in resonance interactions between the phosphane lone pair and the cyclopentadienyl π system, which could change the genuine properties of the two components resulting in a different kind of ligand system. Moreover, the formation of chelate complexes using a direct bridge seems to be unlikely due to the geometric problems[9]. We were therefore interested for some time in complexes with [ω-(phosphanyl)alkyl]cyclopentadienyl ligands in which the cyclopentadienyl and the phosphane part are separated from each other by an alkyl chain. The possibility of chelate formation is a reason for the popularity of ligands with other functional groups in the side chain, for example alkenylcyclopentadienyl complexes[10–15] or aminoalkyl derivatives[3,5,16,17].




**1**

Chelate cobalt complexes like **1** are formed by treatment of the anionic (ω-phosphanylalkyl)cyclopentadienyl ligands with $ICo(CO)_4$[18,19]. Normally, complexes with an ethylene bridge are obtained in higher yields than those with a propylene bridge. In our hands complexes with *tert*-butyl substituents at the P atom gave the highest yields and were those which gave the best crystals. The anionic ligand of **1** is easily accessible by nucleophilic ring opening of spiro[2.4]hepta-4,6-diene with lithium di-*tert*-butylphosphide[20]. The relatively inert nature of the carbonyl complex **1**[19] made us look for more reactive derivatives, and we resorted to the method of Kölle[21], which offered an alternative route to the desired class of complexes. In this paper we report in detail on the synthesis of complexes bearing alkene, alkyne, and vinylidene ligands instead of CO. Parts of the results reported here were published in a preliminary communication[22].

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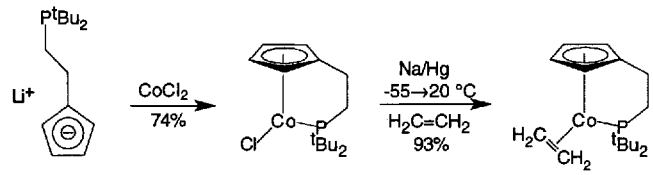
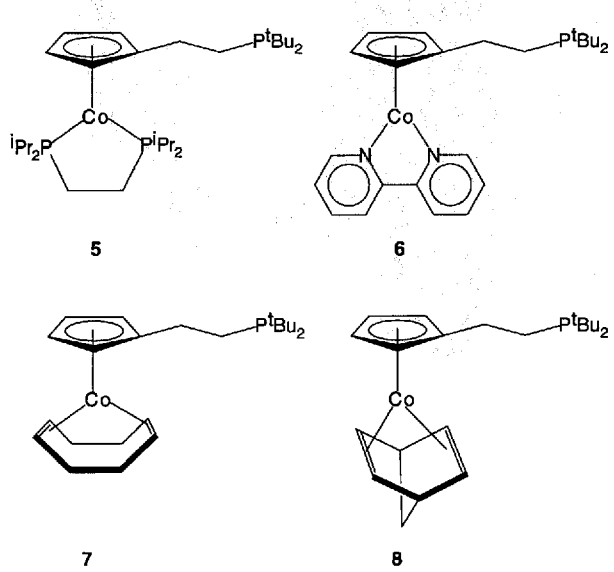
Applying the method introduced by Kölle for the pentamethylcyclopentadienyl ligand to our ligand, we treated anion **2**[19] with anhydrous cobalt(II) chloride at −30°C and subsequently warmed the mixture to 20°C. Paramagnetic chloride **3** was obtained in 74% yield as black-violet plates. Chloride **3** is well soluble in THF, but poorly in all other common solvents. All analytical data are in accord with the formulation of **3**. In analogy to similar chemistry by Kölle[21,23,24] and Okuda[10,12–14], for some time a dimeric constitution was assumed for **3**[22]. However, the ESR spectrum did not only show the signal splitting caused by the cobalt I = 7/2 nucleus but also that caused by the phosphorus I = 1/2 indicating coordination of the phosphane arm, which is in accord with **3**, but not with the assumed dimeric constitution[25]. Compound **3** was reduced by treatment with sodium amalgam at −55°C in the presence of ethene bubbling through the reaction flask to give the ethene complex **4** in 93% yield as a black-red crystalline material, which is well soluble in all common organic solvents. Complex **4** was fully characterized, including by means of an X-ray structural analysis[22]. One interesting feature of the molecule is the rotation of the ethene ligand around the alkene-cobalt coordination axis: At 300 K the signals of the ethene ligand appear as an AA'BB' line system at δ = 1.87 and 2.27. With increasing temperature the signals become broader, and coalescence is observed at 326 K, giving rise to a signal at δ = 2.02 at higher temperatures. This corresponds to estimated $\Delta G^{\ddagger} \approx 62$ kJ/mol (326 K)[26]. This barrier is similar to that of other known $\eta^2$-bonded ethene complexes[27], although it is remarkable that the closely related ($\eta^5$-cyclopentadienyl)($\eta^2$-ethene)(triphenylphosphane)-cobalt(I) does not show this phenomenon up to 55°C[28].




**2** **3** **4**

The ethene ligand in **4** can be more easily replaced by other ligands than the carbonyl ligand in **1**. Bidendate ligands replace ethene in **4** when the reaction mixture is stirred at 20°C, and irradiation is not required. Thus, treatment of **4** with 1,2-bis(diisopropylphosphanyl)ethane gives the chelate complex **5** in 93% yield with decoordination of the phosphane arm of the heterobidendate ligand, as clearly indicated by the spectroscopic data, especially the $^{31}$P-NMR spectrum. Analogously, reaction of **4** with 2,2'-bipyridine results in a 88% yield of the corresponding bipyridine complex **6**, again with decomplexation of the phosphane side arm. The 1,5-cyclooctadiene complex **7** has previously been obtained in 41% yield from **1** by irradiation in 1,5-cyclooctadiene solution[19]. The reaction of **4** with 1,5-cyclooctadiene at 20°C leads without irradiation to **7** in 82% yield, and similar treatment of **4** with norbornadiene results in a 87% yield of **8**. These ligand exchange reactions demonstrate that the ethene complex **4** is a suitable starting material for the synthesis of complexes such as **5**–**8** in high yield under mild reaction conditions. They further demonstrate that the phosphane side arm in **4** can be decoordinated under equally mild reaction conditions, which supports our thesis that the phosphane side arm acts as an intramolecular protecting group for a vacant coordination site[19].




**5** **6**




**7** **8**

Reactions of (cyclopentadienyl)cobalt(I) complexes with alkynes have been extensively investigated and usually result in the formation of coupling products, for example arenes, cyclobutadiene complexes or cyclopentadienone complexes[29–31]. Few alkyne(cyclopentadienyl)cobalt(I) complexes are known[14,32]. To investigate how far the (phosphanylalkylcyclopentadienyl)cobalt(I) systems behave analogously, reactions of **4** with alkynes were performed.

Complex **4** reacts smoothly with diphenylethyne to give the alkyne complex **9** in 83% yield. Compound **9** has previously been obtained in only 39% yield by reaction of **1** with diphenylethyne under photochemical reaction conditions[19].

Crystals of **9** suitable for an X-ray structure analysis were obtained from diethyl ether. The structure of **9** is given in Figure 1 and shows the typical bending back of the substituents on the alkyne ligand upon coordination to a metal. In this compound the deviation of the alkyne from linearity is 31.3(4)°. Interestingly, the alkyne is not bound straight to the Co atom, but distorted so that the plane through the atoms C2, C1, C1*, and C2* forms an angle of 14(2)° to that through Co1, C1, and C1*, presumably as a result of steric interaction between the phenyl groups and the *tert*-butyl groups on the P atom. In the isoelectronic (but-3-enyltetramethylcyclopentadienyl)bis(trimethylsilylethyne)-cobalt(I)[14] the distortion is smaller (7°) and in the opposite direction for a similar steric reason. Disorder of the bridging ethylene chain between the cyclopentadienyl ring and the P atom prevents a detailed discussion of its geometry, but it is evident that the twisted form makes the compound chiral, at least in the solid. The relevant torsion angles are

Co1–P1–C8–C9 32(2) and P1–C8–C9–C10 −45(2)°. In principle, disorder in the ethylene chain may be accompanied by disorder in the cyclopentadienyl ring and the *tert*-butyl groups attached to P, but this could not be confirmed[14].

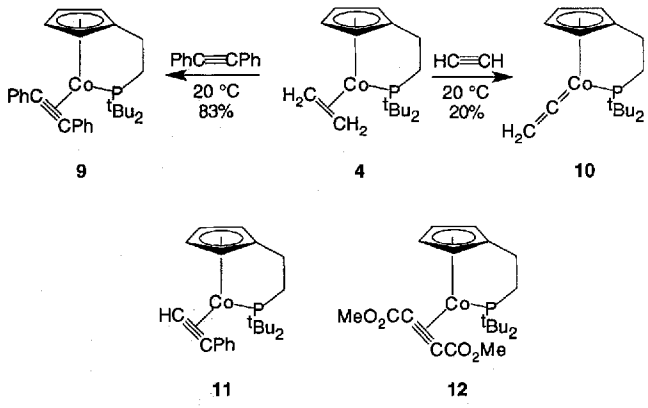
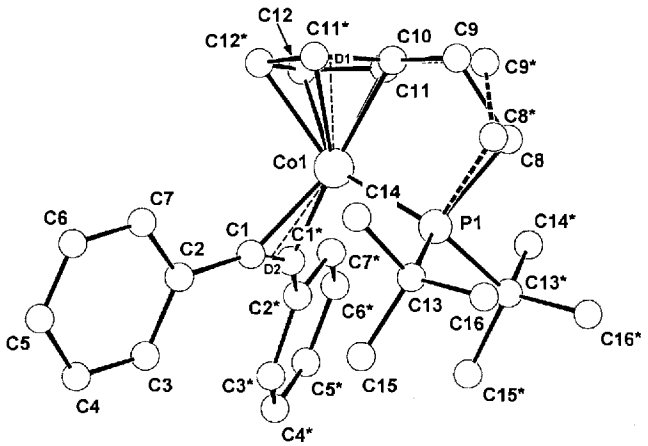



Figure 1. Structure of one molecule of **9** in the crystal (the two independent molecules are identical within error, C8 and C9 have half occupancy, symmetry-related atoms denoted by *); H atoms omitted for clarity; selected interatomic distances [Å] and angles [°]: Co1–P1 2.203(2), Co1–C1 1.961(3), Co1–C10 2.039(6), Co1–C11 2.071(4), Co1–C12 2.102(5), Co1–D1 1.72(2), Co1–D2 1.86(2), P1–C8 1.887(6), P1–C13 1.893(5), C1–C1* 1.272(5), C1–C2 1.450(5), C8–C9 1.58(1), C10–C11 1.380(5), C11–C12 1.381(8), C12–C12* 1.357(8); P1–Co1–D1 121(1), P1–Co1–D2 101.7(5), D1–Co1–D2 137(1), Co1–P1–C8–C9 32(2), P1–C8–C9–C10 −45(2), plane(Co1,C1,C1*)–plane(C2,C1,C1*, C2*) 14(2)




When the ethene complex **4** was treated with ethyne at 20 °C, the vinylidene complex **10** was obtained in 20% yield. Compound **10** is one of the very few reported vinylidene complexes of cobalt[33–36]. It was completely characterized by spectroscopic methods and exhibits a chemical shift of $\delta = 303.7$ for the vinylidene carbon atom. The formation of a vinylidene complex is unexpected considering that the reactivity of the (cyclopentadienyl)cobalt(I) system with alkynes was extensively investigated in connection with cyclooligomerization reactions mentioned above. We explain the formation of **10** instead of cycloologomerization products as resulting from the chelated phosphane side arm, which apparently inhibits the cyclooligomerization reactions under the reaction conditions chosen.

The formation of the alkyne complex **9** and that of the vinylidene complex **10** raises the question, what is the result of the reaction of **4** with phenylethyne? The reaction can be carried out at 0 °C and affords the phenylethyne complex **11** in almost quantitative yield. To our knowledge, **11** is the first known alkyne(cyclopentadienyl)cobalt(I) complex containing a terminal alkyne ligand. In contrast to the room-temperature reaction leading to **9**, this reaction has to be carried out at 0 °C, because **11** decomposes at higher temperatures. Like the other alkyne complexes, **11** dissolves to give a green solution. As observed for the reaction leading to vinylidene complex **10**, the solution of **11** in THF changes its color to brown at higher temperatures. However, the suggested rearrangement to the vinylidene complex corresponding to **10** has not yet been proven. Dimethyl butynedioate, an electron-poor acetylenic ligand, can be introduced by reaction with ethene complex **4** to give **12** in 89% yield.

The vinylidene complex **10** is an interesting substrate for further syntheses and its use might, for example, lead to the rare cobalt carbene complexes. However, to realize these syntheses, the yield of **10** had to be improved. For this purpose, the formation of ethene complex **4** was skipped, and the direct reaction of chloride **3** with ethyne in the presence of sodium amalgam at temperatures between −55 and 20 °C was performed. It gave an 88% yield of the vinylidene complex **10**, which is now accessible in preparative quantities. One experiment showed that the ethyne complex **13** is most likely an intermediate in the reaction leading to **10**. Thus, when the reaction mixture was stored at −78 °C for 2 d, air-stable, black-green crystals (59%, m.p. 232.5 °C) were obtained whose $^1$H-NMR and MS data are in accord with the formulation of **13**. In solution the rearrangement to **10** is so fast that it was impossible to obtain any $^{13}$C-NMR data of **13**. Attempts to obtain an X-ray crystal structural analysis of **13** have failed so far.

In order to investigate how far the one-step reaction of the chloride **3** with alkynes in the presence of sodium amalgam is generally applicable, **3** was treated with 2-butyne, 3-hexyne, and cyclopropyl(trimethylsilyl)ethyne. It gave the corresponding alkyne complexes **14**–**16** in 74, 87, and 95% yield, respectively. The method appears to be limited to nonaromatic alkynes. The reaction with aromatic alkynes normally results in a complicated mixture of products. Maybe an electron transfer process between the sodium amalgam and the aromatic moieties gives rise to side reactions. 3,3-Dimethyl-1-butyne was chosen as an example of a terminal alkyne and its use resulted in a 40% yield of alkylvinylidene complex **17**, which was characterized spectroscopically. The carbon atom resonance at $\delta = 302.7$ is particularly characteristic of its constitution. It is remarkable that this signal is rather broad ($\Delta\nu_{1/2} = 100$ Hz). Investigations regarding to a possible dynamic behavior of our compounds are in progress.

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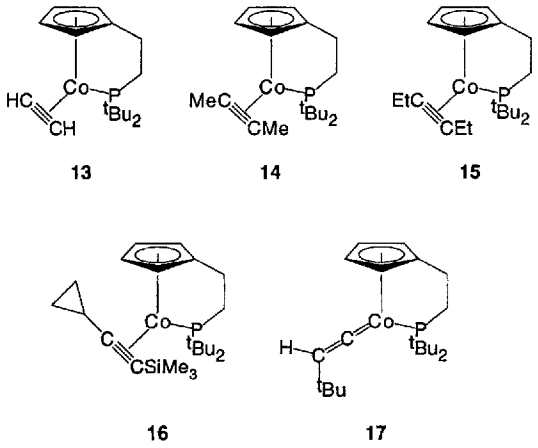


13 14 15

16 17

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## Experimental

*General:* See ref.[19]. All cobalt complexes reported are stable at 25°C under argon. – NMR: APT = attached proton test; + = positive, – = negative phase of signal. – ESR: Bruker ESP 300 (X-Band).

*Chloro{[2-(di-tert-butylphosphanyl-P)ethyl]cyclopentadienyl}-cobalt(II)* (**3**): To a cooled (−30°C) solution of 7.35 g (30.1 mmol) of lithium [2-(di-*tert*-butylphosphanyl)ethyl]cyclopentadicnide[19] in 120 ml of THF in a 250-ml Schlcnk flask equipped with a magnetic stirring bar was added 1.95 g (15.0 mmol) of cobalt(II) chloride. The Bordeaux red suspension was stirred for 20 min and allowed to warm from −30 to 20°C. Then the mixture was stirred at 20°C for anothr 60 min. THF was condensed into a cold trap at 1 mbar, and the residue was taken up in 10 portions of 250 ml of diethyl ether. The red-violet ethereal solution was stored at −78°C. Precipitation gave 7.33 g (11.4 mmol, 74%) of **3** as black-violet plates (m.p. 192°C, DSC). – IR (KBr): $\tilde{\nu}$ = 3117 $cm^{-1}$ (w), 3080 (w, Cp), 3004 (m), 2985 (m), 2965 (s), 2945 (s, $CH_2$, $CH_3$), 2899 (s, $CH_2$, $CH_3$), 2863 (s, $CH_2$, $CH_3$), 1741 (w), 1475 (m), 1422 (w), 1389 (m, *t*Bu), 1367 (m, *t*Bu), 1344 (w), 1307 (w), 1238 (w), 1227 (w), 1180 (m, *t*Bu), 1167 (m, *t*Bu), 1102 (w), 1058 (w), 1036 (m), 1018 (m, Cp-R), 932 (w), 856 (w), 828 (w), 801 (s, Cp), 784 (m), 678 (m), 661 (w), 618 (w), 602 (w). – ESR (toluene, 9.41 GHz, 150 K): $g_z$ = 2.312 (octet of doublets, $A_z$ = 73.6, 20.5 G). – MS (70 cV), *m/z* (%): 331 (97) [$M^+$], 275 (14) [$M^+ - C_4H_8$], 239 (65) [$M^+ - C_4H_8 - HCl$], 183 (100) [$M^+ - 2(C_4H_8) - HCl$], 137 (17), 84 (16), 59 (11) [$Co^+$], 57 (31) [$C_4H_9^+$]. – $C_{30}H_{52}Cl_2Co_2P_2$ (663.5): calcd. C 54.31, H 7.90, Cl 10.69, Co 17.77, P 9.34; found C 54.19, H 7.84, Cl 10.66, Co 17.89, P 9.31.

*{η⁵:η¹[2-(Di-tert-butylphosphanyl-P)ethyl]cyclopentadienyl}(η²-ethene)cobalt(I)* (**4**): In a 1000-ml three-necked round-bottom flask equipped with a gas inlet tube and a magnetic stirring bar at −55°C an excess of ethene was bubbled through a solution of 6.80 g (10.2 mmol) of **3** in 400 ml of THF. After 10 min 301.5 g of 1% sodium amalgam (152 mmol Na) was added by means of pipette to the cooled red-violet solution. The mixture was stirred for 1 h and warmed to 20°C. The muddy brown mixture was filtered through a P4 frit, and the volume of the red filtrate was reduced to 20 ml by condensation of the solvent into a cold trap at reduced pressure. The product was crystallized at −78°C to give 6.15 g (19 mmol, 93%) of **4** as red-black crystals (m.p. 115°C, DSC). – IR (KBr): $\tilde{\nu}$ = 3095 $cm^{-1}$ (w, Cp), 3084 (w, Cp), 3042 (w, coord. $C_2H_4$), 2980 (s), 2960 (s, $CH_2$, $CH_3$), 2895 (s, $CH_2$, $CH_3$), 2860 (s, $CH_2$, $CH_3$), 1559 (w, coord. $C_2H_4$), 1468 (s), 1413 (w), 1385 (w, *t*Bu), 1367 (m, *t*Bu), 1308 (w), 1266 (w), 1162 (s, coord. $C_2H_4$), 1037 (m, Cp-R), 1026 (m, Cp-R), 1017 (m, Cp-R), 929 (w), 888 (w), 824 (m), 808 (m), 794 (s, Cp-R), 766 (w), 667 (m), 653 (w), 619 (w). – $^1$H NMR (400 MHz, 300 K; [D$_8$]toluene): δ = 1.06 (d, 18H, 9-H, $^3J_{P,H}$ = 11.4 Hz), 1.81 (m, 2H, 6-H, $^3J_{P,H}$ = 19.0 Hz), 1.87 (m, 4H, 7-H, *H*HC=C*H*H, $^2J_{P,H}$ = 7.0 Hz), 2.27 (m, 2H, HHC=CHH, Σ*J* = 9.0 Hz), 3.50, 5.39 [AA'BB' line system, 4H, 2(5)-H, 3(4)-H, $\Sigma^3J_{2(5),3(4)}$ = 4.0 Hz]. – $^{13}$C NMR (50.3 MHz, 193 K, [D$_8$]toluene): δ = 22.4 (dt, C-10), 24.8 (dt, C-6, $^2J_{C,P}$ = 5.4 Hz), 29.7 (dq, C-9), 34.7 (d, C-8, $^1J_{C,P}$ = 7.7 Hz), 37.8 (dt, C-7, $^1J_{C,P}$ = 21.0 Hz), 79.8 [dd, C 2(5)], 80.1 [d, C-3(4)], 110.3 (d, C-1, $^3J_{C,P}$ = 6.7 Hz). – $^{13}$C NMR (50.3 MHz, 313 K, [D$_8$]toluene): δ = 22.3 (dt, C-10, $^1J_{C,H}$ = 151 Hz, $J_{C,P}$ = not resolved), 25.1 (dt, C-6, $^1J_{C,H}$ = 130, $^2J_{C,P}$ = 7.0 Hz), 30.5 (dq, C-9, $^1J_{C,H}$ = 127, $^2J_{C,P}$ = 4.1 Hz), 35.1 (d, C-8, $^1J_{C,P}$ = 6.8 Hz), 38.7 (dt, C-7, $^1J_{C,H}$ = 129, $^1J_{C,P}$ = 19.9 Hz), 80.1 [dd, C 3(4), $^1J_{C,H}$ = 172, $^5J_{C,P}$ = 5.8 Hz], 80.7 [d, C 2(5), $^1J_{C,H}$ = 171 Hz], 109.8 (d, C-1, $^3J_{C,P}$ = 6.8 Hz). – $^{31}$P NMR (121.5 MHz, 193 K, [D$_8$]toluene): δ = 91.2. – $^{31}$P NMR (121.5 MHz, 313 K, [D$_8$]toluene): δ = 92.6. – MS (70 eV), *m/z* (%): 324 (28) [$M^+$], 296 (97) [$M^+ - C_2H_4$], 254 (16), 240 (58) [$M^+ - C_2H_4 - C_4H_8$], 184 (100) [$M^+ - C_2H_4 - 2(C_4H_8)$], 137 (26), 59 (19) [$Co^+$], 28 (13) [$C_2H_4^+$]. – $C_{17}H_{30}CoP$ (324.3): calcd. C 62.96, H 9.32, Co 18.17, P 9.55; found C 62.93, H 9.27, Co 18.10, P 9.65.

*{η²-1,2-Bis(diisopropylphosphanyl-P)ethane}{η⁵[2-(di-tert-butylphosphanyl)ethyl]cyclopentadienyl}cobalt(I)* (**5**): A solution of 393 mg (1.2 mmol) of **4** and 317 mg of 1,2-bis(diisopropylphosphanyl)ethane in 20 ml of THF was stirred for 40 h at 20°C. The solvent was condensed into a cold trap at 1 mbar, and the residue was taken up in a small volume of diethyl ether. 623 mg (1.1 mmol, 93%) of **5** was crystallized at −78°C as red crystals (m.p. 82°C, DSC). – IR (KBr): $\tilde{\nu}$ = 3105 $cm^{-1}$ (w), 3091 (w), 3063 (w), 2964 (m, $CH_2$, $CH_3$), 2948 (m, $CH_2$, $CH_3$), 2932 (m, $CH_2$, $CH_3$), 2886 (m, $CH_2$, $CH_3$), 2862 (m, $CH_2$, $CH_3$), 1465 (s), 1375 (m, *t*Bu), 1359 (m, *t*Bu), 1262 (w), 1237 (w), 1174 (m), 1152 (m), 1018 (m), 880 (m), 843 (w), 810 (m), 778 (w), 753 (m), 690 (s), 674 (m), 640 (m), 625 (s), 594 (w). – $^1$H NMR (200 MHz, [D$_8$]THF): δ = 1.04 (dd, 6H, 11-H, $^3J_{10,11}$ = 6.8, $^3J_{P2,H}$ = 5.2 Hz), 1.10 (d, 18H, 9-H, $^3J_{P1,H}$ = 10.5 Hz), 1.12 (dd, 6H, 12-H, $^3J_{10,12}$ = 7.1, $^3J_{P2,H}$ = 6.8 Hz), 1.26 (d, 4H, 13-H, $^2J_{P2,H}$ = 9.5 Hz), 1.57 (m, 2H, 6-H or 7-H, $J_{P1,H}$ = 3.8 Hz), 1.94 (dsept, 4H, 10-H, $^2J_{P2,H}$ = 8.6 Hz), 2.52 (m, 2H, 6-H or 7-H), 4.37, 4.42 [AA'BB' line system, 4H, 2(5)-H, 3(4)-H]. – $^{13}$C NMR (50.3 MHz, [D$_8$]THF): δ = 19.3 (q, C-11 or C-12, $^1J_{C,H}$ = 126 Hz), 20.0 (q, C-11 or C-12, $^1J_{C,H}$ = 126 Hz), 23.1 (tt, C-13, $\Sigma J_{P1,C \text{ and } JP2,C}$ = 44.6 Hz), 26.3 (dt, C-6 or C-7, $J_{C,P}$ = 25.0 Hz), 28.9 (dt, C-10, $\Delta J_{P1,C \text{ and } P2,C}$ = 17.2 Hz), 30.2 (dq, C-9, $^1J_{C,H}$ = 126, $^2J_{P1,C}$ = 14.0 Hz), 31.8 (d, C-8, $^1J_{P1,C}$ = 23.5 Hz), 32.7 (dt, C-6 or C-7, $J_{P1,C}$ = 28.8 Hz), 75.6 [d, C-2(5), C-3(4), $^1J_{C,H}$ = 171 Hz), 99.4 (d, $^3J_{P1,C}$ = 17.4 Hz). – $^{31}$P NMR (81 MHz, [D$_8$]THF): δ = 30.1 (s, 1P, P-1), 114.1 (s, 2 P, P-2). – MS (70 eV), *m/z* (%): 558 (100) [$M^+$], 401 (35), 296 (38) [$M^+ - C_{14}H_{32}P_2$], 237 (36), 195 (37), 153 (26), 57 (70) [$C_4H_9^+$]. – $C_{29}H_{58}CoP_3$ (558.6): calcd. C 62.35, H 10.47, Co 10.55, P 16.63; found C 62.28, H 10.39, Co 10.59, P 16.68.

*(η²-2,2'-Bipyridine){η⁵-[2-(di-tert-butylphosphanyl)ethyl]-cyclopentadienyl}cobalt(I)* (**6**) A red solution of 360 mg (1.1 mmol) of **4** and 356 mg (2.3 mmol) of 2,2'-bipyridine in 30 ml of THF was stirred for 18 h at 20°C. The color changed to violet, and the solvent was condensed into a cold trap at 1 mbar. Excess 2,2'-bipyridine was removed by sublimation at 0.001 mbar; the residue was crystallized from a small volume of diethyl ether. 442 mg (1.0

mmol, 88%) of **6** was obtained as a black-violet solid (m.p. 79°C, DSC). – IR (KBr): $\tilde{\nu}$ = 3071 $cm^{-1}$ (w), 3059 (w), 2937 (s, $CH_2$, $CH_3$), 2894 (m, $CH_2$, $CH_3$), 2859 (m, $CH_2$, $CH_3$), 1581 (m), 1560 (w), 1517 (m), 1468 (m), 1450 (s), 1362 (m, *t*Bu), 1346 (m, *t*Bu), 1303 (m), 1151 (m), 1021 (m), 814 (m, Cp-R), 736 (s), 690 (w). – $^1$H NMR (200 MHz, [D$_8$]THF): δ = 1.01 (d, 18H, $CH_3$, $^3J_{P,H}$ = 10.4 Hz), 1.72 (m, 2H, 6-H or 7-H), 2.70 (m, 2H, 6-H or 7-H), 4.50, 4.59 [AA'BB' line system, 4H, 2(5)-H, 3(4)-H, $\Sigma^3J_{2(5),3(4)}$ = 3.8 Hz], 6.71 (ddd, 2H, 11-H, $^3J_{11,12}$ = 6.4 Hz), 7.30 (ddd, 2H, 12-H, $^3J_{12,13}$ = 8.6 Hz), 7.46 (ddd, 2H, 13-H), 10.20 (2H, 10-H, $^3J_{10,11}$ = 6.4 Hz). – $^{13}$C NMR (50.3 MHz, [D$_8$]THF): δ = 25.0 (dt, C-6, $J_{C,P}$ = 23.5 Hz), 29.2 (dt, C-7, $J_{C,P}$ = 30.5 Hz), 30.0 (dq, C-10, $^1J_{C,H}$ = 126, $^2J_{C,P}$ = 14.0 Hz), 31.7 (d, C-8, $^1J_{C,P}$ = 23.5 Hz), 76.5 [d, C-2(5), $^1J_{C,H}$ = 171 Hz], 77.5 [d, C-3(4), $^1J_{C,H}$ = 174 Hz], 99.1 (d, C-1, $^3J_{C,P}$ = 15.7 Hz), 116.7 (d, C-11 or C-12 or C-13, $^1J_{C,H}$ = 163 Hz), 121.3 (d, C-11 or C-12 of C-13, $^1J_{C,H}$ = 164 Hz), 123.2 (d, C-11 or C-12 or C-13, $^1J_{C,H}$ = 160 Hz), 143.3 (s, C-14), 156.2 (d, C-10, $^1J_{C,H}$ = 178 Hz). – $^{31}$P NMR (81 MHz, [D$_8$]THF): δ = 30.2. – MS (70 eV), *m/z* (%): 452 (13) [M$^+$], 296 (24) [M$^+$ – bipy], 240 (1) [M$^+$ – bipy – $C_4H_7$], 215 (20), 184 (29) [M$^+$ – bipy – 2($C_4H_7$)], 156 (100), 128 (20), 78 (22), 59 (10) [Co$^+$]. – HRMS, $C_{25}H_{34}CoN_2P$: calcd. 452.17915; found 452.17922.

*(η$^4$-1,5-Cyclooctadiene){η$^5$-[2-(di-tert-butylphosphanyl)ethyl]-cyclopentadienyl}cobalt(I)* (**7**)[19]: A solution of 392 mg (1.2 mmol) of **4** in 30 ml of 1,5-cyclooctadiene was stirred at 20°C for 2 d. The 1,5-cyclooctadiene was condensed into a cold trap at 1 mbar, and the red, viscous residue was dissolved in 3 ml of pentane. The solution was transferred to a P4 frit covered by a 5 cm thick layer of silica. The silica was eluted with 200 ml of pentane. Then **7** was eluted with diethyl ether to give 404 mg (1.0 mmol, 82%) of red crystals (m.p. 62°C, DSC); identified by a comparison of the spectroscopic data (IR, $^1$H NMR, $^{13}$C NMR, $^{31}$P NMR, MS) with those of an authentic sample[19].

*{η$^5$-[2-(Di-tert-butylphosphanyl)ethyl]cyclopentadienyl}(η$^4$-norbornadiene)cobalt(I)* (**8**): A solution of 211 mg (0.65 mmol) of **4** in 20 ml of norbornadiene was stirred at 20°C for 4 d. The norbornadiene was condensed into a cold trap, the brown oily residue was dissolved in 10 ml of diethyl ether and the solution filtered through a P4 frit covered with a 2 cm thick layer of Celite. The filtrate was cooled stepwise (+7, –18, –78°C to give 212 mg (0.55 mmol, 84%) of **8** as bright yellow needles (m.p. 64.4°C). – IR (KBr): $\tilde{\nu}$ = 3053 $cm^{-1}$ (br, s), 2947 (s), 1470 (s), 1387 (m), 1367 (s), 1294 (m), 1261 (w), 1166 (s), 1099 (w), 1057 (m), 1019 (s), 990 (w), 927 (w), 893 (m), 809 (s), 449 (s). – $^1$H NMR (200 MHz, $C_6D_6$): δ = 0.98 (t, 2H, 12-H, *J* = 1.5 Hz), 1.21 (d, 18H, 9-H, $^3J_{P,H}$ = 10.8 Hz), 1.80 (m, 2H, 6-H), 2.4 (m, 2H, 7-H), 2.81 (m, 2H, 11-H or 10-H, *J* ≈ 1.5 Hz), 3.29 (m, 2H, 10-H or 11-H, *J* = 1.5 Hz), 4.83 + 4.49 [AA'BB' line system, 4H, 2(5)-H, 3(4)-H, $\Sigma^3J_{2(5),3(4)}$ = 2 Hz]. – $^{13}$C NMR (50 MHz, $C_6D_6$, APT): δ = 23.77 (+, d, C-6, *J* = 23.4 Hz), 26.13 (–, C-10), 29.98 (+, d, C-8, *J* = 30.4 Hz), 30.3 (–, d, C-9, *J* = 13.8 Hz), 31.8 (+, d, C-7, *J* = 22.8 Hz), 44.37 (–, C-11), 55.67 (+, C-12), 81.07 [–, C-3(4) or C-2(5)], 82.46 [–, C-3(4) or C-2(5)], 101.95 (+, d, C-1, *J* = 15.8 Hz). – $^{31}$P NMR (81 Hz, $C_6D_6$): δ = 29.08 (s). – MS (70 eV, 60°C), *m/z* (%): 388 (12) [M$^+$], 296 (100) [M$^+$ – $C_7H_8$], 240 (27) [M$^+$ – $C_7H_8$ – $C_4H_8$], 184 (31) [M$^+$ – $C_7H_8$ – 2 $C_4H_8$], 162 (8), 137 (8), 115 (11), 91 (14), 66 (7). – HRMS, $C_{22}H_{34}CoP$: calcd. 388.17301; found 388.17313.

*{η$^5$:η$^1$-[2-(Di-tert-butylphosphanyl-P)ethyl]cyclopentadienyl}(η$^2$-diphenylethyne)cobalt(I)* (**9**)[19]: A solution of 318 mg (1.0 mmol) of **4** and 178 mg (1.0 mmol) of diphenylethyne in 20 ml THF was stirred for 14 h at 20°C. The solvent was removed from the green-black solution by condensation into a colt trap at 1 mbar. Crystallization of the residue from 8 ml of diethyl ether gave 394 mg (0.8 mmol, 83%) of **9**[19] (m.p. 218°C, DSC); identified by comparison of the spectroscopic data (IR, $^1$H NMR, $^{13}$C NMR; $^{31}$P NMR, MS) with those of an authentic sample.

*X-Ray Crystal Structure Analysis of* **9**[37]: $C_{29}H_{36}CoP$, *M* = 474.5 g $mol^{-1}$, colour black, crystal size 0.39 × 0.46 × 0.25 mm, *a* = 16.671(1), *b* = 16.894(1), *c* = 17.954(1) Å, *V* = 5056.4(6) Å$^3$, *T* = 293 K, $D_c$ = 1.25 g $cm^3$, μ = 7.52 $cm^{-1}$, *F*(000) = 2016 e, *Z* = 8, orthorhombic, space group *Pbam* [No. 55], Enraf-Nonius CAD4 diffractometer, λ = 0.71069 Å, measuring method ω-2Θ, 12695 measured reflections (±*h*, +*k*, +*l*), $[(\sin)\Theta/\lambda]_{max}$ 0.65 Å$^{-1}$, 5942 independent reflections, 3676 observed reflections [$I \geq 2\sigma(I)$] for 281 refined parameters, structure solved by direct methods, non H atoms, except C8, C9, C10, C28, C29, and C30, refined anisotropically, H atom positions for nondisordered C atoms calculated and fixed ($U_H$ = 0.05 Å$^2$) in the final refinement stages, $\Sigma w(F_o - F_c)^2$ minimized, *R* = 0.053, $R_w$ = 0.061 [$w = 1/\sigma^2(F_o)$], max. shift/error 0.28, final difference Fourier = ρ 0.50 e Å$^{-3}$.

*{η$^5$:η$^1$-[2-(Di-tert-butylphosphanyl-P)ethyl]cyclopentadienyl}-(vinylidene)cobalt(I)* (**10**): In a 50-ml Schlenk flask 110 mg (0.3 mmol) of **4** was dissolved in 15 ml of pentane. The pressure in the flask was reduced, and a threefold excess of ethyne was added to the solution. After stirring at 20°C for 10 min, the solution darkened. It was stirred at 20°C for another 18 h and then cooled to –78°C. After removal of the solvent, 20 mg (0.06 mmol, 20%) of **10** was obtained as a black solid; purity 95% ($^1$H, $^{13}$C, $^{31}$P NMR). – IR (KBr): $\tilde{\nu}$ = 1654 $cm^{-1}$ (m, C=C). – $^1$H NMR (400 MHz, ([D$_8$]THF): δ = 1.33 (d, 18H, 9-H, $^2J_{P,H}$ = 12.6 Hz), 2.08 (m, 2H, 6-H, $^3J_{6,7}$ = 7.4, $^3J_{P,H}$ = 19.3 Hz), 2.09 (d, 2H, 10-H, $J_{P,H}$ = 9.6 Hz), 2.80 (m, 2H, 7-H, $^2J_{P,H}$ = 7.8 Hz), 4.49 [m, 2H, 2(5)-H or 3(4)-H, $\Sigma^3J_{2(5),3(4)}$ = 3.8 Hz], 5.03 [m, 2H, 2(5)-H or 3(4)-H]. – $^{13}$C NMR (100.6 MHz, [D$_8$]THF): δ = 25.8 (dt, C-6, $^1J_{C,H}$ = 128, $^2J_{C,P}$ = 5.2 Hz), 30.1 (dq, C-9, $^1J_{C,H}$ = 126, $^2J_{C,P}$ = 3.6 Hz), 36.6 (d, C-8, $^1J_{C,P}$ = 15.0 Hz), 41.0 (dt, C-7, $^1J_{C,H}$ = 128, $^1J_{C,P}$ = 18.2 Hz), 80.0 [d, C-2(5), $^1J_{C,H}$ = 174 Hz], 81.6 [d, C-3(4), $^1J_{C,H}$ = 174, $J_{C,P}$ = 5.4 Hz], 106.2 (dt, Co=C=*C*H$_2$, $^1J_{C,H}$ = 160, $J_{C,P}$ = 2.0 Hz), 112.3 (d, C-1, $^3J_{C,P}$ = 7.8 Hz), 303.7 (d, Co=*C*=CH$_2$, $J_{C,P}$ = 38.9 Hz). – $^{31}$P NMR (81 MHz, [D$_8$]THF): δ = 111.7. – MS (70 eV), *m/z* (%): 322 (14) [M$^+$], 296 (51) [M$^+$ – $C_2H_2$], 254 (13), 240 (47) [M$^+$ – $C_2H_2$ – $C_4H_8$], 184 (100) [M$^+$ – $C_2H_2$ – 2 ($C_4H_8$)], 137 (44), 59 (33) [Co$^+$], 57 (16) [$C_4H_9^+$]. – HRMS, $C_{17}H_{28}CoP$: calcd. 322.12606; found 322.12277.

*{η$^5$:η$^1$-[2-(Di-tert-butylphosphanyl-P)ethyl]cyclopentadienyl}-(phenylethyne)cobalt(I)* (**11**): At 0°C 110 mg (1.1 mmol) of phenylethyne was added to a solution of 347 mg (1.1 mmol) of **4** in THF. The red solution was stirred at 0°C for 12 d, the red color changed to green. The solvent and phenylethyne were condensed into a cold trap at 0°C under reduced pressure to afford 434 mg (1.1 mmol, 98%) of **11** as a green-black oil. – IR (KBr): $\tilde{\nu}$ = 3093 $cm^{-1}$ (m, Cp-R), 3071 (m, Cp-R), 3021 (m), 2976 (s), 2942 (s), 2918 (s), 2897 (s), 1748 (s, C≡C), 1587 (m, Ph), 1475 (m), 1439 (m), 1386 (m, *t*Bu), 1364 (m, *t*Bu), 1306 (w), 1176 (m, *t*Bu), 1166 (m, *t*Bu), 1099 (w), 1968 (w), 1038 (w), 1021 (w), 794 (m, Cp-R), 756 (s, Ph), 691 (s, Ph). – $^1$H NMR (400 MHz, [D$_8$]THF): δ = 1.03 (d, 9H, 9-H, $^3J_{P,H}$ = 11.8 Hz), 1.33 (d, 9H, 9'-H, $^3J_{P,H}$ = 11.8 Hz), 2.06 (m, 2H, 6-H), 2.29 (m, 2H, 7-H, 3.72 (s, 1H, 2-H or 5-H), 3.76 (s, 1H, 2-H or 5-H), 4.98 (s, 1H, ≡CH), 5.31 (s, 1H, 3-H or 4-H), 5.99 (s, 1H, 3-H or 4-H), 7.08 (t, 1H, *p*-H), 7.23 (t, 2H, *m*-H), 7.38 (d, 2H, *o*-H). – $^{13}$C NMR (100.6 MHz, [D$_8$]THF): δ = 25.9 (dt, C-6, $^1J_{C,H}$ = 128, $^2J_{C,P}$ = 6.4 Hz), 29.5 (dq, C-9, $^1J_{C,H}$ = 127, $^2J_{C,P}$ = 3.8 Hz), 30.1 (dq, C-9, $^1J_{C,H}$ = 127, $^2J_{C,P}$ = 2.3 Hz), 35.4 (d, C-8 or C-8', $^1J_{C,P}$ = 8.1 or 5.3 Hz), 35.5 (d, C-8 or C-8', $^1J_{C,H}$ =

13.0 or 10.2 Hz), 38.0 (dt, C-7, $^1J_{C,H}$ = 127, $^1J_{C,P}$ = 20.1 Hz), 77.3 (dd, C-2 or C-5, $^1J_{C,H}$ = 173, $J_{C,P}$ = 9.3 Hz), 77.9 (dd, ≡CH, $^1J_{C,H}$ = 206, $J_{C,P}$ = 14.2 Hz), 78.1 (dd, C-3 or C-4, $^1J_{C,H}$ = 176, $J_{C,P}$ = 1.2 Hz), 80.6 (dd, C-3 or C-4, $^1J_{C,H}$ = 174 Hz), 84.0 (dd, C-2 or C-5, $^1J_{C,H}$ = 173, $J_{C,P}$ = 8.9 Hz), 87.4 (d, HC≡*C*Ph, $^2J_{C,H}$ = 13, $J_{C,P}$ = 5.3 Hz), 111.5 (d, C-1, $^1J_{C,P}$ = 7.1 Hz), 125.6 (dd, *p*-C, $^1J_{C,H}$ = 161, $^3J_{C,H}$ = 8 Hz), 128.2 (dd, *m*-C, $^1J_{C,H}$ = 158, $^3J_{C,H}$ = 8 Hz), 131.5 (dd, *o*-C, $^1J_{C,H}$ = 159, $^3J_{C,H}$ = 7 Hz), 134.0 (d, *ipso*-C, $^3J_{C,H}$ = 7, $J_{C,P}$ = 1.7 Hz). – $^{31}$P NMR (81 MHz, [D$_8$]THF: δ = 97.3. – MS (70 eV), *m/z* (%): 398 (31) [M$^+$], 296 (100) [M$^+$ – $C_8H_6$], 240 (46) [M$^+$ – $C_8H_6$ – $C_4H_8$], 184 (50) [M$^+$ – $C_8H_6$ – 2($C_4H_8$)], 59 (11) [Co$^+$]. – HRMS: $C_{23}H_{32}CoP$: calcd. 398.15736; found 398.15746.

*{η$^5$:η$^1$-[2-(Di-tert-butylphosphanyl-P)ethyl]cyclopentadienyl}-(η$^2$-dimethyl butynedioate)cobalt(I)* (**12**)[19]: A solution of 160 mg (0.5 mmol) of **4** and 86 mg (0.5 mmol) of dimethyl butynedioate in 20 ml of THF was stirred for 12 h at 20°C. The solvent was removed from the green-black solution by condensation into a cold trap at 1 mbar. 385 mg (0.9 mmol, 89%) of **12** was obtained as brown-black crystals, m.p. 117.8°C. – IR (film): $\tilde{\nu}$ = 3090 cm$^{-1}$ (w), 2948 (s, 2905 (m), 2885 (m), 1808 (br., m), 1740 (br., m), 1684 (s), 1615 (m), 1538 (w), 1464 (m), 1432 (s), 1391 (w), 1370 (w), 1329 (w), 1202 (very br., s, C–O), 1117 (w), 1040 (m), 1000 (w), 934 (w), 896 (w), 810 (m), 758 (w). – $^1$H NMR (200 MHz, $C_6D_6$): δ = 1.2 [d, 18H, 9-H, $^3J_{P,H}$ = 12 Hz], 1.3–2 (m, 4H, 6,7-H), 3.69 (s, 6H, $OCH_3$), 4.53 [m, 2H, 3(4)-H or 2(5)-H, Σ*J* = 1 Hz], 5.27 [m, 2H, 3(4)-H or 2(5)-H, Σ*J* = 1 Hz]. – $^{13}$C NMR (50 MHz, $C_6D_6$): δ = 25.2 (+, d, C-6, $^2J_{P,C}$ = 5.5 Hz), 29.4 [–, d, C-9, $^2J_{P,C}$ = 3.5 Hz], 34.8 (+, d, C-8, $^1J_{P,C}$ = 8.7 Hz), 37.2 (+, d, C-7, $^1J_{P,C}$ = 20.6 Hz), 51.4 (–, s, $OCH_3$), 78.5 [–, s, C-2(5) or C-3(4)], 81.9 [–, d, C-2(5) or C-3(4), $^1J_{P,C}$ = 8.3 Hz], 97.8 [+, d, *C*C(O)OCH$_3$, $^3J_{P,C}$ = 11.2 Hz], 113.6 (+, d, C-1, $^2J_{P,C}$ = 7.6 Hz), 165.0 [+, d, C*C*(O)OCH$_3$, $^4J_{P,C}$ = 2.3 Hz]. – $^{31}$P NMR (81 MHz, $C_6D_6$): δ = 95.9. – MS (70 eV), *m/z* (%): 438 (13) [M$^+$], 380 (9) [M$^+$ – $CO_2CH_3$], 321 (21) [M$^+$ – 2 $CO_2CH_3$], 296 (100) [M$^+$ – $C_6H_6O_4$], 265 (20), 240 (40), [M$^+$ – $C_6H_6O_4$ – $C_4H_8$], 184 (60) [M$^+$ – $C_6H_6O_4$ – 2 $C_4H_8$], 137 (36), 115 (4), 91 (12), 74 (10). – HRMS, $C_{21}H_{32}CoO_4P$: calcd. 438.13702; found 438.13695. – $C_{21}H_{32}CoO_4P$ (438.4): calcd. C 57.54, H 7.36; found C 56.96, H 7.25.

*General Procedure for Reductive Complexation Reactions Starting from Chloride* **3**: A solution of **3** in THF was cooled below –50°C. The alkyne was slowly added at –50°C. After stirring of the mixture for 5 min, sodium amalgam was added by means of a pipette. The mixture was allowed to warm slowly, the sodium amalgam melted at about –45°C. Stirring was continued at this temp. for 10 min, then the reaction mixture was allowed to warm to 20°C. After stirring for 2 h at 20°C, the THF was condensed into a cold trap at 1 mbar. The residue was taken up in diethyl ether, and the ethereal solution was filtered through a P4 frit covered with a 3 cm thick layer of Celite. The celite was washed with diethyl ether until the filtrate was colourless. Further purification of the product was carried out by crystallization or by column chromatography.

*(η$^2$-2-Butyne){η$^5$:η$^1$-[2-(di-tert-butylphosphanyl-P)ethyl]-cyclopentadienyl}cobalt(I)* (**14**) *from Chloride* **3**: General procedure, 0.043 ml (0.55 mmol) of 2-butyne, 181 mg (0.27 mmol) of **3**, 50 ml of THF, 27 g of 1% sodium amalgam. 140 mg (0.4 mmol, 74%) of **14**, blue-black crystals, m.p. 128.5°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3074 cm$^{-1}$ (w), 2950 (s), 2900 (s), 2887 (s), 1894 (w), 1474 (s), 1392 (m), 1366 (m), 1261 (m), 1147 (s), 817 (s). – $^1$H NMR (200 MHz, $C_6D_6$): δ = 1.28 (d, 18H, 9-H, $^3J_{P,H}$ = 11.5 Hz), 1.6–2.0 (m, 4H, 6,7-H), 2.43 (d, 6H, 11-H, $^4J_{P,H}$ = 1.5 Hz), 3.91 + 5.58 [2 m, 4H, AA′BB′ line system, Σ*J* = 3 Hz, 2(5)-H, 3(4)-H]. – $^{13}$C NMR (50 MHz, $C_6D_6$, APT): δ = 13.2 (–, d, ≡C*C*H$_3$, $^3J_{C,P}$ = 1.5 Hz), 25.3 (+, d, C-6, $^2J_{C,P}$ = 7.5 Hz), 29.7 (–, d, C-9, $^2J_{C,P}$ = 4.4 Hz), 34.3 (+, d, C-8, $^1J_{C,P}$ = 5.4 Hz), 38.0 (+, d, C-7, $^1J_{C,P}$ = 19.1 Hz), 63.2 (+, d, ≡*C*CH$_3$, $^3J_{C,P}$ = 8.6 Hz), 79.2 [–, C-2(5) or C-3(4)], 80.0 [–, C-2(5) or C-3(4)], 108.2 (+, d, C-1, $^1J_{C,P}$ = 6.5 Hz). – $^{31}$P NMR (81 MHz,$C_6D_6$): δ = 97.5. – MS (70 eV, 60°C), *m/z* (%): 350 (25) [M$^+$], 296 (100) [M$^+$ – $C_4H_6$], 240 (30) [M$^+$ – $C_4H_6$ – $C_4H_8$], 184 (45) [M$^+$ – $C_4H_6$ – 2 $C_4H_8$], 137 (12), 120 (5). – $C_{19}H_{32}CoP$ (350.4): calcd. C 65.13, H 9.21; found C 65.47, H 8.81.

*Vinylidene Complex* **10** *from Chloride* **3**

a) General procedure, excess ethyne, 815 mg (1.2 mmol) of **3** in 20 ml of THF, 42.51 g of 1% sodium amalgam (18.5 mmol Na). 701 mg (2.2 mmol, 88%) of **10**.

b) In one case the reaction mixture was stored at –78°C for 2 d after addition of the sodium amalgam. Ethyne complex **13** was obtained as a crystalline material. Upon dissolution in [D$_8$]THF a quantitative rearrangement to vinylidene complex **10** started and was complete after 20 min. Attempt to reproduce this observation failed so far. – $^1$H-NMR (**13**, [D$_8$]THF): δ = 1.36 (d, 18H, 9-H, $^3J_{P,H}$ = 11.7 Hz), 2.09 (dt, 2H, 6-H, $^3J_{6,7}$ = 7.5, $^3J_{P,H}$ = 19 Hz), 2.38 (dt, 2H, 7-H, $^2J_{P,H}$ = 7.2 Hz), 3.62 [m, 2H, 2(5)-H or 3(4)-H, $\Sigma J_{2(5),3(4)}$ = 4.2 Hz], 4.46 (d, 2H, *HCCH*, $^3J_{P,H}$ = 2.6 Hz), 5.61 [m, 2H, 2(5)-H or 3(4)-H].

*{η$^5$:η$^1$-[2-(Di-tert-butylphosphanyl-P)ethyl]cyclopentadienyl}-(η$^2$-3-hexyne)cobalt(I)* (**15**) *from Chloride* **3**: General procedure, 0.015 ml (1.15 mmol) of 3-hexyne, 382 mg (0.58 mmol) of **3**, 20 ml of THF, 13.6 g of sodium amalgam. A solution of **15** in diethyl ether was filtered through a P4 frit because of decomposition of the compound on Celite. 383 mg (1.0 mmol, 87%) of **15**, green-violet-black crystals, m.p. 110.7°C. – IR (film): $\tilde{\nu}$ = 3086 cm$^{-1}$ (w), 2959 (w), 2926 (w), 2868 (s), 1870 (m), 1473 (s), 1386 (m), 1366 (s), 1305 (w), 1267 (w), 1181 (w), 1040 (w), 1017 (w), 932 (w), 909 (w), 809 (s), 792 (s), 672 (w), 620 (w), 595 (w), 576 (w), 497 (w), 471 (w). – $^1$H NMR (200 MHz, $C_6D_6$): δ = 1.26 [d, 18H, 9-H, $^3J_{P,H}$ = 11 Hz], 1.45 (t, 6H, $CH_2CH_3$, $^3J$ = 7 Hz), 1.88 (m, 4H, 6,7-H), 2.9 (q, 4H, $CH_2CH_3$, $^3J$ = 7 Hz), 3.94 [m, 2H, 2(5)-H or 3(4)-H], 5.62 [m, 2H, 2(5)-H or 3(4)-H]. – $^{13}$C NMR (50 MHz, $C_6D_6$, APT): δ = 15.7 (–, s, $CH_2CH_3$), 22.3 (+, d, $CH_2CH_3$, $^3J_{P,C}$ = 1.6 Hz), 25.4 (+, d, C-6, $^2J_{P,C}$ = 7.1 Hz), 29.8 [–, d, C-9, $^2J_{P,C}$ = 4.3 Hz], 34.3 [+, d, C-8, $^1J_{P,C}$ = 5.3 Hz], 37.9 (+, d, C-7, $^1J_{P,C}$ = 19.1 Hz), 70.2 (+, d, *C*CH$_2$CH$_3$, $^2J_{P,C}$ = 8.3 Hz), 79.3 [–, C2(5) or C-3(4)], 79.7 [–, C2(5) or C-3(4), $^2J_{P,C}$ = 9.8 Hz], 107.8 (+, C-1, $^1J_{P,C}$ = 6.7 Hz). – $^{31}$P NMR (81 MHz, $C_6D_6$): δ = 96.4. – MS (70 eV), *m/z* (%): 378 (4) [M$^+$], 310 (1), 296 (33) [M$^+$ – $C_6H_{10}$], 254 (4), 240 (15) [M$^+$ – $C_6H_{10}$ – $C_4H_8$], 184 (40) [M$^+$ – $C_6H_{10}$ – 2 $C_4H_8$], 137 (24), 82 (77), 67 (100). – HRMS, $C_{21}H_{36}CoP$: calcd. 378.18866; found 378.18865.

*[η$^2$-Cyclopropyl(trimethylsilyl)ethyne]{η$^5$:η$^1$-[2-(di-tert-butylphosphanyl-P)ethyl]cyclopentadienyl}cobalt(I)* (**16**) *from Chloride* **3**: General procedure, 0.166 ml (133 mg, 0.97 mmol) of cyclopropyl(trimethylsilyl)ethyne, 320 mg (0.48 mmol) of **3**, 20 ml of THF, 20.3 g of sodium amalgam. 395 mg (0.91 mmol, 95%) of **16**, viscous oil. – IR (film): $\tilde{\nu}$ = 3084 cm$^{-1}$ (m), 3018 (s), 2959 (s), 2918 (s), 2898 (s), 1808 (s), 1474 (s), 1457 (m), 1387 (m), 1367 (m), 1309 (w), 1261 (s), 1241 (s), 1183 (m), 1115 (s), 1040 (s), 1017 (s), 963 (s), 922 (w), 908 (w), 852 (s), 832 (s), 752 (m), 672 (m), 620 (w), 608 (w), 576 (w), 497 (w), 469 (m). – $^1$H NMR (200 MHz, $C_6D_6$): δ = 0.45 [s, 9H, Si(CH$_3$)$_3$], 0.82 (m, 2H, cyclopropyl CH$_2$, Σ*J* = 2 Hz), 1.01 [m, 2H, cyclopropyl CH$_2$, Σ*J* = 3 Hz], 1.23 [d, 9H, C(CH$_3$)$_3$, $^3J_{P,H}$ = 11.8 Hz], 1.32 [d, 9H, C(CH$_3$)$_3$, $^3J_{P,H}$ = 11.8 Hz], 1.85 (m, 4H, 6,7-H), 2.48 (m, 1H, cyclopropyl CH), 3.62 (m, 1H, cyclopentadienyl H, Σ*J* = 1 Hz), 4.09 (m, 1H, cyclopentadienyl H, Σ*J* = 1

Hz), 5.17 (m, 1H, cyclopentadienyl H, $\Sigma J$ = 1 Hz), 6.07 (m, 1H, cyclopentadienyl H, $\Sigma J$ = 1 Hz). – $^{13}$C NMR (50 MHz, $C_6D_6$, APT): δ = 2.3 [–, $Si(CH_3)_3$], 10.8 (–, d, cyclopropyl CH, $^3J_{P,C}$ = 2 Hz), 12.1 (+, cyclopropyl $CH_2$), 12.2 (+, cyclopropyl $CH_2$), 25.4 (+, d, C-6, $^2J_{P,C}$ = 7 Hz), 29.9 [–, d, $C(CH_3)_3$, $^2J_{P,C}$ = 3.9 Hz], 30.0 [–, d, $C(CH_3)_3$, $^2J_{P,C}$ = 3.9 Hz], 34.2 [+, d, C-9, $^1J_{P,C}$ = 7.7 Hz], 34.9 [+, d, C-8, $^1J_{P,C}$ = 3 Hz], 37.4 (+, d, C-7, $^1J_{P,C}$ = 19.7 Hz), 54.0 (+, cyclopropyl $CH_2$), 54.1 (+, cyclopropyl $CH_2$), 76.8 (–, C-2 or C-3 or C-4 or C-5), 79.0 (–, C-2 or C-3 or C-4 or C-5, $J_{P,C}$ = 8.8 Hz), 80.0 (–, d, C-2 or C-3 or C-4 or C-5, $J_{P,C}$ = 9.9 Hz), 81.4 (–, C-2 or C-3 or C-4 or C-5), 108.1 (+, d, C-1, $J_{P,C}$ = 6.8 Hz). – $^{31}$P NMR (81 MHz, $C_6D_6$): δ = 96.8. – MS (70 eV, 90°C), *m/z* (%): 434 (3) [$M^+$], 433 (9) [$M^+$ – H], 361 (27) [$M^+$ – $SiMe_3$], 296 (29) [$M^+$ – $Me_3SiCCC_3H_5$], 237 (28) [$H_4C_5CH_2CH_2PtBu_2$], 181 (26) [$H_4C_5CH_2CH_2PHtBu$], 148 (100), 123 (93), 105 (44), 75 (54). – HRMS, $C_{23}H_{40}CoPSi$: calcd. 434.19689; found 434.19699

*{η⁵:η¹-[2-(Di-tert-butylphosphanyl-P)ethyl]cyclopentadienyl}-(3,3-dimethyl-1-butenylidene)cobalt(I)* (**17**): General procedure, 0.07 ml (0.7 mmol) of 3,3-dimethyl-1-butyne, 230 mg (0.34 mmol) of **3**, 25 ml of THF, 20.3 g of sodium amalgam. 103 mg (0.27 mmol, 40%) of **17** as a brown oil. – IR (film): $\tilde{\nu}$ = 3095 cm$^{-1}$ (w), 2949 (s), 2900 (s), 2865 (s), 1575 (s), 1475 (s), 1391 (s), 1366 (s), 1147 (s), 1020 (m), 935 (w), 816 (s). – $^1$H NMR (200 MHz, $C_6D_6$): δ = 1.22 (d, 18H, 9-H, $^3J_{P,H}$ = 13 Hz), 1.29 (s, 9H, 13-H), 1.79 (m, 2H, 6-H), 2.21 (m, 2H, 7-H), 3.13 (d, 1H, 11-H, $^4J_{P,H}$ = 9.5 Hz), 4.5 [m, 2H, 2(5)-H or 3(4)-H], 5.25 [br. s, 2H, 2(5)-H or 3(4)-H]. – $^{13}$C NMR (100 MHz, $C_6D_6$): δ = 25.3 (d, C-6, $^2J_{C,P}$ = 5.4 Hz), 27.3 (d, C-8, $^1J_{C,P}$ = 4.2 Hz), 29.3 (s, C=CH$C(CH_3)_3$), 29.8 (d, C-9, $^2J_{P,C}$ = 16 Hz), 32.5 [=CHC($CH_3$)$_3$], 40.3 (d, C-7, $^1J_{C,P}$ = 18.1 Hz), 79.6 [br d, C-3(4) or C-2(5) $^1J_{C,H}$ = 169.1 Hz], 81.5 [d, C-3(4) or C-2(5), $^1J_{C,H}$ = 175.4 Hz], 110.8 (d, C-1, $^1J_{C,P}$ = 7.2 Hz), 136.9 (d, Co=C=CH*t*Bu, $^1J_{C,H}$ = 151.8 Hz), 302.7 (very br, Co=*C*=CH*t*Bu, $\Delta\nu_{1/2}$ = 100 Hz). – $^{31}$P NMR (162 MHz, $C_6D_6$): δ = 110.3 (very br). – MS (70 eV, 70°C), *m/z* (%): 378 (7) [$M^+$], 296 (67) [$M^+ - C_6H_{10}$], 240 (61) [$M^+ - C_6H_{10} - C_4H_8$], 184 (100) [$M^+ - C_6H_{10} - 2\,C_4H_8$], 162 (20), 137 (45), 106 (37), 91 (18), 67 (32). – HRMS, $C_{21}H_{36}CoP$: calcd. 378.18866; found 378.18867.


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