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New carbene and vinylidene chelate complexes of cyclopentadienylcobalt bearing a phosphorus tether

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Abstract

The {η^5[2-(di-*tert*-butylphosphanyl-*P*)ethyl]cyclopentadienyl}cobalt chelate was treated with trimethylsilylethyne to give the corresponding alkyne complex along with the trimethylsilylvinylidene complex. In a similar way, the bis(trimethylsilyl)ethyne complex was obtained. Silyl migration to give the bis(trimethylsilyl)vinylidene complex was observed at elevated temperature and represents the first cobalt example of this reaction. As the first cobalt vinylidene complex the bis(trimethylsilyl)vinylidene complex was characterized by an X-ray structure analysis. Reaction of the cobalt chelate with an Arduengo type carbene unexpectedly gave a non-chelated cobalt complex bearing the carbene ligand and ethene at the same metal atom. This complex was also structurally characterized. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Since their discovery by Fischer in 1964 [1], carbene complexes of almost all the transition metals have been prepared. While in the sixties and in the seventies of the last century many structural and theoretical aspects of carbene complexes were investigated, the last decades have been dominated by applications of carbene complexes in organic chemistry. Prominent examples are the Dötz benzanellation reaction [2–7] and metathesis reactions catalyzed by carbene complexes [8–14]. The variety of carbene ligands has also broadened significantly. In addition to typical Fischer or Schrock type carbene complexes, bearing alkynyl or vinyl carbene, vinylidene and cumulenylidene ligands, bidendate carbene ligands and carbene ligands, that are stable without a metal (Arduengo carbenes) have been reported. Many of the complexes of these ligands show interesting chemical properties, and the most highly unsaturated ones, in particular, are now being applied to the chemistry of self-organizing and supramolecular materials [15–29].

Most of the work in the field of Fischer type carbene complexes has involved Group 6 metals, with emphasis on chromium and tungsten [5]. Catalytic applications recently focus on ruthenium carbene complexes. Some metals, however, have been rather neglected.

We have contributed to the chemistry of cyclopentadienylcobalt complexes bearing a pendant phosphane ligand. This chemistry allows for the preparation of stable alkyne [30], bicyclopropyilidene [31], and 3,3-diphenylvinylcarbene complexes [32], facilitates new rearrangement reactions of strained cyclopropene ligands [32,33], and even allows the complete cleavage of a phosphorus carbon triple bond in a phosphaalkyne [34]. We wish to report here the syntheses and some structures of new cobalt vinylidene and carbene complexes.

2. Vinylidene complexes

The chemistry of cyclopentadienylmetal complexes in which a pendant phosphane ligand is used to facilitate

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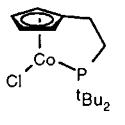
chelation is a rapidly growing field [35]. In many cases, the presence of the bridge leads to the stabilization of complexes that are not otherwise observed in the usual chemistry of cyclopentadienyl metal complexes. Thus in contrast to non-chelating systems, the reaction of the cobalt chelate **2**, which is easily obtained from chloride **1**, with ethyne gave vinylidene complex **3**, which has been fully characterized and represents the first vinylidene complex of a cyclopentadienylcobalt system. **3** is obtained in higher yield if it is prepared from **1** with Na/Hg as the reducing reagent [30,36].

As the chemistry of cyclopentadienylcobalt complexes with alkynes is dominated by cyclooligomerization reactions [37], cobalt vinylidene complexes are rarely observed. The only other examples are those reported by Bianchini upon the reaction of a cobalt(0) tripod complex with terminal alkynes [38–40]. Subsequently we reported the synthesis of the *tert*-butylvinylidene complex corresponding to **3** upon reaction of 3,3-dimethyl-1-butyne with **1** and Na/Hg [30].



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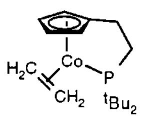

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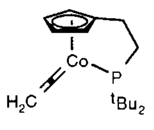

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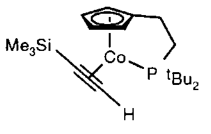
When cobalt(II) chloride **1** was treated with trimethylsilylethyne and Na/Hg in THF at temperatures between − 50 and 20°C for 2 h, a mixture of the alkyne and vinylidene complexes **4** and **5** was obtained in 79% overall yield. Extension of the reaction time to 24 h gave trimethylsilylvinylidene complex **5** as the only product in 54% yield. **4** and **5** were characterized spectroscopically. Attempts to deprotonate **5** failed (BuLi at − 78 and 20°C, *t*-BuLi at − 78°C).



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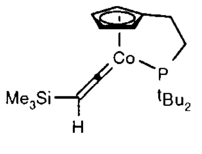

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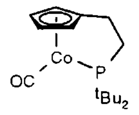
The chemistry of the vinylidene complex **3** was briefly explored. Although many attempted reactions resulted in the formation of decomposed material only, some reactions with sources of CO (CO gas, arenetricarbonylchromium complex, diironenneacarbonyl) resulted in the formation of the known carbonyl complex **6** [41,42].



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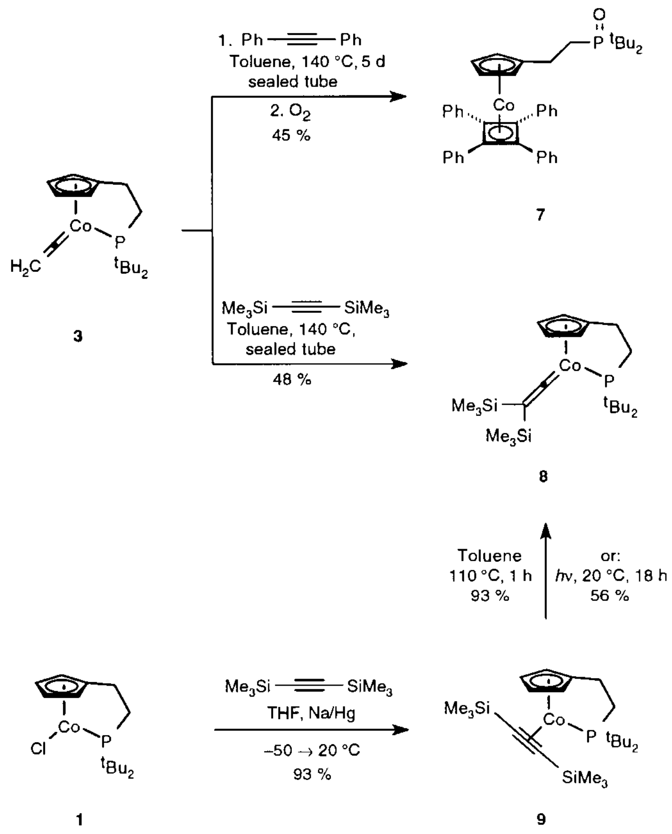
In order to perform a codimerization reaction, the vinylidene complex **3** was treated with diphenylethyne and bis(trimethylsilyl)ethyne at 140°C in a sealed tube. The reaction with diphenylethyne gave, after chromatographic work-up in air, a cyclobutadiene complex, the phosphane oxide **7**. The corresponding phosphane is a known compound [34]. Apparently the reaction involves a displacement of the vinylidene ligand by diphenylethyne. Decomplexation of the phosphane arm enables the coordination of a second diphenylethyne ligand followed by cyclization. A reversed order of steps seems less likely, since the vinylidene ligand is not involved in the coupling process.

The reaction of **1** with bis(trimethylsilyl)ethyne gave the bis(trimethylsilyl)vinylidene complex **8** as the only product in 48% yield. This is in accord with the observation that bis(trimethylsilyl)ethyne does not usually cyclooligomerize. To confirm that this is indeed the result of a silylalkyne complexation, followed by a silyl migration, the bis(trimethylsilyl)ethyne complex **9** was prepared from the chloride **1** and bis(trimethylsilyl)ethyne in 93% yield.



The DSC (differential scanning calorimetry) analysis of **9** does not show a melting point of the complex, but rather reveals that a highly exothermic reaction occurs at 86°C. In an analogous experiment, **9** was heated in toluene at 110°C for 1 h, and a clean rearrangement was observed, resulting in a 93% yield of the bis(trimethylsilyl)vinylidene complex **8**. Alternatively, **8** was obtained from **9** photochemically within 18 h at 20°C in 56% yield. **7**–**9** have been characterized spectroscopically. The IR spectrum of alkyne complex **9** brought to light an interesting property of the compound. Whereas the ^{1}H-NMR spectrum indicated the pure compound, the IR spectrum (KBr) exhibited an unmistakable vinylidene absorption at 1595 cm^{-1} in addition to the alkyne absorption at 1749 cm^{-1}. More importantly, its relative intensity increased when the pressure during the preparation of the KBr pellet was increased or applied for a longer time. This clearly indicates, at least qualitatively, that the silyl migration in the reaction of **9** to **8** is facilitated by pressure. Although a more detailed interpretation of this effect must be based on quantitative investigation, it is worth mentioning that the effect indicates a negative activation volume, which is in accord with an insertion of cobalt with formation of a $Me_3Si–Co–C{\equiv}C–SiMe_3$ fragment.

Crystallization of **8** from toluene gave crystals suitable for an X-ray structure analysis (Fig. 1). **8** is the first neutral cobalt vinylidene complex to be structurally characterized. The molecules crystallize in the centrosymmetric space group *Pnma* with an exact mirror plane passing through the Co atom, the centroid of the Cp ring, the ethylene bridge, P, and C6 and C7 of the vinylidene ligand. The relatively high ratio of maximum to minimum principle mean square atomic displacements of atom C5 (3.0) indicates that the ethylene chain linking the Cp ring to the P atom may be disordered, but attempts to refine the structure in the acentric space group $Pna2_1$ or using a disordered model were unsuccessful, suggesting that deviations from ideal symmetry are slight. The Cp–Co–P angle [120.4(6)°] is, however, comparable with that found in structures of other cobalt complexes containing the 2-(di-*tert*-butyl-phosphino)ethylcyclopentadienyl group (mean, 121°). The C=C double bond distance (C6–C7) is 1.319(4) Å and is similar to those in other vinylidene complexes (1.25–1.41 Å) [43,44]. The Co=C bond length (Co–C6) at 1.724(3) Å is shorter than those observed in Co carbene complexes (mean, 1.881 Å) and almost as short as the Co–C bond in the analogous carbonyl complex, carbonyl(η^5-2-(di-*tert*-butylphosphino)ethylcyclopentadienyl)cobalt(I) (**6**) [1.702(3) Å], indicating considerable double bond character in this bond. It is also similar to that in the cobalt tripod cation $[(PP3)Co\{C{=}C(H)Ph\}]^+$ [1.71(3) Å] [30], though the high error associated with this latter bond distance prevents a useful comparison. The Cp–Co–C6 angle at 136(1)° and the P–Co–C6 angle at 103.2(1)° are respectively smaller and larger than the corresponding angles in the CO complex **6** [140.8(1) and 97.2(1)°]. This, together with the smaller than expected Co–C6–C7 angle of 172.6(3)°, is probably the result of repulsive steric interaction between the *tert*-butyl groups on the P atom and the methyl groups on the Si atoms. Unfortunately, we have not been able

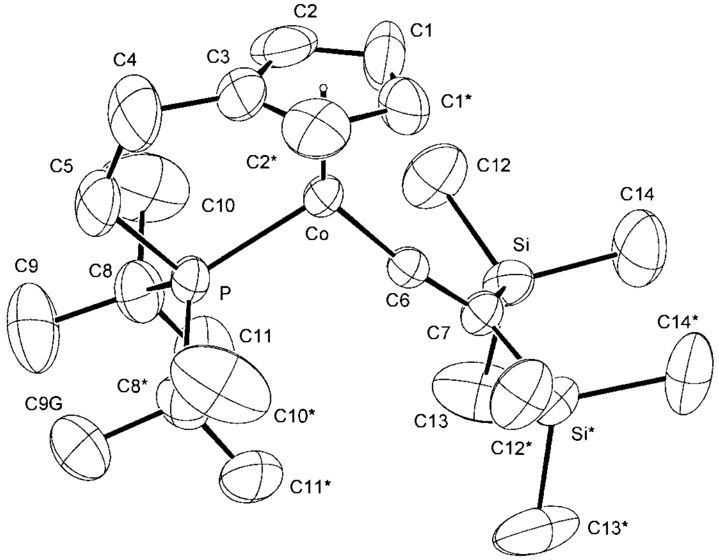
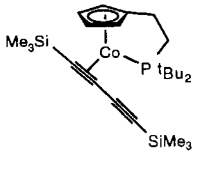


Fig. 1. Structure of **8** in the crystal. Selected bond lengths (Å) and angles (°) (Cp is the centroid of the cyclopentadienyl ligand; the numbering scheme is arbitrary): Co–C1 2.069(3), Co–C2 2.091(3), Co–C3 2.055(4), Co–Cp 1.68(1), C3–C4 1.499(6), C4–C5 1.434(7), C5–P 1.854(4), Co–P 2.160(1), Co–C6 1.724(3), C6–C7 1.319(4), C7–Si 1.870(2), C6–Co–P 103.2(1), Cp–Co–P 120.4(3), Cp–Co–C6 136(1), Co–C6–C7 172.6(3), C6–C7–Si 117.84(8), Si–C7–Si* 124.3(2).

to obtain crystals of the bis(trimethylsilyl)ethyne complex **9**, but a computer simulation of **9** based on the geometry of the analogous diphenylethyne complex, in which the phenyl groups are bent by 13° out of the coordination plane away from the phosphine [39], indicates that **9** is highly sterically crowded, suggesting that the rearrangement of **9** to **8** probably results in a considerable loss of steric repulsion.

Although the observation of such silyl migrations from silylalkyne to silylvinylidene ligands in mononuclear metal complexes is rare, there is some literature precedence. The reaction was first mentioned by Sakurai in 1987, who reported the effect in a manganese complex [45]. In 1991 Werner et al. reported this type of reaction in coordinatively unsaturated rhodium complexes [46–49]. Connelly et al. found the reaction to take place in an arene chromium complex, and, most interestingly, that a one-electron oxidation of the bis(trimethylsilyl)vinylidene complex favored the reverse reaction back to the alkyne complex. More recently Berke found that the reaction also works with an 18-electron iron system [50]. The reaction of **9** to **8** is the first example using cobalt.

The mononuclear bis(trimethylsilyl)butadiyne complex **10** was obtained in 72% yield by treatment of the ligand with an equimolar amount of **1** and Na/Hg. Heating of **10** at 110°C in toluene for 5 days resulted in some decomposition and a poor yield of a product, which on the basis of its IR and MS data has been tentatively characterized as the cyclobutadiene complex **11**. Irradiation of **10** also did not give a vinylidene complex. Treatment of bis(trimethylsilyl)butadiyne with two equivalents of **1** and Na/Hg presumably gives the dinuclear vinylidene complex **12**, which has only been incompletely characterized and which decomposed during the ^{13}C-NMR measurement. The identification of **12** is strongly based on the IR spectrum, which in contrast to that of **10** does not show an alkyne absorption band but instead an intense absorption at 1607 cm^{-1}, which we attribute to the vinylidene valence vibration. In addition, the ^{1}H-NMR spectrum shows a singlet for the trimethylsilyl groups at $\delta = 0.39$ and doublet at $\delta = 1.30$ for the *tert*-butyl groups ($^{3}J_{P,H} = 13$ Hz). The chelated cobalt systems give rise to an AA′BB′ line system and two multiplets for the ethylene bridges. These data and the number of signals are in accord with the formation of **12**.



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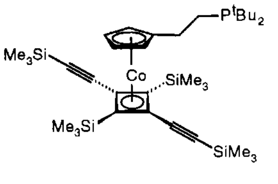

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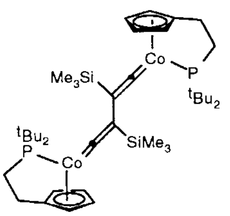

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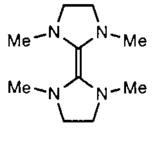
3. Carbene complexes

As in the case for the non-bridging cobalt vinylidene complexes, non-bridging cobalt carbene complexes are also comparatively rare [51,52]. Recently, metal complexes of stable heterocyclic carbenes (Arduengo type carbenes) have gained in importance in processes such as hydroformylation and catalytic ring closing metathesis [53–55]. Complexes with carbene ligands of this type had previously been prepared from the respective alkenes, like **13**, which gives the cobalt complex **14** upon reaction with CpCo(CO)$_2$ [56].



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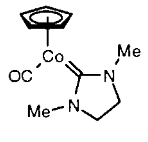

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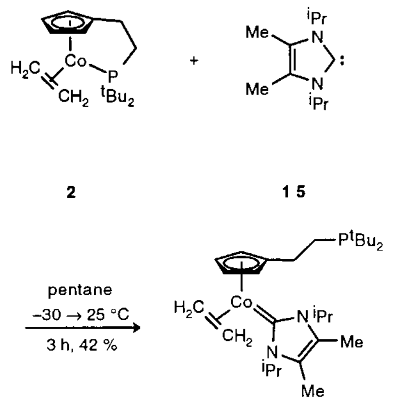
In an attempt to attach an Arduengo type carbene to the cobalt chelate, 1,3-diisopropyl-3,4-dimethyl-2,3-dihydro-1*H*-imidazol-2-ylidene (**15**) [57] was treated with the ethene complex **2**. In accord with all other experiments in which **2** was used for ligand exchange reactions with monodendate ligands, it was anticipated that the ethene ligand would be replaced by the Arduengo carbene. The reaction took place between −30 and 20°C and unexpectedly gave a 42% yield of the non-chelated complex **16**. Instead of loss of the ethene ligand, the phosphane side arm became uncoordinated. Complexes like **16**, which bears a carbene and an ethene ligand at one metal atom, are rarely observed [58–61]. Formally such a complex represents the very first step of a metathesis reaction.

16 has been characterized spectroscopically. The carbene carbon atom shows a broad ^{13}C-NMR signal at $\delta = 241.4$ ($\nu_{1/2} \approx 220$ Hz), possibly the highest chemical shift observed for the carbene carbon atom of an Arduengo type carbene complex so far and a value considerably higher than that found for **14** ($\delta = 207.38$, 218.46 for CO and carbene carbon atoms) [56]. This may be a result of backbonding or anisotropy effects associated with the ethene ligand. The ethene ligand in **16** produces a signal at $\delta = 14.9$ ($\nu_{1/2} \approx 170$ Hz). The ethene ligand in **2** resonates at $\delta = 22.3$. The signals of the carbene ligand and that of the ethene ligand are



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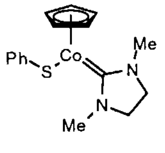
extraordinarily broad, presumably due to the cobalt quadrupol moment (Fig. 2). In the ^{31}P-NMR spectrum a signal at $\delta = 29.7$ indicates an uncoordinated phosphane side arm. **16** was crystallized from pentane, and a suitable crystal has been subjected to a crystal structure analysis (Fig. 3).

The analysis confirms the constitution of **16**, in which the phosphane side arm is uncoordinated and the carbene and the ethene ligand are simultaneously attached to one cobalt atom. The bond length C27–C28 [1.355(13) Å] in the ethene ligand is shorter than the C,C bond length in the ethene ligand of **2** [1.396(5)] [36]. The cobalt carbene bond length Co1–C16 [1.929(8) Å] is longer than the corresponding bond in the structurally characterized complex **17** [1.902(3) Å] [56] but shorter than that in the Fischer carbene cobalt(I) complex **18** [1.989(4) Å], which has also been structurally characterized [62]. Usually the carbene metal bonds in Arduengo carbene complexes are longer than those in Fischer type carbene complexes [53]. However, since **16** represents a carbene complex with ethene as a ligand at the same metal atom, such a comparison is difficult. It appears that the molecular geometry is a result of a competition between the electron donating and accepting properties of the two ligands. Thus, the relatively short bond length in the ethene ligand and the relatively short metal–carbene bond indicate that a back donation to the carbene is preferred. The isopropyl groups are bent away from the ethene ligand, presumably for steric reasons, causing a slight distortion of the carbene ligand, which is bent out of planarity by about 3° [C16–N2–C17–C18 −2.6(19)°, C16–N1–C18–C17 −3.6(19)°].



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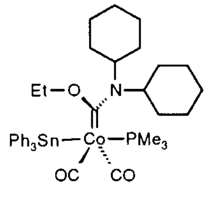

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So far no intramolecular cyclization of the ethene and the Co,C double bonds with formation of a cobaltacyclobutane has yet been observed for **16**. Consequently, no metathetic activity has been found.

4. Conclusions

The synthesis of silylvinylidene chelate complexes has been reported. These include the first observation of a silyl migration with vinylidene formation at a cobalt atom. Bis(trimethylsilyl)cobalt chelate **8** was prepared and strucuturally characterized. The synthesis of a carbene complex with an ethene ligand at the same metal gave **16**, which also was structurally characterized. Structural and spectroscopic data indicate that the ethene and carbene ligands compete for electron density from the metal.

5. Experimental

5.1. General

All operations involving air sensitive materials were performed under argon using standard Schlenk techniques. Diethyl ether, THF, benzene, and toluene were dried over Na/K–benzophenone. Silica gel was heated at reduced pressure and then put under normal pressure with argon. This was repeated five times. Starting materials were either purchased or prepared according to literature procedures. IR: Bruker ISS 25, Perkin–Elmer FT 580, FT 1710. ^{1}H-NMR: Bruker AVS 200 (200.1 MHz), AVS 400 (400.1 MHz). ^{13}C-NMR: Bruker AVS 200 (50.3 MHz), AVS 400 (100.6 MHz). Spectra were obtained with the DEPT and with the APT techniques. + and − indicate positive (C, CH_2) and negative phase (CH, CH_3), respectively. ^{31}P-NMR: H decoupled, Bruker AVS 400 (161.9 MHz), 85% aqu. H_3PO_4 as external standard. MS, FAB-MS, HRMS: Finnigan AM 400, Fisons VG Autospec. Elemental analyses: Haeraeus CHN-Rapid. Melting points: Büchi apparatus according to Dr Tottoli, uncorrected.

*5.2. {[2-Di(tert-butylphosphanyl-P)ethyl]cyclopentadienyl}chlorocobalt(II) (**2**) [30]: improved procedure*

At 0°C 25.7 ml (41.1 mmol) of a 1.6 M solution of butyllithium in hexane was added dropwise to a stirred solution of 6.00 g (41.1 mmol) of di-*tert*-butylphosphane in 150 ml of THF. After completed addition, the pale yellow solution was stirred for 1 h. At 25°C 3.78 g (41.1 mmol) of spiro[2.4]hepta-4,6-diene [63] was added dropwise. The mixture was heated at reflux until it became colorless. At −50°C 5.34 g (41.1 mmol) of

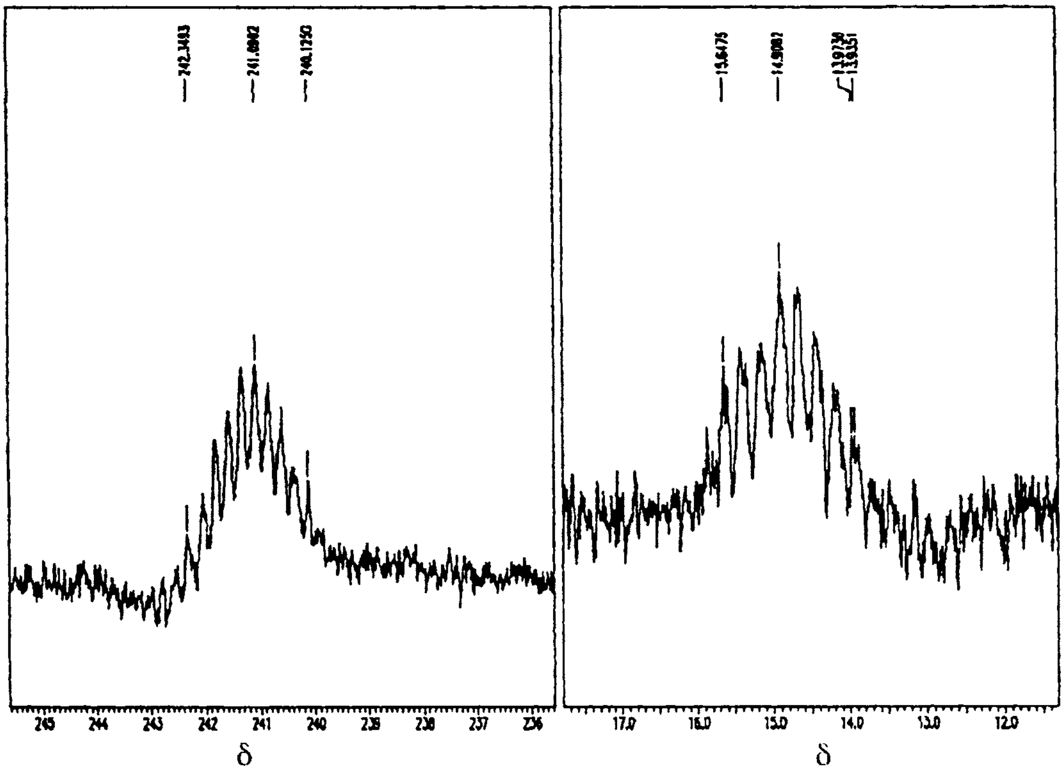

Fig. 2. ^{13}C-NMR signals of the carbene (left) and the ethene ligands (right) in **16**.

anhydrous cobalt(II)chloride was added to the obtained solution of lithium [2-di(*tert*-butylphosphanyl)ethyl]-cyclopentadienide. The mixture was warmed to 25°C over 4 h and stirred at 25°C for another hour. After condensation of the THF into a cold trap the residue was extracted five times with 50 ml of diethyl ether each time. The combined organic extracts were filtered through a P4 frit covered with a 3 cm thick layer of Celite. After solvent condensation into a cold trap 10.1 g (30.5 mmol, 74%) of **2** was obtained as a black–violet solid.

5.3. {η^5:η^1-[2-(Di-*tert*-butylphosphanyl-*P*)ethyl]cyclopentadienyl}(trimethylsilylethyne)cobalt(I) (4) and {η^5:η^1-[2-(di-*tert*-butylphosphanyl-*P*)ethyl]-cyclopentadienyl}(trimethylsilyl-1-ethenylidene)cobalt(I) (5)

(a) 110 mg (0.11 mmol) of trimethylsilylethyne was added dropwise to a −50°C cold solution of 374 mg (0.11 mmol) of **2** in 20 ml of THF. After 5 min 20.0 g of sodium amalgam was added, and the solution was slowly warmed to −45°C. After stirring the mixture at this temperature for 10 min it was warmed slowly to 20°C and then stirred for 1 h. The THF was condensed into a cold trap, and the residue was taken up with diethyl ether and filtered through a P4 frit covered with a 3 cm thick layer of Celite. The Celite was washed with diethyl ether until the filtrate remained colorless. After solvent removal into a cold trap the residue was separated by column chromatography (petroleum ether–diethyl ether 3:1).

Fraction I: 169 mg (0.043 mmol, 38%) of **4** as blue–green crystals (m.p. 106°C). IR (film): $\tilde{\nu} = 3295$ cm^{-1} (m, ≡C–H), 3080 (m, Cp–H), 2960 (s, CH_2, CH_3), 2898 (s, CH_2, CH_3), 2864 (s, CH_2, CH_3), 1715 (s, C≡C), 1601 (s), 1472 (s), 1385 (m, *t*-Bu), 1365 (s, *t*-Bu), 1240 (s), 1180 (m), 1168 (m), 1038 (m, Cp–R),

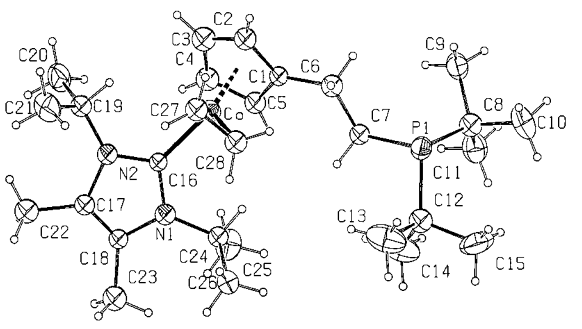

Fig. 3. Structure of **16** in the crystal. Selected bond lengths (Å) and angles (°): Co1–C1 2.07(2), Co1–C2 2.03(2), Co1–C3 2.07(2), Co1–C4 2.04(2), Co1–C5 2.08(2), Co1–C16 1.929(8), Co1–C27 1.97(2), Co1–C28 1.91(2), C16–N1 1.39(2), C16–N2 1.35(2), C27–C28 1.355(13), Co1–C27–C28 67.2(13), Co1–C28–C27 71.9(13), C27–Co1–C16 91.6(6), C28–Co1–C16 95.2(7)

1017 (m, Cp–R), 930 (m), 860 (s, C–Si), 845 (s, C–Si), 790 (s, Cp), 752 (s), 672 (s), 620 (m), 585 (m), 492 (m). ^{1}H-NMR (200 MHz, [D$_6$]benzene): $\delta = 0.55$ (s, 9H, 12-H), 1.21 (d, 18H, 9-H, $^{3}J_{P,H} = 11.5$ Hz), 1.6–1.95 (m, 5H, 6-H, 7-H, 10-H), 3.85 [m, 2H, 2(5)-H or 3(4)-H], 6.03 [m, 2H, 2(5)-H or 3(4)-H]. ^{13}C-NMR (100 MHz, [D$_6$]benzene): $\delta = 1.2$ (s, C-12), 25.3 (d, C-6, $^{2}J_{C,P} = 6.8$ Hz), 29.8 (s, C-9), 34.7 (d, C-8, $^{1}J_{C,P} = 6.4$ Hz), 37.1 (d, C-7, $^{1}J_{C,P} = 19.3$ Hz), 76.4 [s, C-2(5) or C-3(4)], 80.3 (s, C-2(5) or C-3(4)], 108.3 (d, C-1, $^{3}J_{C,P} = 7.2$ Hz), signals for C-10, C-11 were not observed. MS (70 eV, 90 °C): m/z (%): 394 (41) [M$^+$], 378 (11) [M$^+$ − CH$_4$], 336 (35) [M$^+$ − Si(CH$_3$)$_2$], 321 (12) [M$^+$ − Si(CH$_3$)$_3$], 296 (35) [M$^+$ − C$_5$H$_{10}$Si], 279 (53) [M$^+$ − Si(CH$_3$)$_2$–C$_4$H$_8$], 265 (34) [M$^+$ − Si(CH$_3$)$_3$–C$_4$H$_8$], 239 (88) [M$^+$ − C$_5$H$_{10}$Si–C$_4$H$_9$], 183 (100) [M$^+$ − C$_5$H$_{10}$Si–C$_4$H$_9$–C$_4$H$_8$], 137 (43), 118 (35), 106 (35), 91 (34), 73 (49).

Fraction II: 183 mg (0.46 mmol, 41%) of **5**, brown oil. IR (film): $\tilde{\nu} = 3095$ cm^{-1} (w, Cp–H), 2950 (s, CH$_2$, CH$_3$), 2900 (m, CH$_2$, CH$_3$), 2870 (m, –CH$_2$–, CH$_3$), 1605 (br. m, vinylidene), 1475 (m), 1392 (w, *t*-Bu), 1370 (m, *t*-Bu), 1247 (m), 1149 (br. m), 840 (br. s, C–Si), 818 (s, Cp), 760 (w), 495 (w). ^{1}H-NMR (200 MHz, [D$_6$]benzene): $\delta = 0.37$ (s, 9H, 12-H), 1.30 (d, 18H, 9-H, $^{3}J_{P,H} = 12.7$ Hz), 1.72–1.85 (m, 2H, 6-H), 2.15–2.22 (m, 2H, 7-H), 2.62 (d, 1H, 11-H, $^{4}J_{P,H} = 9.6$ Hz), 4.61 [br. s, 2H, 2(5)-H or 3(4)-H], 4.91 [br. s, 2H, 2(5)-H or 3(4)-H]. ^{13}C-NMR (100 MHz, [D$_6$]benzene): $\delta = 1.2$ (s, C-12), 25.1 (d, C-6, $^{2}J_{C,P} = 5.7$ Hz), 29.8 (d, C-9, $^{2}J_{C,P} = 2.8$ Hz), 35.7 (d, C-8, $^{1}J_{C,P} = 14.6$ Hz), 40.2 (d, C-7, $^{1}J_{C,P} = 17.8$ Hz), 80.3 [s, C-2(5) or C-3(4)], 81.36 [d, C-2(5) or C-3(4), $^{2}J_{C,P} = 5.1$ Hz], 108.3 (s, C-11), 110.5 (d, C-1, $^{3}J_{C,P} = 7.6$ Hz), 302.4 (br., C-10, $\nu_{1/2} = 100$ Hz). ^{31}P-NMR (162 MHz, [D$_6$]benzene): $\delta = 115.2$. MS (70 eV, 90 °C): m/z (%): 394 (43) [M$^+$], 378 (8) [M$^+$ − CH$_4$], 336 (25) [M$^+$ − Si(CH$_3$)$_2$], 321 (32) [M$^+$ − Si(CH$_3$)$_3$], 296 (47) [M$^+$ − C$_5$H$_{10}$Si], 279 (53), 265 (22) [M$^+$ − Si(CH$_3$)$_3$–C$_4$H$_8$], 239 (79) [M$^+$ − C$_5$H$_{10}$Si–C$_4$H$_9$], 183 (100) [M$^+$ − C$_5$H$_{10}$Si–C$_4$H$_9$–C$_4$H$_8$], 137 (65), 118 (25), 106 (36), 91 (24), 73 (62). HRMS (C$_{20}$H$_{36}$PSiCo): calc. 394.16559; found 394.16554.

(b) To a stirred solution of 204 mg (0.63 mmol) **2** in 30 ml of THF 60 mg (0.63 mmol) trimethylsilylethyne was added at −30°C. After removing the ice-bath and warming up to 25°C, the solution was stirred for 24 h at ambient temperature. During this time the color changed to reddish brown. After removal of all volatiles into a cold trap, the residue was taken up with 50 ml of a 2:1 mixture of diethylether and pentane. Filtration through a frit covered with a 2 cm layer of Celite and washing the filter pad once with a small amount of diethyl ether gave a red solution, which was evaporated to dryness, affording 132 mg (0.34 mmol, 54%) of **5** as a red–brown powder. This was identified by comparison of the spectroscopic data (^{1}H-NMR, IR).

*5.4. Reaction of **3** with diphenylethyne*

585 mg (1.82 mmol) of **3** and 160 mg (0.90 mmol) of diphenylethyne in 20 ml of toluene in a sealed glass ampule were heated at 140°C for 5 days. The solvent was condensed into a cold trap at reduced pressure, and the residue was chromatographed on silica gel (petroleum ether–diethyl ether 1:1). Oxidation in air gave 270 mg (0.41 mmol, 45%) of [η^5-2-(di-*tert*-butylphosphoranyl)ethylcyclopentadienyl](η^4-tetraphenylcyclobutadiene)cobalt(I) (**7**) as a yellow, microcrystalline powder (m.p. 78°C).

IR (KBr): $\tilde{\nu} = 3080$ cm^{-1} (w), 3056 (m), 3026 (w), 2961 (m, CH$_2$, CH$_3$), 2870 (m, CH$_2$, CH$_3$), 1598 (m), 1499 (s), 1475 (m), 1445 (m), 1309 (w), 1157 (br., m, *t*-Bu), 1025 (w, Cp–R), 817 (m, Cp), 772 (m, arom.), 745 (m, arom.), 698 (s, arom.), 590 (m), 565 (m). ^{1}H-NMR (200 MHz, CDCl$_3$): $\delta = 1.12$ (d, 18H, 9-H, $^{3}J_{P,H} = 13$ Hz), 1.6–1.75 (m, 2H, 6-H), 2.20–2.40 (m, 2H, 7-H), 4.52 [s, 4H, 2(5)-H, 3(4)-H], 7.20 [m, 12H, 11(15)-H, 13-H], 7.44 [m, 8H, 12(14)-H]. MS (70 eV, 190°C): m/z (%): 669 (100) [M$^+$], 506 (78) [M$^+$ − P(O)tBu$_2$], 416 (17), 327 (18) [M$^+$ − 2(C$_4$H$_8$)–3(C$_6$H$_5$)], 312 (73) [M$^+$ − Ph$_4$C$_4$], 256 (12), 237 (10), 178 (16) [C$_{14}$H$_{10}^{+}$], 150 (15), 105 (7). Anal. Calc. for C$_{43}$H$_{46}$CoOP (668.74): C 77.23, H 6.93. Found: C 76.32, H 7.00%.

*5.5. {η^5:η^1-[2-(Di-tert-butylphosphanyl-P)ethyl]cyclopentadienyl}[bis(trimethylsilyl)vinylidene]cobalt(I) (**8**) from **3***

A solution of 120 mg (0.37 mmol) of **3** and 94 mg (0.37 mmol) of bis(trimethylsilyl)ethyne in 20 ml of toluene in a sealed tube was heated at 140°C for 5 days. Chromatography at silica gel (petroleum ether–diethyl ether 3:1) followed by recrystallization from toluene gave 83 mg (0.18 mmol, 48%) of {η^5:η^1-[2-(di-*tert*-butylphosphanyl-*P*)ethyl]cyclopentadienyl}[bis(trimethylsilyl)vinylidene]cobalt(I) (**8**), which was identified spectroscopically (see below).

*5.6. {η^5:η^1-[2-(Di-tert-butylphosphanyl-P)ethyl]cyclopentadienyl}[η^2-bis(trimethylsilyl)ethyne]cobalt(I) (**9**)*

153 mg (0.90 mmol) of bis(trimethylsilyl)ethyne was added dropwise at −50°C to a solution of 290 mg (0.88 mmol) of **1** in 20 ml of THF. After 5 min 14.0 g of Na/Hg was added, and the mixture was stirred at −45°C for 10 min and then stirred for 1 h at 20°C. The THF was condensed into a cold trap, and the residue was taken up with diethyl ether and filtered through a P4 frit covered with a 3 cm thick layer of Celite. The

Celite was washed with diethyl ether until the solution became colorless. The diethyl ether was condensed into a cold trap. Crystallization from diethyl ether gave 379 mg (0.81 mmol, 93%) of **9** as blue–green crystals [m.p. (DSC) 86°C, exothermic reaction to **8**].

IR (KBr): $\tilde{\nu} = 3095$ cm^{-1} (w, Cp), 2953 (s, CH_2, CH_3), 2898 (s, CH_2, CH_3), 1749 (s, alkyne, compl.), 1594 (m), 1557 (m), 1474 (s), 1367 (m, *t*-Bu), 1243 (s), 1182 (w), 1147 (m), 1019 (Cp–R), 932 (w), 854 (br. s, C–Si), 792 (m), 754 (m), 687 (m), 672 (m), 467 (w). ^{1}H-NMR (200 MHz, [D$_6$]benzene): $\delta = 0.54$ (s, 18H, 11-H), 1.21 (d, 18H, 9-H, $^3J_{P,H} = 12.0$ Hz), 1.80 (m, 4H, 6-H, 7-H), 3.65 + 5.69 [AA′BB′ line system, 4H, 2(5)-H, 3(4)-H, $\Sigma J = 4.0$ Hz]. ^{13}C-NMR (50 MHz, [D$_6$]benzene, APT): $\delta = 2.5$ (−, s, C-11), 25.2 (+, d, C-6, $^2J_{C,P} = 7.4$ Hz), 29.9 (−, d, C-9, $^2J_{C,P} = 4.2$ Hz), 34.3 (+, d, C-8, $^1J_{C,P} = 5.2$ Hz), 38.5 (+, d, C-7, $^1J_{C,P} = 20.0$ Hz), 78.9 [−, d, C-2(5) or C-3(4), $^2J_{C,P} = 8.6$ Hz], 79.2 (−, s, C-2(5) or C-3(4)], 106.9 (+, d, C-1, $^3J_{C,P} = 6.7$ Hz), 115.0 (+, br. d, C-10, $^2J_{C,P} = 5.3$ Hz). ^{31}P-NMR (81 MHz, [D$_6$]benzene): $\delta = 96.6$. MS (70 eV, 50 °C) *m*/*z* (%): 466 (2) [M$^+$], 295 (31) [$M^+ - C_8H_{19}Si_2$], 240 (6) [$M^+ - C_8H_{18}Si_2 – C_4H_8$], 184 (8) [$M^+ - C_8H_{18}Si_2 – 2(C_4H_8)$], 170 (12) [$C_8H_{18}Si_2^+$], 155 (100) [$C_8H_{18}Si_2^+ – CH_3$], 137 (4), 107 (3), 97 (5), 73 (23). Anal. Calc. for $C_{23}H_{44}Si_2PCo$ (466.68): C 59.25, H 9.51. Found: C 59.92, H 9.17%.

5.7. {*η*^{5}:*η*^{1}-[2-(Di-tert-butylphosphanyl-P)ethyl]cyclopentadienyl}[bis(trimethylsilyl)vinylidene]cobalt(I) (**8**) from **9**

74 mg (0.16 mmol) of **9** in 10 ml of toluene was heated at 110°C for 1 h. The mixture was filtered through a P4 frit covered with a 3 cm thick layer of Celite, which was washed with toluene until the filtrate became colorless. The volume of the solution was reduced to 5 ml. Crystallization at −30°C gave 69 mg (0.15 mmol, 93%) of **8** as red crystals [m.p. 137°C (DSC)].

IR (KBr): $\tilde{\nu} = 3095$ cm^{-1} (w, Cp–H), 2953 (m, $–CH_2–$, CH_3), 2898 (m, $–CH_2–$, CH_3), 1595 (s, vinylidene), 1473 (m), 1367 (w, *t*-Bu), 1244 (m), 1153 (w), 1019 (w, Cp–R), 862 (s, C–Si), 840 (s, C–Si), 805 (m, Cp), 758 (w), 685 (w), 624 (w), 580 (w), 528 (w), 468 (w). ^{1}H-NMR (200 MHz, [D$_6$]benzene): $\delta = 1.30$ (d, 18H, 9-H, $^3J_{P,H} = 13.0$ Hz), 1.75 (dt, 2H, 6-H, $J = 7.0$ Hz, $^3J_{P,H} = 19.0$ Hz), 2.15 (dt, 2H, 7-H, $J = 7$ Hz, $^2J_{C,P} = 8.0$ Hz), 4.71 + 5.06 [AA′BB′ line system, 2 × 2H, 2(5)-H, 3(4)-H, $\Sigma J = 4.0$ Hz]. ^{13}C-NMR (100 MHz, [D$_6$]benzene): $\delta = 2.5$ (s, C-12), 25.2 (d, C-6, $^2J_{C,P} = 5.7$ Hz), 29.9 (d, C-9, $^2J_{C,P} = 4.3$ Hz), 35.5 (d, C-8, $^1J_{C,P} = 13.4$ Hz), 39.8 (d, C-7, $^1J_{C,P} = 18.9$ Hz), 81.1 [d, C-2(5) or C-3(4), $^2J_{C,P} = 4.7$ Hz], 81.3 [s, C-2(5) or C-3(4)], 109.7 (d, C-1, $^3J_{C,P} = 7.0$ Hz), 110.5 (s, C-11), 298.4 (br., C-10). ^{31}P-NMR (81 MHz, [D$_6$]benzene): $\delta = 117.2$. MS (70 eV, 160 °C): *m*/*z* (%): 466 (4) [M$^+$], 393 (6) [$M^+ - SiMe_3$], 295 (27) [$M^+ - C_8H_{19}Si_2$], 239 (6) [$M^+ - C_8H_{18}Si_2 – C_4H_8$], 183 (9) [$M^+ - C_8H_{18}Si_2 – C_4H_8 – C_4H_9$], 170 (15) [$C_8H_{18}Si_2^+$], 155 (100) [$C_8H_{18}Si_2^+ – CH_3$], 137 (4), 106 (7), 91 (6), 75 (27). Anal. Calc. for $C_{23}H_{44}Si_2PCo$ (466.68): C 59.20, H 9.51. Found: C 59.21, H 9.40%.

5.8. Crystal structure analysis of **8**

$C_{23}H_{44}CoPSi_2$, MW = 466.7, dark red prism 0.28 × 0.46 × 0.53 mm, orthorhombic *Pnma* [no. 62], $a = 18.694(1)$, $b = 14.808(1)$, $c = 9.600(1)$ Å, $U = 2657.4(4)$ Å^3, $T = 293$ K, $Z = 4$, $D_x = 1.17$ g cm^{-3}, $\lambda = 0.71073$ Å, $\mu(\text{Mo–K}_\alpha) = 0.803$ mm^{-1}, Enraf–Nonius CAD-4 diffractometer, $2.39 < \theta < 27.41°$, 3147 independent measured reflections, 2307 with $I > 2\sigma(I)$. Structure solved by direct methods and refined by least-squares using Chebyshev weights on F_o^2 to $R_1 = 0.040$ [$I > 2\sigma(I)$], $wR_2 = 0.141$, 133 parameters, H atoms riding, $S = 0.928$, residual electron density +0.415/ −0.609 e Å^{-3}.

5.9. [*η*^{2}-Bis(trimethylsilyl)butadiyne]{*η*^{5}:*η*^{1}-[2-(di-tert-butylphosphanyl-P)ethyl]cyclopentadienyl}cobalt(I) (**10**)

101 mg (0.52 mmol) of bis(trimethylsilylbutadiyne was added to 173 mg (0.52 mmol) of **1** in 30 ml of THF. 20.0 g of Na/Hg was added, and the mixture was warmed to −45°C. After 10 min the mixture was slowly warmed to 20°C and stirred for 1 h. The THF was condensed into a cold trap, the residue was taken up with diethyl ether and filtered through a P4 frit covered with a 3 cm thick layer of Celite. The Celite was washed with diethyl ether until the filtrate became colorless. The diethyl ether was condensed into a cold trap. 184 mg (0.38 mmol, 72%) of **10**, green, viscous oil.

IR (film): $\tilde{\nu} = 3094$ cm^{-1} (w, Cp), 2958 (s, CH_2, CH_3), 2894 (s, CH_2, CH_3), 2104 (s, C≡C), 2070 (s, C≡C), 1777 (s, C≡C coord.), 1562 (m), 1473 (s), 1398 (m, *t*-Bu), 1388 (m, *t*-Bu), 1368 (m, *t*-Bu), 1245 (s), 1182 (m), 1065 (m, Cp–R), 1027 (m, Cp–R), 839 (br. s, C–Si), 756 (s), 698 (m), 672 (m), 654 (w), 577 (w), 467 (m). ^{1}H-NMR (200 MHz, [D$_6$]benzene): $\delta = 0.42$ (s, 9H, 16-H or 17-H), 0.50 (s, 9H, 16-H or 17-H), 1.09 (d, 9H, 9-H or 11-H, $^3J_{P,H} = 12.0$ Hz), 1.46 (d, 9H, 9-H or 11-H, $^3J_{P,H} = 12.0$ Hz), 1.60–1.90 (m, 4H, 6-H, 7-H), 3.62 (m, 1H, 2-H or 3-H or 4-H or 5-H), 4.31 (m, 1H, 2-H or 3-H or 4-H or 5-H), 5.11 (m, 1H, 2-H or 3-H or 4-H or 5-H), 5.80 (m, 1H, 2-H or 3-H or 4-H or 5-H). ^{13}C-NMR (50 MHz, [D$_6$]benzene, APT): $\delta = 0.5$ (−, C-16 or C-17), 1.3 (−, s, C-16 or C-17), 25.3 (+, d, C-6, $^2J_{C,P} = 6.9$ Hz), 29.4 (−, d, C-9 or C-11, $^2J_{C,P} = 4.0$ Hz), 30.1 (−, d, C-9 or C-11, $^2J_{C,P} = 4.0$ Hz), 34.6 (+, d, C-8 or C-10, $^1J_{C,P} = 3.6$ Hz), 35.3 (+, d, C-8 or C-10, $^1J_{C,P} = 10.2$ Hz), 37.0 (+, d, C-7, $^1J_{C,P} = 20.2$

Hz), 77.4 (−, C-2 or C-3 or C-4 or C-5), 78.9 (−, d, C-2 or C-3 or C-4 or C-5, $^2J_{C,P} = 8.9$ Hz) 80.5 (−, C-2 or C-3 or C-4 or C-5), 83.5 (−, d, C-2 or C-3 or C-4 or C-5, $^2J_{C,P} = 7.6$ Hz), 96.4 (+, d, C-12 or C-13, $^2J_{C,P} = 8.8$ Hz), 103.2 (+, s, C-14 or C-15), 103.9 (+, s, C-14 or C-15), 110.8 (+, d, C-1, $^3J_{C,P} = 7.3$ Hz). ^{31}P-NMR (81 MHz, [D$_6$]benzene): $\delta = 94.0$. MS (70 eV, 50 °C): m/z (%): 490 (10) [M$^+$], 434 (2) [$M^+ - C_4H_8$], 393 (2) [$M^+ - C_2SiMe_3$], 375 (2) [$M^+ - 2(C_4H_9)$], 296 (49) [$M^+ - Me_3SiC_4SiMe_3$], 240 (8) [$M^+ - Me_3SiC_4SiMe_3 - C_4H_8$], 195 (10) [$Me_3SiC_4SiMe_3H^+$], 179 (45) [$Me_3SiC_4SiMe_3^+ - CH_4$], 162 (7), 147 (7), 106 (9), 84 (30), 74 (100) [$HSiCH_3^+$]. HRMS ($C_{25}H_{44}PSi_2Co$): calc. 490.2051; found 490.2044.

5.10. Thermolysis of ***10***

122 mg (0.25 mmol) of **10** in 10 ml of toluene was heated at 110°C for 5 days. The color of the mixture changed from green to brown. The toluene was condensed into a cold trap, and the residue was taken up with diethyl ether and filtered through a P4 frit. After solvent removal into a cold trap 67 mg of a brown–black oil was obtained, which was tentatively characterized as the cyclobutadiene complex **11**.

IR (film): $\tilde{\nu} = 2956$ (s), 2925 (s), 2875 (m), 2110 (w), 2060 (w), 2000 (w), 1472 (m), 1399 (w), 1368 (w), 1247 (m), 1020 (w), 842 (s), 758 (w). MS (70 eV, 170 °C): m/z (%): 684 (4), 628 (2), 540 (4), 295 (20), 239 (35), 183 (48), 147 (100), 73 (37).

5.11. Bis(vinylidene) complex ***12***

64 mg (0.33 mmol) of bis(trimethylsilyl)butadiyne was added to 219 mg (0.66 mmol) of **1** at −50°C. After 5 min 15.0 g of Na/Hg was added and the mixture was warmed to −45°C. After 10 min the mixture was slowly warmed to 20°C and stirred for 1 h. The solution was separated from the Na/Hg, and the THF was condensed into a cold trap. The residue was taken up with diethyl ether and 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 colorless. After solvent condensation into a cold trap 171 mg (0.22 mmol, 66%) of **12** was obtained, as a brown, microcrystalline powder.

IR (KBr): $\tilde{\nu} = 3095$ cm^{-1} (w, Cp), 2961 (s, $-CH_2-$, CH_3), 2951 (m, $-CH_2-$, CH_3), 1607 (br, m, vinylidene), 1475 (m), 1367 (m, *t*-Bu), 1261 (s), 1098 (br., s), 1028 (br., s, Cp–R), 843 (br., s, C–Si), 802 (s, Cp), 755 (w), 450 (w), 419 (w). ^{1}H-NMR (200 MHz, [D$_6$]benzene): $\delta = 0.39$ (s, 18H, 12-H), 1.30 (d, 36H, 9-H, $^3J_{P,H} = 13$ Hz), 1.62 (m, 4H, 6-H), 2.20 (m, 4H, 7-H), 4.62 + 5.31 [AA′BB′ line system, 2 × 2H, 2(5)-H, 3(4)-H, $\Sigma J = 3.0$ Hz]. The sample decomposed during the ^{13}C-NMR measurement. ^{31}P-NMR of the decomposed material (81 MHz, [D$_6$]benzene): $\delta = 29.2$, 56.5, 69.9, 106.8, 114.8.

*5.12. {η^5[2-(Di-tert-butylphosphanyl-P)ethyl]cyclopentadienyl}-(1,3-diisopropyl-4,5-dimethyl-2-dehydro-1H-imidazol-2-ylidene)(η^2-ethene)cobalt (I) (**16**)*

422 mg (2.35 mmol) of 1,3-diisopropyl-3,4-dimethyl-2,3-dihydro-1*H*-imidazol-2-ylidene (**15**) was added at −50°C to 760 mg (2.35 mmol) of **2** in 75 ml of pentane. After stirring for 3 h and warming up to 20°C the mixture was filtered through a P4 frit covered with a 3 cm thick layer of Celite. Crystallization from the filtrate at −30°C gave 493 mg (0.98 mmol, 42%) of **16**, red crystals (m.p. 134°C, dec.).

IR (KBr): $\tilde{\nu} = 3688$ (w) cm^{-1}, 2960 (s, CH_3, $-CH_2-$), 1668 (m), 1640 (m), 1600 (m), 1464 (m), 1396 (m), 1368 (m), 1188 (w), 1132 (m), 1080 (m), 1020 (m), 912 (w), 808 (m), 756 (w), 654 (w), 516 (w). ^{1}H-NMR (400.1 MHz, [D$_6$]benzene): $\delta = 1.15$ (d, $^3J_{P,H} = 10.3$ Hz, 18H, 9-H, 13-H), 1.33 (d, $^3J_{H,H} = 6.1$ Hz, 12H, 17-H, 19-H), 1.62 (s, 6H, 21-H, 23-H), 1.78–2.00 (m, 4H, 14-H), 2.35 (m, 2H, 6-H or 7-H), 2.75 (m, 2H, 6-H or 7-H), 4.14 (m, 2H, 16-H, 18-H), 4.53 (s, 1H, 2-H or 3-H or 4-H or 5-H), 4.92 (s, 1H, 2-H or 3-H or 4-H or 5-H), 5.24 (s, 1H, 2-H or 3-H or 4-H or 5-H), 5.45 (s, 1H, 2-H or 3-H or 4-H or 5-H). ^{13}C-NMR (100.6 MHz, [D$_6$]benzene, APT): $\delta = 10.2$ (−, s, C-21, C-23), 14.9 (+, m, C-14, $\nu_{1/2} \approx 170$ Hz), 22.5 (−, s, C-17, C-19), 23.0 (+, $^1J_{C,P} = 23.1$ Hz, C-8 or C-12), 25.0 (+, $^1J_{C,P} = 7.0$ Hz, C-7), 30.0 (−, $^2J_{C,P} = 14.0$ Hz, C-9, C-13), 34.8 (+, d, $^2J_{C,P} = 7.0$ Hz, C-6), 53.5 (−, s, C-16, C-18), 79.0 (−, s, C-2 or C-3 or C-4 or C-5), 80.0 (−, d, $^2J_{C,P} = 5.1$ Hz, C-2 or C-3 or C-4 or C-5), 80.6 (−, d, $^2J_{C,P} = 5.7$ Hz, C-2 or C-3 or C-4 or C-5), 109.7 (+, d, $^3J_{C,P} = 6.4$ Hz, C-1), 124.6 (+, s, C-20, C-22), 241.4 (+, m, C-15, $\nu_{1/2} \approx 220$ Hz). ^{31}P{^{1}H}-NMR ([D$_6$]benzene): $\delta = 29.7$ (s). MS (70 eV, 90°C): m/z (%) 506 (8) [$M^+ + 2$], 505 (11) [$M^+ + 1$], 504 (31) [M$^+$], 478 (1) [$M^+ - C_2H_4$], 421 (1) [$M^+ - C_2H_4 - C_3H_7N$], 364 (1) [$M^+ - C_2H_4 - (C_3H_7N)_2$], 296 (5) [$M^+ - C_{11}H_{20}N_2$], 281 (24), 240 (4), 196 (47), 154 (26), 112 (100), 91 (16), 73 (24), 65 (2).

5.13. Crystal structure analysis of ***16***

$C_{28}H_{50}N_2PCo$, molecular weight 504.60, crystal system orthorhombic, space group $Pna2_1$, $a = 23.805(2)$, $b = 11.073(1)$, $c = 11.130(1)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 90°$, $V = 2933.8(4)$ Å^3, $Z = 4$, $d_{ber} = 1.142$ g cm^{-3}, $F(000) = 1096$ e, $\mu = 6.56$ cm^{-1}, red crystal, crystal size 0.33 × 0.30 × 0.11 mm, Stoe IPDS (area detector) diffractometer, $T = 300(2)$ K, Mo–K$_\alpha$ = 0.71073 Å, $2\theta_{min} = 2.03°$, $2\theta_{max} = 20.96°$, 10376 measured reflections (±23; −10–11; ±11), 3085 independent, 1434 observed ($I > 2\sigma$) reflections, completeness of data

99.7%, $R(I) = 0.1441$, absorption correction none, extinction correction none, refinement program SHELXL-93, full-matrix least-squares on F^2, $R(F, F > 4\sigma(f)) = 0.1360$, $wR(F^2, \text{all}) = 0.1551$, minimum/maximum residual electron density $-0.406/0.538$ e Å^{-3}.

6. Supplementary material

Crystallographic data (without structural factors) of the structures described in this publication have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 147197 (**8**) and 146998 (**16**). Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http//www.ccdc.cam.ac.uk).

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