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

Jan Foerstner^b, Ralf Kettenbach^a, Richard Goddard^a, and Holger Butenschön*^{a,b}

Max-Planck-Institut für Kohlenforschung^a, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr, Germany

Institut für Organische Chemie, Universität Hannover^b, Schneiderberg 1B, D-30167 Hannover, Germany

Received October 2, 1995

Key Words: $\{[\omega], (Phosphanyl)alkyl]cyclopentadienyl\}cobalt(I) / Cobalt complexes / Bidentate ligand / Alkynes$

An improved synthesis of [(2-phosphanylethyl)cyclopenta-dienyl]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

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

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.

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].



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].

319

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 $\delta = 1.87$ and 2.27. With increasing temperature the signals become broader, and coalescence is observed at 326 K, giving rise to a signal at $\delta = 2.02$ at higher temperatures. This corresponds to estimated $\Delta G^{\ddagger} \approx 62 \text{ kJ/mol} (326 \text{ K})^{[26]}$. This barrier is similar to that of other known n²-bonded ethene complexes^[27], although it is remarkable that the closely related $(\eta^5$ -cyclopentadienyl)(η^2 -ethene)(triphenylphosphane)cobalt(I) does not show this phenomenon up to 55°C^[28].



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 ³¹P-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 1,5cyclooctadiene 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].



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 tertbutyl groups on the P atom. In the isoelectronic (but-3enyltetramethylcyclopentadienyl)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

FULL PAPER

Co1-P1-C8-C9 32(2) and P1-C8-C9-C10 $-45(2)^{\circ}$. 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 [A] 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-C01-D1 121(1), P1-C01-D2 101.7(5), D1-C01-D2 137(1), C01-P1-C8-C9 32(2), P1-C8-C9-C10 -45(2), plane(C01,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 ¹H-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 ¹³C-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 ($\Delta v_{1/2} = 100$ Hz). Investigations regarding to a possible dynamic behavior of our compounds are in progress.

We thank Dr. M. Baumgarten, Max-Planck-Institut für Polymerforschung, Mainz, for the ESR measurement. This work was kindly supported by the Fonds der Chemischen Industrie, the Deut-



sche Forschungsgemeinschaft, and the Max-Planck-Gesellschaft. We thank BASF, Chemetall, Preussag, and Hüls for gifts of chemicals.

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(H) (3): To a cooled (-30 °C) solution of 7.35 g (30.1 mmol) of lithium [2-(di-tert-butylphosphanyl)ethyl]cyclopentadienide^[19] in 120 ml of THF in a 250-ml Schlenk 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): $\tilde{v} = 3117 \text{ cm}^{-1}$ (w), 3080 (w, Cp), 3004 (m), 2985 (m), 2965 (s), 2945 (s, CH₂, CH₃), 2899 (s, CH₂, CH₃), 2863 (s, CH₂, CH₃), 1741 (w), 1475 (m), 1422 (w), 1389 (m, tBu), 1367 (m, tBu), 1344 (w), 1307 (w), 1238 (w), 1227 (w), 1180 (m, tBu), 1167 (m, tBu), 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 eV), m/z(%): 331 (97) [M⁺], 275 (14) [M⁺ - C₄H₈], 239 (65) [M⁺ - C₄H₈ - HCl], 183 (100) [M⁺ - 2(C₄H₈) - HCl], 137 (17), 84 (16), 59 (11) $[Co^+]$, 57 (31) $[C_4H_4^+]$. - $C_{30}H_{52}Cl_2Co_2P_2$ (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.

{ $\eta^5: \eta^1 [2-(Di-tert-butylphosphanyl-P) ethyl]cyclopentadienyl}(\eta^2-ethene) cobalt(I)$ (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): $\tilde{v} = 3095$ cm⁻¹ (w, Cp), 3084 (w, Cp), 3042 (w, coord.

C₂H₄), 2980 (s), 2960 (s, CH₂, CH₃), 2895 (s, CH₂, CH₃), 2860 (s, CH₂, CH₃), 1559 (w, coord. C₂H₄), 1468 (s), 1413 (w), 1385 (w, tBu), 1367 (m, tBu), 1308 (w), 1266 (w), 1162 (s, coord. C₂H₄), 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; [D₈]toluene): $\delta = 1.06$ (d, 18 H, 9-H, ${}^{3}J_{PH} = 11.4$ Hz), 1.81 (m, 2H, 6-H, ${}^{3}J_{PH} = 19.0$ Hz), 1.87 (m, 4H, 7-H, HHC=CHH, ${}^{2}J_{P,H} = 7.0$ Hz), 2.27 (m, 2H, HHC=CHH, $\Sigma J = 9.0$ Hz), 3.50, 5.39 [AA'BB' line system, 4H, 2(5)-H, 3(4)-H, $\Sigma^3 J_{2(5),3(4)} = 4.0$ Hz]. $- {}^{13}$ C NMR (50.3 MHz, 193 K, [D₈]toluene): $\delta = 22.4$ (dt, C-10), 24.8 (dt, C-6, ${}^{2}J_{CP} = 5.4$ Hz), 29.7 (dq, C-9), 34.7 (d, C-8, ${}^{1}J_{C,P} = 7.7$ Hz), 37.8 (dt, C-7, ${}^{1}J_{C,P} =$ 21.0 Hz), 79.8 [dd, C 2(5)], 80.1 [d, C-3(4)], 110.3 (d, C-1, ${}^{3}J_{C,P} =$ 6.7 Hz). - ¹³C NMR (50.3 MHz, 313 K, [D₈]toluene): $\delta = 22.3$ (dt, C-10, ${}^{1}J_{C,H} = 151$ Hz, $J_{C,P} =$ not resolved), 25.1 (dt, C-6, ${}^{1}J_{C,H} = 130, {}^{2}J_{C,P} = 7.0 \text{ Hz}), 30.5 \text{ (dq, C-9, } {}^{1}J_{C,H} = 127, {}^{2}J_{C,P} = 4.1 \text{ Hz}), 35.1 \text{ (d, C-8, } {}^{1}J_{C,P} = 6.8 \text{ Hz}), 38.7 \text{ (dt, C-7, } {}^{1}J_{C,H} = 129,$ ${}^{1}J_{C,P} = 19.9$ Hz), 80.1 [dd, C 3(4), ${}^{1}J_{C,H} = 172$, ${}^{5}J_{C,P} = 5.8$ Hz], 80.7 [d, C 2(5), ${}^{1}J_{C,H} = 171$ Hz], 109.8 (d, C-1, ${}^{3}J_{C,P} = 6.8$ Hz). -³¹P NMR (121.5 MHz, 193 K, [D₈]toluene): $\delta = 91.2. - {}^{31}P$ NMR (121.5 MHz, 313 K, $[D_8]$ toluene): $\delta = 92.6. - MS$ (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) [C₂H₄⁺]. – C₁₇H₃₀CoP (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.

 $\{\eta^2-1, 2-Bis(diisopropylphosphanyl-P)ethane\} \{\eta^5[2-(di-tert-bu$ tylphosphanyl)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): $\tilde{v} = 3105 \text{ cm}^{-1}$ (w), 3091 (w), 3063 (w), 2964 (m, CH₂, CH₃), 2948 (m, CH₂, CH₃), 2932 (m, CH₂, CH₃), 2886 (m, CH₂, CH₃), 2862 (m, CH₂, CH₃), 1465 (s), 1375 (m, tBu), 1359 (m, tBu), 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, [D₈]THF): $\delta = 1.04$ (dd, 6H, 11-H, ${}^{3}J_{10,11} = 6.8$, ${}^{3}J_{P2,II} = 5.2$ Hz), 1.10 (d, 18H, 9-H, ${}^{3}J_{\text{P1,H}} = 10.5 \text{ Hz}$, 1.12 (dd, 6H, 12-H, ${}^{3}J_{10,12} = 7.1$, ${}^{3}J_{\text{P2,H}} = 6.8$ Hz), 1.26 (d, 4H, 13-H, ${}^{2}J_{P2,H} = 9.5$ Hz), 1.57 (m, 2H, 6-H or 7-H, $J_{P1,H} = 3.8$ Hz), 1.94 (dsept, 4H, 10-H, ${}^{2}J_{P2,H} = 8.6$ 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, [D₈]THF): $\delta = 19.3$ (q, C-11 or C-12, ${}^{1}J_{C,H} = 126$ Hz), 20.0 (q, C-11 or C-12, ${}^{1}J_{C,H} = 126$ 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 $(dq, C-9, {}^{1}J_{C,H} = 126, {}^{2}J_{P1,C} = 14.0 \text{ Hz}), 31.8 (d, C-8, {}^{1}J_{P1,C} = 23.5 \text{ Hz})$ Hz), 32.7 (dt, C-6 or C-7, $J_{P1,C} = 28.8$ Hz), 75.6 [d, C-2(5), C-3(4), ${}^{1}J_{C,H} = 171$ Hz), 99.4 (d, ${}^{3}J_{P1,C} = 17.4$ Hz). - ${}^{31}P$ NMR (81 MHz, $[D_8]$ THF): $\delta = 30.1$ (s, 1P, P-1), 114.1 (s, 2 P, P-2). - MS (70 eV), m/z (%): 558 (100) [M⁺], 401 (35), 296 (38) [M⁺ - C₁₄H₃₂P₂], 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.

 $(\eta^2-2,2'-Bipyridine) \{\eta^5-[2-(di-tert-butylphosphanyl)ethyl]$ $cyclopentadienyl}cobalt(1) (6) A red solution of 360 mg (1.1 mmol)$ of 4 and 356 mg (2.3 mmol) of 2,2'-bipyridine in 30 ml of THFwas stirred for 18 h at 20°C. The color changed to violet, and thesolvent was condensed into a cold trap at 1 mbar. Excess 2,2'bipyridine was removed by sublimation at 0.001 mbar; the residuewas 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): $\tilde{v} = 3071 \text{ cm}^{-1}$ (w), 3059 (w), 2937 (s, CH₂, CH₃), 2894 (m, CH₂, CH₃), 2859 (m, CH₂, CH₃), 1581 (m), 1560 (w), 1517 (m), 1468 (m), 1450 (s), 1362 (m, tBu), 1346 (m, tBu), 1303 (m), 1151 (m), 1021 (m), 814 (m, Cp-R), 736 (s), 690 (w). -¹H NMR (200 MHz, [D₈]THF): $\delta = 1.01$ (d, 18H, CH₃, ³J_{PH} = 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)-II, 3(4)-H, $\Sigma^3 J_{2(5),3(4)}$] = 3.8 Hz], 6.71 (ddd, 2 H, 11-H, ${}^{3}J_{11,12} = 6.4$ Hz), 7.30 (ddd, 2 H, 12-H, ${}^{3}J_{12,13} = 8.6$ Hz), 7.46 (ddd, 2H, 13-H), 10.20 (2H, 10-H, ${}^{3}J_{10.11} = 6.4$ Hz). $- {}^{13}$ C NMR (50.3 MHz, [D₈]THF): $\delta = 25.0$ (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, ${}^{1}J_{C,H} = 126$, ${}^{2}J_{C,P} = 14.0$ Hz), 31.7 (d, C-8, ${}^{1}J_{C,P} = 23.5$ Hz), 76.5 [d, C-2(5), ${}^{1}J_{C,H} = 171$ Hz], 77.5 [d, C-3(4), ${}^{1}J_{C,H} = 174$ Hz], 99.1 (d, C-1, ${}^{3}J_{C,P} = 15.7$ Hz), 116.7 (d, C-11 or C-12 or C-13, ${}^{1}J_{C,H} = 163$ Hz), 121.3 (d, C-11 or C-12 of C-13, ${}^{1}J_{C,H} = 164$ Hz), 123.2 (d, C-11 or C-12 or C-13, ${}^{1}J_{C,H} = 160$ Hz), 143.3 (s, C-14), 156.2 (d, C-10, ${}^{1}J_{C,H} = 178$ Hz). $- {}^{31}P$ NMR (81 MHz, [D₈]THF): $\delta = 30.2. - MS$ (70 eV), mlz (%): 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, C₂₅H₃₄CoN₂P: calcd. 452.17915; found 452.17922.

 $(\eta^{4}-1.5$ -Cyclooctadiene) { η^{5} -[2-(di-tert-butylphosphanyl)ethyl]cyclopentadienyl}cobalt(1) (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, ¹H NMR, ¹³C NMR, ³¹P NMR, MS) with those of an authentic sample^[19].

 $\{\eta^5 - [2 - (Di - tert - butylphosphanyl)ethyl] cyclopentadienyl\}(\eta^4 - nor$ bornadiene) 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): $\tilde{v} = 3053$ 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, C₆D₆): $\delta = 0.98$ (t, 2H, 12-H, J = 1.5 Hz), 1.21 (d, 18H, 9-H, ${}^{3}J_{PH} = 10.8$ Hz), 1.80 (m, 2H, 6-H), 2.4 (m, 2H, 7-H), 2.81 (m, 2H, 11-H or 10-H, $J \approx$ 1.5 Hz), 3.29 (m, 2H, 10-H or 11-H, J = 1.5 Hz), 4.83 + 4.49 $[AA'BB' line system, 4H, 2(5)-H, 3(4)-H, \Sigma^{3}J_{2(5),3(4)} = 2 Hz]. -$ ¹³C NMR (50 MHz, C₆D₆, 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). - ³¹P NMR (81 Hz, C_6D_6): $\delta = 29.08$ (s). - MS (70 eV, 60 °C), m/z (%): 388 (12) [M⁺], 296 (100) $[M^+ - C_7 H_8]$, 240 (27) $[M^+ - C_7 H_8 - C_4 H_8]$, 184 (31) $[M^+ - C_7H_8 - 2 C_4H_8]$, 162 (8), 137 (8), 115 (11), 91 (14), 66 (7). - HRMS, C₂₂H₃₄CoP: calcd. 388.17301; found 388.17313.

 $\{\eta^5: \eta^1-[2-(Di-tert-butylphosphanyl-P)ethyl]cyclopenta$ $dienyl<math>\{(\eta^2-diphenylethyne)cobalt(I)$ (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, ¹H NMR, ¹³C NMR; ³¹P NMR, MS) with those of an authentic sample.

X-Ray Crystal Structure Analysis of $9^{[37]}$: C₂₉H₃₆CoP, M = 474.5 g mol⁻¹, colour black, crystal size $0.39 \times 0.46 \times 0.25$ mm, a = 16.671(1), b = 16.894(1), c = 17.954(1) Å, V = 5056.4(6) Å³, T = 293 K, $D_c = 1.25$ g cm³, $\mu = 7.52$ cm⁻¹, F(000) = 2016 e, Z = 8, orthorhombic, space group *Pbam* [No. 55], Enraf-Nonius CAD4 diffractometer, $\lambda = 0.71069$ Å, measuring method ω -20, 12695 measured reflections ($\pm h$, $\pm k$, $\pm l$), $[(\sin)\Theta/\lambda]_{max}$ 0.65 Å⁻¹, 5942 independent reflections, 3676 observed reflections [$I \ge 2\sigma(I)$] 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 ($U_{\rm H} = 0.05$ Å²) 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.

 $\{\eta^5: \eta^1 - [2 - (Di - tert - buty| phosphany| - P) ethyl \} cyclopentadieny| \}$ -(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% (¹H, ¹³C, ³¹P NMR). - IR (KBr): $\tilde{v} = 1654 \text{ cm}^{-1}$ (m, C=C). - ¹H NMR (400 MHz, ([D₈]THF): $\delta = 1.33$ (d, 18 H, 9-H, ${}^{2}J_{P,H} = 12.6$ Hz), 2.08 (m, 2 H, 6-H, ${}^{3}J_{6,7} = 7.4$, ${}^{3}J_{P,H} = 19.3$ Hz), 2.09 (d, 2 H, 10-H, $J_{P,H} = 9.6$ Hz), 2.80 (m, 2H, 7-H, ${}^{2}J_{P,H} = 7.8$ Hz), 4.49 [m, 2H, 2(5)-H or 3(4)-H, $\Sigma^3 J_{2(5),3(4)} = 3.8$ Hz], 5.03 [m, 2H, 2(5)-H or 3(4)-H]. -¹³C NMR (100.6 MHz, [D₈]THF): $\delta = 25.8$ (dt, C-6, ¹ $J_{C,H} = 128$, ${}^{2}J_{C,P} = 5.2$ Hz), 30.1 (dq, C-9, ${}^{1}J_{C,H} = 126$, ${}^{2}J_{C,P} = 3.6$ Hz), 36.6 (d, C-8, ${}^{1}J_{C,P} = 15.0$ Hz), 41.0 (dt, C-7, ${}^{1}J_{C,H} = 128$, ${}^{1}J_{C,P} = 18.2$ Hz), 80.0 [d, C-2(5), ${}^{1}J_{C,H} = 174$ Hz], 81.6 [d, C-3(4), ${}^{1}J_{C,H} = 174$, $J_{C,P} = 5.4$ Hz], 106.2 (dt, Co=C=CH₂, ${}^{1}J_{C,H} = 160$, $J_{C,P} = 2.0$ Hz), 112.3 (d, C-1, ${}^{3}J_{C,P} = 7.8$ Hz), 303.7 (d, Co=C=CH₂, $J_{C,P} =$ 38.9 Hz). $-{}^{31}$ P NMR (81 MHz, [D₈]THF): $\delta = 111.7. - MS$ (70 eV), m/z (%): 322 (14) [M⁺], 296 (51) [M⁺ - C₂H₂], 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.

 $\{\eta^5: \eta^1 - [2 - (Di-tert-buty] phosphany l-P) ethyl] cyclopentadienyl\}$ -(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, tBu), 1364 (m, tBu), 1306 (w), 1176 (m, tBu), 1166 (m, tBu), 1099 (w), 1968 (w), 1038 (w), 1021 (w), 794 (m, Cp-R), 756 (s, Ph), 691 (s, Ph). $- {}^{1}$ H NMR (400 MHz, [D₈]THF): $\delta = 1.03$ (d, 9H, 9-H, ${}^{3}J_{PH} = 11.8$ Hz), 1.33 (d, 9H, 9'-H, ${}^{3}J_{PH} = 11.8$ 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, 1 H, 2-H or 5-H), 4.98 (s, 1 H, \equiv CH), 5.31 (s, 1 H, 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). – ¹³C NMR (100.6 MHz, [D₈]THF): δ = 25.9 (dt, C-6, ${}^{1}J_{C,H} = 128$, ${}^{2}J_{C,P} = 6.4$ Hz), 29.5 (dq, C-9, ${}^{1}J_{C,H} = 127$, ${}^{2}J_{C,P} = 3.8$ Hz), 30.1 (dq, C-9, ${}^{1}J_{C,H} = 127$, ${}^{2}J_{C,P} = 2.3$ Hz), 35.4 (d, C-8 or C-8', ${}^{1}J_{C,P} = 8.1$ or 5.3 Hz), 35.5 (d, C-8 or C-8', ${}^{1}J_{C,H} =$

FULL PAPER

13.0 or 10.2 Hz), 38.0 (dt, C-7, ${}^{1}J_{C,H} = 127$, ${}^{1}J_{C,P} = 20.1$ Hz), 77.3 (dd, C-2 or C-5, ${}^{1}J_{C,H} = 173$, $J_{C,P} = 9.3$ Hz), 77.9 (dd, =CH, ${}^{1}J_{C,H} = 206$, $J_{C,P} = 14.2$ Hz), 78.1 (dd, C-3 or C-4, ${}^{1}J_{C,H} = 176$, $J_{C,P} = 1.2$ Hz), 80.6 (dd, C-3 or C-4, ${}^{1}J_{C,H} = 174$ Hz), 84.0 (dd, C-2 or C-5, ${}^{1}J_{C,H} = 173$, $J_{C,P} = 8.9$ Hz), 87.4 (d, HC=CPh, ${}^{2}J_{C,H} = 13$, $J_{C,P} = 5.3$ Hz), 111.5 (d, C-1, ${}^{1}J_{C,P} = 7.1$ Hz), 125.6 (dd, *p*-C, ${}^{1}J_{C,H} = 161$, ${}^{3}J_{C,H} = 8$ Hz), 128.2 (dd, *m*-C, ${}^{1}J_{C,H} = 158$, ${}^{3}J_{C,H} = 8$ Hz), 131.5 (dd, *o*-C, ${}^{1}J_{C,H} = 159$, ${}^{3}J_{C,H} = 7$ Hz), 134.0 (d, *ipso*-C, ${}^{3}J_{C,H} = 7$, $J_{C,P} = 1.7$ Hz). $-{}^{31}P$ NMR (81 MHz, [D₈]THF: $\delta = 97.3$. - 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: C₂₃H₃₂CoP: calcd. 398.15736; found 398.15746.

 $\{\eta^5: \eta^1 - [2 - (Di-tert-buty] phosphany] - P \}$ ethyl] cyclopentadieny] - P $(\eta^2$ -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): $\tilde{v} = 3090$ 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, C₆D₆): $\delta = 1.2$ [d, 18H, 9-H, ${}^{3}J_{P,H} = 12$ Hz], 1.3-2 (m, 4H, 6,7-H), 3.69 (s, 6H, OCH₃), 4.53 [m, 2H, 3(4)-H or 2(5)-H, $\Sigma J = 1$ Hz], 5.27 [m, 2H, 3(4)-H or 2(5)-H, $\Sigma J = 1$ Hz]. $- {}^{13}$ C NMR (50 MHz, C₆D₆): $\delta =$ 25.2 (+, d, C-6, ${}^{2}J_{P,C} = 5.5$ Hz), 29.4 [-, d, C-9, ${}^{2}J_{P,C} = 3.5$ Hz], 34.8 (+, d, C-8, ${}^{1}J_{P,C} = 8.7$ Hz), 37.2 (+, d, C-7, ${}^{1}J_{P,C} = 20.6$ Hz), 51.4 (-, s, OCH₃), 78.5 [-, s, C-2(5) or C-3(4)], 81.9 [-, d, C-2(5) or C-3(4), ${}^{1}J_{P,C} = 8.3$ Hz], 97.8 [+, d, CC(O)OCH₃, ${}^{3}J_{P,C} = 11.2$ Hz], 113.6 (+, d, C-1, ${}^{2}J_{P,C} = 7.6$ Hz), 165.0 [+, d, CC(O)OCH₃, ${}^{4}J_{PC} = 2.3$ Hz]. $-{}^{31}P$ NMR (81 MHz, C₆D₆): $\delta = 95.9$. - MS (70 eV), m/z (%): 438 (13) [M⁺], 380 (9) [M⁺ - CO₂CH₃], 321 (21) $[M^+ - 2 CO_2 CH_3]$, 296 (100) $[M^+ - C_6 H_6 O_4]$, 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, C₂₁H₃₂CoO₄P: calcd. 438.13702; found 438.13695. - C₂₁H₃₂CoO₄P (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.

 $(\eta^2 - 2 - Butyne) \{\eta^5 : \eta^1 - [2 - (di-tert-butylphosphanyl-P)ethyl]$ $cyclopentadienyl\}cobalt(I) (14) from Chloride 3: General pro$ cedure, 0.043 ml (0.55 mmol) of 2-butyne, 181 mg (0.27 mmol) of3, 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): $<math>\tilde{v} = 3074 \text{ cm}^{-1}$ (w), 2950 (s), 2900 (s), 2887 (s), 1894 (w), 1474 (s), 1392 (m), 1366 (m), 1261 (m), 1147 (s), 817 (s). – ¹H NMR (200 MHz, C₆D₆): $\delta = 1.28$ (d, 18H, 9-H, ³ $J_{P,H} = 11.5$ Hz), 1.6–2.0 (m, 4H, 6,7-H), 2.43 (d, 6H, 11-H, ⁴ $J_{P,H} = 1.5$ Hz), 3.91 + 5.58 [2 m, 4H, AA'BB' line system, $\Sigma J = 3$ Hz, 2(5)-H, 3(4)-H]. – ¹³C NMR (50 MHz, C₆D₆, APT): $\delta = 13.2$ (-, d, \equiv CCH₃, ${}^{3}J_{C,P} = 1.5$ Hz), 25.3 (+, d, C-6, ${}^{2}J_{C,P} = 7.5$ Hz), 29.7 (-, d, C-9, ${}^{2}J_{C,P} = 4.4$ Hz), 34.3 (+, d, C-8, ${}^{1}J_{C,P} = 5.4$ Hz), 38.0 (+, d, C-7, ${}^{1}J_{C,P} = 19.1$ Hz), 63.2 (+, d, \equiv CCH₃, ${}^{3}J_{C,P} = 8.6$ Hz), 79.2 [-, C-2(5) or C-3(4)], 80.0 [-, C-2(5) or C-3(4)], 108.2 (+, d, C-1, ${}^{1}J_{C,P} = 6.5$ Hz). $-{}^{31}P$ NMR (81 MHz,C₆D₆): $\delta = 97.5$. - MS (70 eV, 60 °C), *m/z* (%): 350 (25) [M⁺], 296 (100) [M⁺ - C₄H₆], 240 (30) [M⁺ - C₄H₆] - C₄H₈], 184 (45) [M⁺ - C₄H₆ - 2 C₄H₈], 137 (12), 120 (5). - C₁₉H₃₂CoP (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 $-78 \,^{\circ}\text{C}$ for 2 d after addition of the sodium amalgam. Ethyne complex 13 was obtained as a crystalline material. Upon dissolution in [D₈]THF a quantitative rearrangement to vinylidene complex 10 started and was complete after 20 min. Attempt to reproduce this observation failed so far. $-^{1}\text{H-NMR}$ (13, [D₈]THF): $\delta = 1.36$ (d, 18H, 9-H, ${}^{3}J_{\text{P,H}} = 11.7$ Hz), 2.09 (dt, 2H, 6-H, ${}^{3}J_{6,7} = 7.5$, ${}^{3}J_{\text{P,H}} = 19$ Hz), 2.38 (dt, 2H, 7-H, ${}^{2}J_{\text{P,H}} = 7.2$ 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*, ${}^{3}J_{\text{P,H}} = 2.6$ Hz), 5.61 [m, 2H, 2(5)-H or 3(4)-H].

 $\{\eta^5: \eta^1 - [2 - (Di - tert - butylphosphanyl - P) + thyl] cyclopentadienyl\}$ - $(\eta^2$ -3-hexyne)cobalt(1) (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, greenviolet-black crystals, m.p. 110.7 °C. – IR (film): $\tilde{v} = 3086$ 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, C₆D₆): $\delta = 1.26$ [d, 18H, 9-H, ${}^{3}J_{P,H} = 11$ Hz], 1.45 (t, 6H, CH₂CH₃, ${}^{3}J = 7$ Hz), 1.88 (m, 4H, 6,7-H), 2.9 (q, 4H, CH_2CH_3 , ${}^{3}J = 7$ Hz), 3.94 [m, 2H, 2(5)-H or 3(4)-H], 5.62 [m, 2H, 2(5)-H or 3(4)-H]. – ¹³C NMR (50 MHz, C_6D_6 , APT): $\delta = 15.7$ (-, s, CH_2CH_3), 22.3 (+, d, CH_2CH_3 , ${}^{3}J_{\rm PC} = 1.6$ Hz), 25.4 (+, d, C-6, ${}^{2}J_{\rm PC} = 7.1$ Hz), 29.8 [-, d, C-9, ${}^{2}J_{P,C} = 4.3$ Hz], 34.3 [+, d, C-8, ${}^{1}J_{P,C} = 5.3$ Hz], 37.9 (+, d, C-7, ${}^{1}J_{P,C} = 19.1$ Hz), 70.2 (+, d, CCH₂CH₃, ${}^{2}J_{P,C} = 8.3$ Hz), 79.3 [-, C2(5) or C-3(4)], 79.7 [-, C2(5) or C-3(4), ${}^{2}J_{P,C} = 9.8$ Hz], 107.8 $(+, C-1, {}^{1}J_{PC} = 6.7 \text{ Hz}). - {}^{31}P \text{ NMR}$ (81 MHz, C_6D_6): $\delta = 96.4$. - 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) $[M^+ - C_6H_{10} - C_4H_8]$ $C_6H_{10} - 2 C_4H_8$, 137 (24), 82 (77), 67 (100). - HRMS, C₂₁H₃₆CoP: calcd. 378.18866; found 378.18865.

[η²-Cyclopropyl(trimethylsilyl)ethyne] {η⁵:η¹-[2-(di-tert-butylphosphanyl-P)ethyl]cyclopentadienyl}cobalt(1) (**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): $\tilde{v} = 3084 \text{ cm}^{-1}$ (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). – ¹H NMR (200 MHz, C₆D₆): $\delta =$ 0.45 [s, 9 H, Si(CH₃)₃], 0.82 (m, 2 H, cyclopropyl CH₂, $\Sigma J = 2$ Hz), 1.01 [m, 2 H, cyclopropyl CH₂, $\Sigma J = 3$ Hz], 1.23 [d, 9 H, C(CH₃)₃, ³J_{P,H} = 11.8 Hz], 1.32 [d, 9 H, C(CH₃)₃, ³J_{P,H} = 11.8 Hz], 1.85 (m, 4H, 6,7-H), 2.48 (m, 1 H, cyclopropyl CH), 3.62 (m, 1 H, cyclopentadienyl H, $\Sigma J = 1$ Hz), 4.09 (m, 1 H, cyclor ntadienyl H, $\Sigma J = 1$

Hz), 5.17 (m, 1H, cyclopentadienyl H, $\Sigma J = 1$ Hz), 6.07 (m, 1H, cyclopentadienyl H, $\Sigma J = 1$ Hz). – ¹³C NMR (50 MHz, C₆D₆, APT): $\delta = 2.3 [-, Si(CH_3)_3], 10.8 (-, d, cyclopropyl CH, {}^{3}J_{P,C} =$ 2 Hz), 12.1 (+, cyclopropyl CH₂), 12.2 (+, cyclopropyl CH₂), 25.4 (+, d, C-6, ${}^{2}J_{PC} = 7$ Hz), 29.9 [-, d, C(CH₃)₃, ${}^{2}J_{PC} = 3.9$ Hz], 30.0 [-, d, C(CH₃)₃, ${}^{2}J_{PC} = 3.9$ Hz], 34.2 [+, d, C-9, ${}^{1}J_{PC} = 7.7$ Hz], 34.9 [+, d, C-8, ${}^{1}J_{PC} = 3$ Hz], 37.4 (+, d, C-7, ${}^{1}J_{PC} = 19.7$ Hz), 54.0 (+, cyclopropyl CH₂), 54.1 (+, cyclopropyl CH₂), 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, $J_{\rm PC} = 8.8$ Hz), 80.0 (-, d, C-2 or C-3 or C-4 or C-5, $J_{\rm PC} = 9.9$ Hz), 81.4 (-, C-2 or C-3 or C-4 or C-5), 108.1 (+, d, C-1, J_{PC} = 6.8 Hz). $-{}^{31}$ P NMR (81 MHz, C₆D₆): $\delta = 96.8$. - MS (70 eV, 90 °C), m/z (%): 434 (3) [M⁺], 433 (9) [M⁺ - H], 361 (27) [M⁺ -SiMe₃], 296 (29) [M⁺ - Me₃SiCCC₃H₅], 237 (28) [H₄C₅CH₂CH₂PtBu₂], 181 (26) [H₄C₅CH₂CH₂PHtBu], 148 (100), 123 (93), 105 (44), 75 (54). – HRMS, $C_{23}H_{40}CoPSi$: calcd. 434.19689; found 434.19699

 $\{\eta^{5}: \eta^{1}-[2-(Di-tert-butylphosphanyl-P)ethyl]cyclopentadienyl\}$ -(3,3-dimethyl-1-butenylidene)cobalt(1) (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): $\tilde{v} = 3095$ 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, C₆D₆): $\delta = 1.22$ (d, 18 H, 9-H, ${}^{3}J_{P,H} = 13$ Hz), 1.29 (s, 9 H, 13-H), 1.79 (m, 2 H, 6-H), 2.21 (m, 2H, 7-H), 3.13 (d, 1H, 11-H, ${}^{4}J_{P,H} = 9.5$ Hz), 4.5 [m, 2H, 2(5)-H or 3(4)-H], 5.25 [br. s, 2H, 2(5)-H or 3(4)-H]. - ¹³C NMR (100 MHz, C₆D₆): $\delta = 25.3$ (d, C-6, ${}^{2}J_{C,P} = 5.4$ Hz), 27.3 (d, C-8, ${}^{1}J_{C,P} = 4.2$ Hz), 29.3 (s, C=CHC(CH₃)₃), 29.8 (d, C-9, ${}^{2}J_{P,C} = 16 \text{ Hz}$, 32.5 [=CHC(*C*H₃)₃], 40.3 (d, C-7, ${}^{1}J_{C,P} = 18.1 \text{ Hz}$), 79.6 [br d, C-3(4) or C-2(5) ${}^{1}J_{C,H} = 169.1$ Hz], 81.5 [d, C-3(4) or C-2(5), ${}^{1}J_{C,H} = 175.4 \text{ Hz}$], 110.8 (d, C-1, ${}^{1}J_{C,P} = 7.2 \text{ Hz}$), 136.9 (d, Co=C=CHtBu, ${}^{1}J_{C,H} = 151.8$ Hz), 302.7 (very br, Co = C = CHtBu, $\Delta v_{1/2} = 100$ Hz). $- {}^{31}P$ NMR (162 MHz, C_6D_6): $\delta = 110.3$ (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.

- ^[1] Comprehensive Organometallic Chemistry (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon Press, Oxford, 1982.
- [2] J. P. Collman, L. S. Hegedus, J. R. Norton, R. G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, California, 1987, p. 989.
- [3] J. Okuda, Comments Inorg. Chem. 1994, 16, 185-205.
 [4] R. L. Halterman, Chem. Rev. 1992, 92, 965-994.
- [5]
- P. Jutzi, U. Siemeling, J. Organomet. Chem. 1995, 500, 175-185.
- C. A. Tolman, Chem. Rev. 1977, 77, 313-348.
- K.-S. Gan, T. S. A. Hor in Ferrocenes: Homogeneous Catalysis. [7] Organic Synthesis, Materials Science (Eds.: A. Togni, T. Hayashi), VCH, Weinheim, 1995, pp. 3-104.

- ^[8] T. Hayashi in ref.^[7], pp. 105-142.
- ^[9] R. M. Bullock, C. P. Casey, Acc. Chem. Res. 1987, 20, 167-173. J. Okuda, K. H. Zimmermann, Chem. Ber. 1980, 123, 1641–1748. ^[10] J.
- [11] J. Okuda, K. H. Zimmermann, J. Organomet. Chem. 1988, 344, C1-C4.
- ^[12] J. Okuda, K. H. Zimmermann, Chem. Ber. 1989, 122, 1645 - 1647
- ^[13] J. Okuda, E. Herdtweck, K. H. Zimmermann in Organic Synthesis via Organometallics (Eds.: K. H. Dötz. R. W. Hoffmann), Vieweg, Braunschweig, 1991; pp. 207–221.
- ^[14] J. Okuda, K. H. Zimmermann, E. Herdtweck, Angew. Chem. 1991, 103, 446-447; Angew. Chem. Int. Ed. Engl. 1991, 30, 430.
- ^[15] K. H. Zimmermann, P. Robert, S. I. Horváth, J. Okuda, Or-ganometallics 1992, 11, 3935-3937.
- ^[16] P. Jutzi, M. O. Kristen, J. Dahlhaus, B. Neumann, H.-G. Stammler, Organometallics 1993, 12, 2980–2985
- ^[17] P. Jutzi, M. O. Kristen, B. Neumann, H.-G. Stammler, Organometallics 1994, 13, 3854-3861. ^[18] R. T. Kettenbach, H. Butenschön, N. J. Chem. 1990, 14,
- 599-601.
- ^[19] R. T. Kettenbach, W. Bonrath, H. Butenschön, Chem. Ber. 1993, 126, 1657-1669.
- ^[20] T. Kauffmann, J. Ennen, H. Lhotak, A. Rensing, F. Steinseifer, A. Woltermann, Angew. Chem. 1980, 92, 321-323; Angew. Chem. Int. Ed. Engl. 1980, 19, 328.
- ^[21] U. Kölle, F. Khouzami, B. Fuss, Angew. Chem. 1982, 94, 132;
 Angew. Chem. Int. Ed. Engl. 1982, 21, 131.
- [22] R. T. Kettenbach, C. Krüger, H. Butenschön, Angew. Chem. 1992, 104, 1052-1054; Angew. Chem. Int. Ed. Engl. 1992, 31, 1066 - 1068
- ^[23] U. Koelle, B. Fuss, M. Belting, E. Raabe, Organometallics 1986, 5,980-987
- ^[24] U. Kölle, F. Khouzami, B. Fuss, Angew. Chem. Suppl. 1982, 250 - 256
- ^[25] We thank one of the referees for a constructive comment regarding this point. ^[26] H. Günther, *NMR-Spektroskopie*, 2nd ed., Georg Thieme Ver-
- lag, Stuttgart, 1983.
- ^[27] R. Benn, Org. Magn. Res. 1983, 21, 723-726.
- ^[28] E. R. Evitt, R. G. Bergman, J. Am. Chem. Soc. 1980, 102, 7003-7011.
- ^[29] K. P. C. Vollhardt, Acc. Chem. Res. 1977, 10, 1-8.
 ^[30] K. P. C. Vollhardt, Angew. Chem. 1984, 96, 525-541; Angew.
- Chem. Int. Ed. Engl. **1984**, 23, 539–556. ^[31] H. Bönnemann, Angew. Chem. **1985**, 97, 264–279; Angew. Chem. Int. Ed. Engl. **1985**, 24, 248–262.
- ^[32] R. D. W. Kemmitt, D. R. Russell in Comprehensive Organometallic Chemistry (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon Press, Oxford, **1982**, vol. 5; pp. 204–209. ^[33] M. I. Bruce, *Chem. Rev.* **1991**, *91*, 197–257.
- ^[34] C. Bianchini, P. Innocenti, A. Meli, M. Peruzzini, F. Zanobini, Organometallics 1990, 9, 2514-2522
- ^[35] C. Bianchini, M. Peruzzini, F. Zanobini, Organometallics 1991, 10, 3415-3417
- ^[36] C. Bianchini, M. Peruzzini, A. Vacca, F. Zanobini, Organometallics 1991, 10, 3697-3707.
- ^[37] Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-59233, the names of the authors, and the journal citation.

[95153]