[ω-(Phosphanyl)alkyl]cyclopentadienyl Complexes☆

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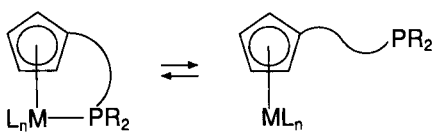
The syntheses and characterisation of the [ω-(phosphanyl)alkyl]cyclopentadienyl anions **2**, **3**, **6**–**8**, **10**, and **11** are described. These anions form metallocenes **12**–**15** and **17**–**19** with $FeCl_2$ 2 THF and with $ZrCl_4 \cdot 2$ THF, respectively. With $ICo(CO)_4$ chelated carbonyl complexes **23**–**25**, **28**, and **29** are formed. The unchelated intermediate **20** has been detected by IR spectroscopy. The carbonyl chelate complexes are thermally stable. Under photochemical conditions, ligand exchange reactions are possible which in the case of 1,5-cyclooctadiene proceed with decomplexation of the phosphane arm. This does not prevent a reaction at the cobalt(I) atom; treatment of **35** with diphenylethyne gives the corresponding tetraphenylcyclobutadiene complex **36** in good yield, the phosphane arm remaining uncoordinated.

Transition metal complexes with cyclopentadienyl ligands have been intensively studied since their initial synthesis in 1951[1]. Special aspects of their chemistry are *ring-slippage* reactions[2] in which the usual η^5 bonding mode changes to an η^3 bonding with temporary decomplexation of one double bond. This raised the question in how far chemical reactions with participation of the temporarily decoordinated double bond might be possible. One result of our work was the ring opening reaction of a (bicyclo[3.2.0]hepta-1,3-dienyl)cobalt(I) complex followed by a cycloaddition of the intermediate *ortho*-quinodimethane species[3]. In these ring-slippage reactions the cyclopentadienyl ligand can formally be regarded as a bidentate "allyl-ene" ligand, whose "ene" fragment decoordinates in the course of the change in hapticity from η^5 to η^3 and is recoordinated later. The process reversibly generates a vacant coordination site, which is capable of participating in chemical reactions[3].

Vacant coordination sites are usually generated by decomplexation of a ligand. If the ligand is not present in large excess in the reaction mixture, it will normally not be recoordinated after use of the vacant coordination site for further reaction. However, if the decomplexed ligand is still attached to the complex by other means than by coordination to the metal atom, it will not leave the molecule as a whole and can be later recoordinated. The ring slippage of a cyclopentadienyl ("allyl-ene") ligand mentioned is a very special case, and more generally this line of thought leads to the use of bi- or multidentate ligands. Most bidentate ligands are combinations of two ligands of the same nature, e.g. diphosphanes, bipyridyl derivatives and similar systems. In contrast, heterobidentate ligands should allow use to be made of the different coordination properties of the two ligands involved. In this context we became interested in combinations of cyclopentadienyl and phosphane ligands, which are among the most thoroughly studied ligands in organometallic chemistry. To avoid any interference from resonance interactions we envisaged a connection of the ligands by an alkyl chain. The two partial ligands have rather different properties: whereas the cyclopentadienyl system is negatively charged, the phosphane ligand is electronically neutral. In neutral complexes of these ligands one has therefore to expect substantial ionic bonding of the cyclopentadienyl part to the metal, while the phosphane part is fixed to the metal mainly by coordinative bonding. As a consequence, the phosphane part will in general be decomplexed more easily than the cyclopentadienyl fragment. The phosphane ligand may therefore be regarded as an "intramolecular protecting group of a vacant coordination site" as illustrated in Scheme 1.

Scheme 1



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In this paper we describe the synthesis and characterisation of some ligands of the type under discussion, the formation of metallocenes of iron and zirconium, as well as carbonylcobalt(I) chelate complexes of these ligands and finally reactions of the latter complexes including some, in which the phosphane arm is decomplexed. Material presented in this paper was in part the subject of preliminary communications[4].

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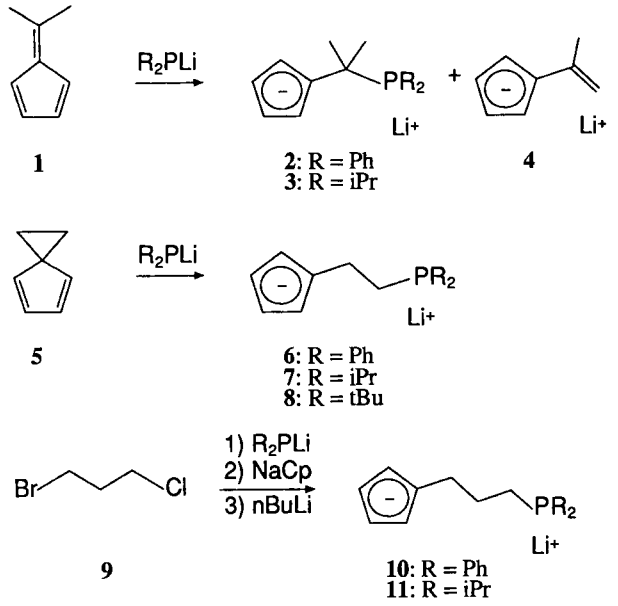
Results and Discussion

[ω-(Phosphanyl)alkyl]cyclopentadienyl complexes have only received limited attention[5]. In an initial attempt to obtain the desired ligands, (2-chloroethyl)diphenylphosphane[6] was treated with sodium cyclopentadienide. However, the ethyl compound was dehydrohalogenated by the basic sodium cyclopentadienide yielding mainly ethenyldiphenylphosphane[7]. Further experiments showed that different synthetic routes had to be applied according to the length of the alkyl chain connecting the cyclopentadienyl and the phosphane parts.

Ligands with a one-carbon bridge can be obtained by nucleophilic addition to pentafulvenes[8]. Treatment of 6,6-dimethylfulvene (**1**) with lithium diphenylphosphide gives ligand **2**[8] in 70% yield besides some deprotonation product **4**. With lithium diisopropylphosphide ligand **3** is obtained in 65% yield in addition to some **4**.



To obtain [ω-(phosphanyl)ethyl]cyclopentadienyl ligands **6**–**8**, the corresponding lithium phosphides were treated with spiro[2.4]hepta-4,6-diene (**5**)[9], giving the desired ligands in 63–92% yield. [ω-(Phosphanyl)propyl]cyclopentadienyl anions **10** and **11** were obtained from 1-bromo-3-chloropropane (**9**) via the corresponding (3-chloropropyl)-phosphanes in 51 and 65% yield, respectively[6,10]. All ligands were obtained as cyclopentadienyl anions since the absence of double bond isomers makes their characterisation easier, and it is also the form in which the ligands are coordinated to metals. The ligands were characterised by NMR spectroscopy (Table 1).

Depending on the substituents at phosphorus, the ^{31}P-NMR chemical shifts range between $\delta = -15$ and $+28$. The ^{31}P-NMR chemical shift of substituted phosphanes is governed by electronic and steric factors. According to Mann[12], an increasing steric demand of the substituents at phosphorus increases the bonding angles, ultimately resulting in an increased shielding of the phosphorus atom. This view is in accordance with the data listed in Table 1.

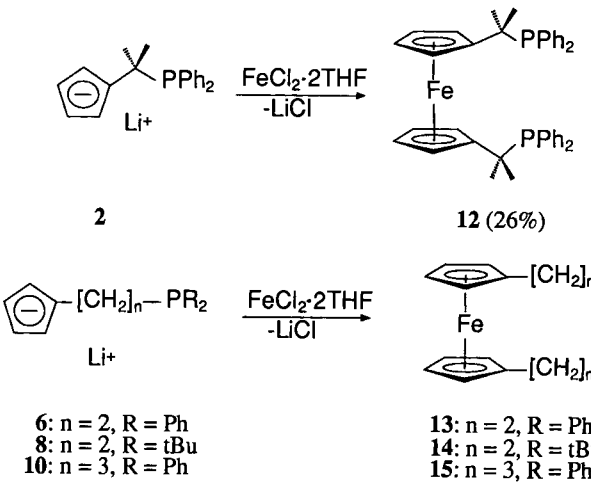
Table 1. [ω-(Phosphanyl)alkyl]cyclopentadienyl anions; counterion Li^+; solvent [D_8]THF

Anion	R	% Yield	^{1}H NMR[a]	^{13}C NMR[b]	^{31}P NMR
2[8]	Ph	70	5.6	103.3 (d) 103.4 (d) 125.7 (s)	+21.2
3	*i*-Pr	65[c]	5.5	–	+2.5
6[5,9]	Ph	63	5.51	102.9 (d) 120.3 (s)	−15.7
7	*i*-Pr	83	5.4	102.6 (d) 102.7 (d) 121.0 (s)	+2.5
8	*t*-Bu	92	5.35	102.7 (d)[d] 121.5 (s)	+28.1
10[11]	Ph	51	5.1	102.5 (d) 103.2 (d) 119.4 (s)	−15.1
11	*i*-Pr	65	5.31	102.4 (d) 103.0 (d) 119.9 (s)	+3.8

[a] AA'BB' System of cyclopentadienyl protons. – [b] δ of cyclopentadienyl carbon atoms. – [c] **3** was detected in the mixture containing the isopropenylcyclopentadienyl anion (**4**). – [d] C-2(5) and C-3(4).

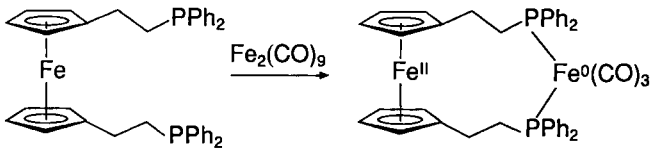
Various cyclopentadienyl anions have been used to prepare metallocenes. Metallocenes bearing phosphane arms are bidendate phosphane ligands themselves and might facilitate coordination of the ligands to another metal atom leading to homo- or heterodimetallic complexes. In these complexes the metal-metal distance is determined by the kind and the conformation of the alkyl chains and might possibly allow interactions between the metal atoms. In the corresponding zirconocenes, the additional possibility of coordinating the phosphane arms to the zirconium atom to give zirconium(II) chelate complexes is attractive.

Ligands **2**, **6**, **8**, and **10** were treated with $FeCl_2 \cdot 2$ THF to afford the corresponding ferrocenes **12**–**15** in 23–75%



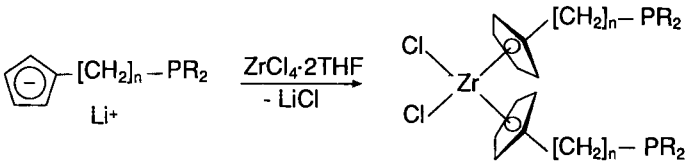
yield, highest yields being obtained with ethylene-bridged ligands. **12–15** are yellow crystalline materials melting between 63 and 129°C.

Attempts to obtain dimetallic complexes by treating ferrocenes **12–15** with (η^5-cyclopentadienyl)bis(ethene)-cobalt(I), tetracarbonyl(η^4-norbornadiene)molybdenum(0), bis(η^4-1,5-cyclooctadiene)nickel(0), or bis(acetonitrile)dichloropalladium(II) were not successful. In most cases the compounds did not react selectively, and a complex mixture of products was obtained. Apparently, the conformationally flexible ferrocenes do not sufficiently differentiate between intra- and intermolecular reactions with the metal reagents. Only the reaction of **13** with $Fe_2(CO)_9$ gave a mixture, whose spectroscopic data indicate the formation of dimetallic complex **16**: In the IR spectrum (KBr) absorptions at $\tilde{\nu} = 1883$ and 1872 cm^{-1} are in accordance with a $Fe(CO)_3$ unit, and in the mass spectrum the signal of the molecular ion is observed at $m/z = 750$ (4%). In addition, the completely decarbonylated fragment ion causes a signal at $m/z = 666$ (46%). Although **16** has not been obtained in pure form, the compound is of interest since it contains the two iron atoms in different oxidation states (0, +2).



13 **16**

The reactions of ligands **6**, **8**, and **10** with $ZrCl_4 \cdot 2$ THF result in the formation of zirconocene dichlorides **17**[5c], **18**[5c], and **19** in 66–92% yield. These compounds were prepared with the view of reducing the Zr(IV) species to give a system in which the phosphane arms would be coordinated to the Zr atom. However, although cyclic voltammetry of **18** indicated reduction steps similar to those in zirconocene dichloride, experiments with activated magnesium or with *n*-butyllithium gave no clear result. In some cases, 10–40% of the decomplexed ligands were detected by ^1H- and ^{13}C-NMR analysis.



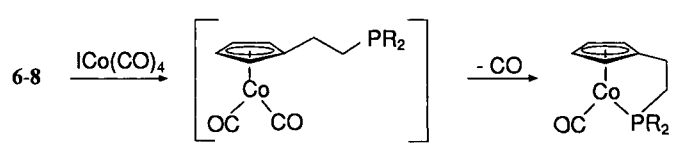
6: n = 2, R = Ph
8: n = 2, R = tBu
10: n = 3, R = Ph

17: n = 2, R = Ph (81%)
18: n = 2, R = tBu (92%)
19: n = 3, R = Ph (66%)

Because cyclopentadienyl complexes of cobalt have been thoroughly studied, the synthesis of cobalt complexes with the bidentate ligands was next attempted. Although there are reports on the synthesis of some complexes of ligand **6** with other metals[5], there are so far no reports involving cobalt(I) complexes of the ligands described here. According to Rausch et al.[13] cyclopentadienyl anions can be coordinated to cobalt by treatment with a reagent prepared from octacarbonyl dicobalt and iodine (1:1). The synthesis of the reagent has recently been modified by Pályi et al.[14], who identified $ICo(CO)_4$ as the reactive species.

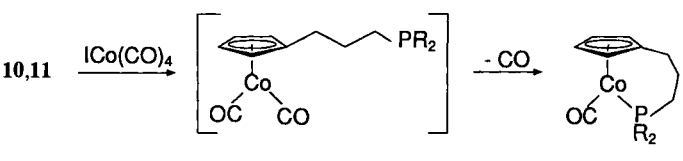
The reaction of ligand **2** with $ICo(CO)_4$ was unselective, giving a mixture of seven phosphorus-containing compounds (^{31}P-NMR spectroscopy) with some spectroscopic evidence for the presence of a non-chelated dicarbonylcobalt(I) complex with ligand **2**. The inspection of molecular models indicates that chelation is difficult to achieve with only a one-carbon bridge present and that it is much easier to realize with a two-carbon bridge while chelation should be possible with a three-carbon bridge, although some steric crowding of the three-carbon chain may introduce some steric hindrance. Therefore we turned to ligands **6–8**, **10**, and **11**, containing ethylene and propylene bridges between the cyclopentadienyl and the phosphane part of the ligand. Initially it was unclear, if chelation had occurred following the complexation, or if an extra transformation step had been necessary. This was the case in the only comparable compound reported in the literature: Mathey et al. prepared the $Mn(CO)_3$ complex of ligand **6** (31%) and induced a loss of CO followed by the chelation in 60% yield by irradiation of the complex[5b] (overall yield 19%). In a related case, the oxidation of a cobalt(I) complex with iodine accompanied by loss of one CO followed by reduction with Na/Hg was necessary to induce chelation[15]. With this literature background in mind we were gratified to obtain chelated complexes **23–25**, **28**, and **29** in 24–56% yield as red crystalline materials directly by treatment of the anionic ligands with $ICo(CO)_4$ (Table 2).

There is no doubt that the reactions proceed via intermediates **20–22** and **26**, **27**. Some evidence for this was obtained in the reaction between ligand **6** and $ICo(CO)_4$: initially, a dark yellow product was isolated which between 20 and 40°C reacted further to the dark red complex **23**. A low-temperature IR spectrum of the reaction mixture at −25°C showed carbonyl absorptions at 1949 and 2013 cm^{-1} as expected for a dicarbonyl intermediate **20**.



20: R = Ph
21: R = iPr
22: R = tBu

23: R = Ph
24: R = iPr
25: R = tBu



26: R = Ph
27: R = iPr

28: R = Ph
29: R = iPr

Table 2. Carbonyl[ω-(phosphanyl)alkyl]cyclopentadienylcobalt(I) complexes

Compd.	Yield (%)	M.p. (°C)	IR (cm^{-1})	^{31}P NMR[a]	$\Delta\delta$ (^{31}P)[d]
20			1957[b] 2018[b]		
23	24	89	1898[c]	85.2	100.9
24	43	83	1886[c]	108.1	105.6
25	56	119	1899[c]	128.9	100.8
28	39	72	1898[c]	62.0	77.1
29	27	68	1903[b]	78.6	74.8

[a] δ values, solvent C_6D_6. — [b] $\tilde{\nu}_{C=O}$ in [D_8]toluene. — [c] $\tilde{\nu}_{C=O}$ in KBr. — [d] $\Delta\delta = \delta_{complex} - \delta_{ligand}$.

Complexes **23**–**25** and **28**, **29** are soluble in most organic solvents. The ethylene-bridged complexes **23**–**25** are less soluble with decreasing solvent polarity and can be crystallized from boiling hexane. Due to their conformational flexibility the propylene-bridged complexes **28** and **29** cannot be easily crystallized. These complexes are less stable than the ethylene-bridged ones and decompose slowly in solution. In addition they are more air-sensitive. The carbonyl chelate complexes **23**–**25**, **28**, and **29** were characterised by their spectroscopic data. The IR carbonyl absorptions (Table 2) do not differ significantly from those of carbonyl(η^5-cyclopentadienyl)(triphenylphosphane)cobalt(I) (1905 cm^{-1}, KBr)[16]. The ^{31}P-NMR chemical shifts of the chelated complexes (Table 2) are significantly different from those of the uncomplexed ligands (Table 1). The calculated $\Delta\delta$ values are almost independent of the substituents R at phosphorus and vary considerably with the length of the alkyl bridge between the cyclopentadienyl and the phosphane parts of the ligands: for the ethylene-bridged complexes $\Delta\delta$ is slightly above 100 (100.8 to 105.6), and for the propylene-bridged complexes it is about 75 (74.8 to 77.1). We suggest that this variation is caused by the differing steric requirements of the ethylene and the propylene bridges. The different chain lengths apparently cause different bonding angles between the phosphorus atom, the cobalt atom and the cyclopentadienyl ligand in the chelate complexes. Presumably, differences in the molecular geometry and the molecular strain determine the $\Delta\delta$ values. In addition to the chemical shift, the shape of the phosphorus resonance signals indicates the coordination of the phosphane arms to the cobalt atoms. Due to the quadrupole moment of ^{59}Co, compounds with a Co–P bond show ^{31}P-NMR signals which are much broader (width at half height 100–170 Hz) than those of uncoordinated phosphorus atoms. In the ^1H-NMR spectra usual coordination shifts are observed. In the ^1H-NMR spectrum of **25** no broadening of the signal of the diastereotopic protons bound to the ethylene bridge appears down to 193 K. This indicates that the exchange between the two enantiomeric *gauche* conformations (Figure 1) is fast relative to the NMR time scale, even at 193 K, resulting in an average spectrum. The ^{13}C-NMR data of the chelate complexes are consistent with the proposed structures. In the mass spectra, in addition to the peak of the molecular ion, the signal of ^{59}Co and peaks resulting from a CO fragmentation and a dissociation of the substituents at phosphorus are significant.

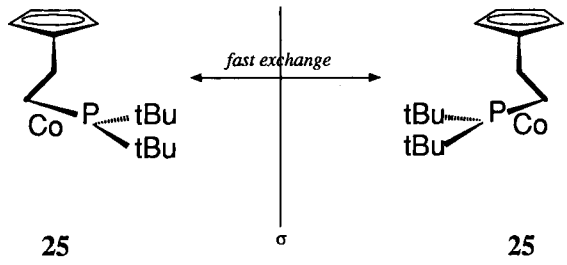


Figure 1. Enantiomeric conformations of **25**

Crystals suitable for an X-ray study of {[2-(di-*tert*-butylphosphanyl-*P*)ethyl]-η^5-cyclopentadienyl}cobalt(I) (**25**) were obtained by crystallization from Et_2O (Figure 2, atomic fractional coordinates see Table 4). The structure does not show significant differences in the C–C bond lengths of the cyclopentadienyl ring. C1 is located about 0.05 Å to the cobalt side of the best plane through C2, C3, C4, C5 (±0.008 Å). This observation is mirrored by the distances between the cobalt atom and the cyclopentadienyl carbon atoms indicating a central location of the metal atom below the cyclopentadienyl ring. The deviation of C1 is caused by the chelation of the phosphane part. The structure clearly shows the torsion of the ethylene bridge with dihedral angles C1–C6–C7–P (36.3°) and C6–C7–P–Co (−26.4°). The co-

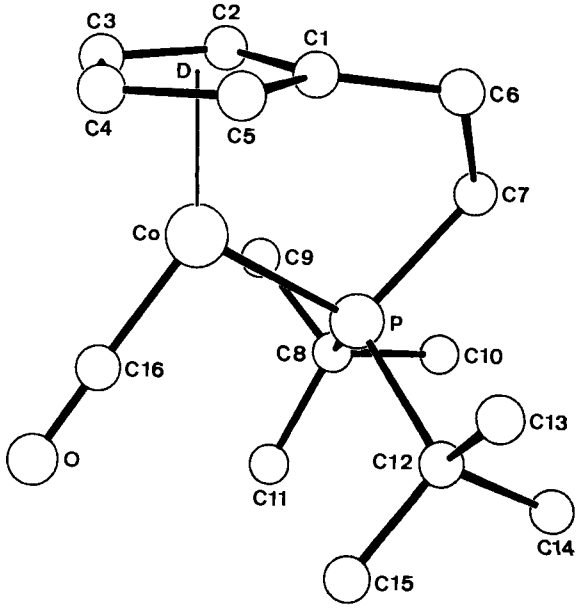
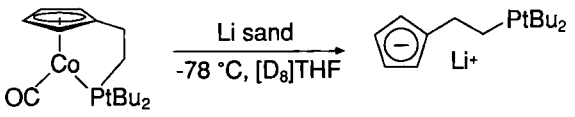


Figure 2. Crystal structure of **25**. Selected bond lengths [Å], bond angles [°], and dihedral angles [°]: Co–P 2.152(1), Co–C1 2.051(2), Co–C2 2.091(3), Co–C3 2.100(3), Co–C4 2.081(3), Co–C5 2.096(3), Co–C16 1.702(3), P–C7 1.858(3), C16–O 1.159(3), C1–C2 1.424(4), C1–C5 1.425(4), C1–C6 1.510(4), C2–C3 1.395(4), C3–C4 1.428(5), C4–C5 1.401(4), C6–C7 1.542(4); C16–Co–P 97.2(1), D–Co–C16 140.8(1), D–Co–P 121.9(1), D–C1–C6 173.9(2); C1–C2–C3–C4 1.0, C1–C5–C4–C3 3.4, C1–C6–C7–P −36.3, C6–C7–P–Co −26.4

balt atom is apparently accessible only from the side of the carbonyl ligand, the *tert*-butyl substituents at the phosphorus atom effectively shield the other side of the metal. A comparable structure of a ruthenium complex with ligand **6** has recently been published[17].

25 is available in good yield, and the bulky *tert*-butyl substituents at the phosphorus atom should support a decomplexation of the phosphane arm. Therefore the studies on the reactivity of the chelate complexes were mainly carried out with this derivative. In some experiments the phenyl-substituted complex **23** was used.

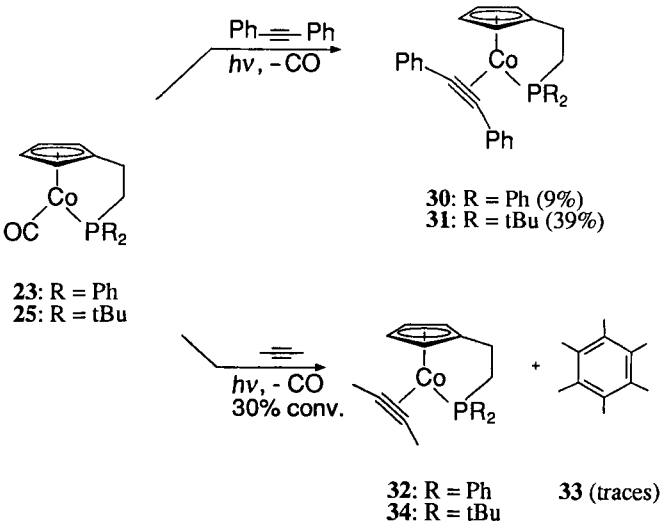
The cyclic voltammogram of **25** shows three reversible reduction steps. Because a two-electron reduction of **25** would lead to a 20*e* complex, which is rather unstable, other possibilities have to be taken into account. Among these is a reversible decomplexation of the phosphane arm, which might allow two electrons to occupy the vacant coordination site created. A vacant coordination site might also be a result of a reversible $\eta^5 \rightarrow \eta^3$ ring slippage reaction of the cyclopentadienyl ligand. To investigate the reduction chemistry of **25** experimentally, the compound was reduced with lithium sand at −78 °C in THF. This method had enabled a $\eta^6 \rightarrow \eta^4$ ring slippage to be detected in (arene)$Cr(CO)_3$ complexes[18]. However, the result of the reaction was a complete decomplexation of the ligand as indicated by ^{1}H-, ^{13}C-, and ^{31}P-NMR analyses. Because in the course of the reaction no precipitate was observed, the cobalt liberated must be present either in solution or, more probably, in the lithium sand. This result resembles that of the reduction experiments carried out on the zirconocene derivative **18**.



25 **8**

To obtain some information on the thermal behaviour of **25**, a DSC analysis was carried out (DSC = Differential Scanning Calorimetry): The compound melts at 119 °C and decomposes above 175 °C. This means that it is rather stable thermally. The DSC analysis was performed in the absence of any other reagent. To exclude the possibility of a ligand exchange reaction in the presence of a ligand, **25** was treated with triphenylphosphane and with diphenylethyne in boiling di-*n*-butyl ether. The DSC result was confirmed; thus, in all cases **25** was recovered in more than 90% yield. After **25** had been refluxed in 1,5-cyclooctadiene for three days, 15% of the starting compound were converted into the 1,5-cyclooctadiene complex **35** with the phosphane arm decoordinated. Although this is certainly not a suitable route to ligand exchange products, the result does indicate that in principle decomplexation of the phosphane arm is possible. Alternative methods of ligand exchange were sought.

The UV spectrum of **25** shows absorptions at 221 nm ($\varepsilon = 1.42 \cdot 10^4$), 319 ($2.75 \cdot 10^3$) and 440 ($3.63 \cdot 10^2$). The absorption at 221 nm is assigned to a $\pi \rightarrow \pi^*$ transition of the cyclopentadienyl system. Irradiation at this wavelength would most likely result in a decomplexation of the cyclopentadienyl system. Therefore solutions of **23** and **25** in toluene were irradiated with Duran-filtered light (>300 nm). In the presence of a threefold excess of diphenylethyne the CO ligands were displaced by the acetylene ligand, and complexes **30** and **31** were obtained in 9 (50 h) and 39% yield (91 h), respectively, demonstrating the higher reactivity of the *tert*-butyl-substituted compound. **30** and **31** can be crystallized from pentane as black crystals (m.p. 127 and 218 °C, resp.), which dissolve with green colour in polar organic solvents. Because (cyclopentadienyl)cobalt(I) complexes are known to trimerise alkynes to give benzene derivatives, in the experiments with **23** and **25** the crude reaction mixtures were analysed for hexaphenylbenzene by GC and by ^{1}H NMR: no hexaphenylbenzene was detected.



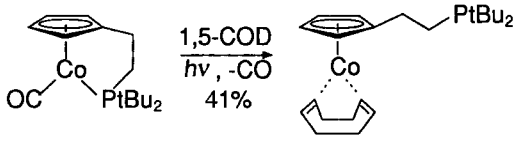
In the ^{31}P-NMR spectrum of **31** the broad ($w_{1/2}$ ca. 200 Hz) signal of the coordinated phosphorus atom appears at $\delta = 94.9$, the coordination shift ($\Delta\delta = 66.8$) being smaller than in the corresponding carbonyl complex ($\Delta\delta = 100.8$, see Table 2). The C≡C stretching vibration is observed in the IR spectrum at 1795 cm^{-1} in contrast to 2221 cm^{-1} for uncomplexed diphenylethyne (Raman)[19].

The reactions of **23** and **25** with 2-butyne under photochemical conditions resulted in only 30% conversion to the alkyne complexes **32** and **34** in addition to starting material. Traces of hexamethylbenzene (**33**) were detected by mass spectrometry and by ^{1}H-NMR spectroscopy.

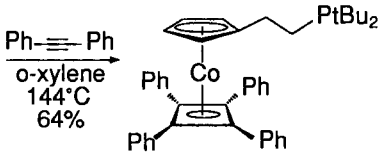
Decomplexation of the phosphane arm in **25** by treatment with bidentate ligands has also been investigated. After partial coordination, a competition between the chelate effects of the new bidendate ligand and that of the [(ω-phosphanyl)alkyl]cyclopentadienyl ligand is to be expected which could finally induce a decomplexation of the phosphane arm. As an additional result of an intermolecular reaction, a coupling of two complexes by a further bidentate ligand might be expected. Treatment of **25** with 1,2-bis(dimethylphosphanyl)ethane and with 2,2′-bipyridyl under photochemical conditions proceeded with incomplete conversion and resulted in mixtures, which according to their analytical

data (^{1}H, ^{31}P NMR) contained the desired products in addition to numerous other compounds. The reaction with 1,5-hexadiyne gave a product mixture, which according to mass spectrometral data contained among others a compound in which two cobalt atoms are coupled by the diacetylenic ligand. Efforts directed to separation of the mixtures have, as yet, been unsuccessful.

The reaction of **25** with 1,5-cyclooctadiene under photochemical conditions was more successful: the 1,5-cyclooctadiene complex **35** with a decomplexed phosphane arm was obtained in 41% yield as red crystals which can be dissolved in all polar organic solvents. The sharp ^{31}P-NMR signal at $\delta = 30.7$ is diagnostic of the decomplexed phosphane arm, the coordination shift being only $\Delta\delta = 2.6$. All other analytical data are also in accordance with **35**. The formation of **35** in good yield can be understood as the result of a competition of the chelate effects of the two bidentate ligands.



25 **35**



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(η^4-1,5-Cyclooctadiene)(η^5-cyclopentadienyl)cobalt(I) complexes have been extensively investigated in connection with cyclisation reactions of alkynes and nitriles, leading to cyclobutadiene complexes or to benzene and pyridine derivatives[20]. This raises the question, whether **35** behaved in a similar manner or whether the phosphane arm recoordinated and thus prevented the use of the vacant coordination sites for a reaction. Refluxing **35** in *ortho*-xylene in the presence of an excess of diphenylethyne led to the formation of the tetraphenylcyclobutadiene complex **36** in 64% yield. In the crude reaction mixture no hexaphenylbenzene was detected. **36** was characterised by its spectroscopic data and elemental analysis. The absence of a C,P coupling between the cyclobutadiene carbon atoms and the phosphorus atom, the ^{31}P-NMR chemical shift of $\delta = 29.8$ and the small width at half height of this signal ($w_{1/2} = 3$ Hz) clearly indicate that the phosphane arm remains decoordinated and thus does not prevent the reaction at the cobalt(I) atom.

We have shown that [ω-(phosphanyl)alkyl]cyclopentadienyl chelate complexes are accessible in good yield. The chelate complexes deserve further attention because the phosphane arm may be regarded as an intramolecular protecting group of a coordination site. The carbonyl complexes with cobalt(I) are thermally unreactive, but under photochemical conditions ligand exchange reactions become possible. The most encouraging results have been obtained with 1,5-cyclooctadiene, which is a bidendate ligand itself and causes a decomplexation of the phosphane arm. The decoordinated phosphane arm does not hinder further reactions at the cobalt(I) atom by recoordination.

We are currently investigating more efficient methods of preparing more reactive chelate complexes containing other than carbonyl ligands.

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Experimental

All operations were performed in flame-dried two- or three-necked round-bottom flasks equipped with a reflux condenser, argon inlet, and magnetic stirring bar under an argon atmosphere. Pentane, hexane, heptane, toluene, benzene, dioxane, and diethyl ether were dried with $NaAlEt_4$ and then distilled from sodium potassium alloy. Dichloromethane and trichloromethane were dried over P_4O_{10} and distilled through a 80-cm Vigreux column. Unless otherwise indicated starting materials were purchased and used without further purification. – ^{1}H NMR: Bruker WH 400-FT (400.1 MHz), AM and AC 200 (200.1 MHz), WP 80 (80 MHz). – ^{13}C NMR: Bruker WH 400-FT (100.6 MHz), AM and AC 200 (50.3 MHz), WM 300 (75.5 MHz). Signal multiplicities were determined by application of the DEPT[21] technique or by inspection of gated spectra. Chemical shifts (^{1}H and ^{13}C) refer to $\delta_{TMS} = 0$ or to residual solvent signals as internal standard[22]. Numbering of the C and H atoms according to Figure 2. – ^{31}P NMR: Bruker AM and AC 200 (81.0 MHz) with H_3PO_4 as external standard. – IR: Nicolet 7199 FT-IR; solution measurements in AgCl or NaCl cuvettes. – Raman: Coderg LRT 800 ($\lambda = 488$ nm). – UV: Varian Cary-2300. – MS: Varian 311 A (fractional evaporation). In all cases the correct isotope ratio is observed; for Zr compounds only peaks referring to ^{90}Zr (natural abundance 51.4%) are reported. – GC/MS: Finnigan MAT CH 7 A + Perkin-Elmer GCF 22. – HRMS: Finnigan MAT 820. – Analytical GC: Becker-Packard 417, Shimadzu GC-8AX (FID), 15–40-m glass capillary columns PS 240 or PS 345.5 or 40-m glass capillary column OV-1, carrier gas H_2. – Flash chromatography[23]: Silica gel Merck, 0.04–0.063 mm (230–400 mesh ASTM), or alumina Fluka 507 C neutral, 100–125 mesh, activity 1. For chromatography of organometallic compounds silica gel was dried for 48 h at 110°C/0.001 mbar and then flushed with argon-satured solvent. – DSC: DuPont 9900. – Melting points: Büchi SMP-20 (uncorr.). – Elemental analyses: Mikroanalytisches Laboratorium Dornis und Kolbe, Mülheim a.d. Ruhr, FRG.

Lithium [1-(Diphenylphosphanyl)-1-methylethyl]cyclopentadienide[8] (**2**): 3.60 g (34.0 mmol) of 6,6-dimethylfulvene (**1**)[24] is added to a solution of 6.48 g (34.0 mmol) of lithium diphenylphosphide[25] in 200 ml of THF at 20°C, the colour of the mixture changing from red to pale yellow. The mixture is stirred at 20°C for 4 h and then refluxed for 15 h. The THF is evaporated into a cold trap, the residue is taken up in 200 ml of diethyl ether and the mixture filtered through a P4 frit. The residue is dried at 0.001 mbar for 8 h; yield 0.94 g (8.3 mmol, 25%) of lithium (1-methylethenyl)cyclopentadienide[5a,f] (**4**), bright grey powder, identified by a comparison of the ^{1}H-NMR data with those of authentic material. The solvent is evaporated from the filtrate into a cold trap and the residue dried at 0.001 mbar for 8 h. Filtration yield 7.09 g [23.8 mmol, 70%, purity 70% (^{1}H NMR)] of **2**, yellow powder. – IR (KBr): $\tilde{\nu} = 3053$

cm^{-1} (m, Cp, Ph), 2955 (m, CH_2, CH_3), 2922 (m, CH_2, CH_3), 2862 (m), 1954 (w), 1888 (w), 1813 (w), 1575 (m, Ph), 1478 (m, Ph), 1433 (s, P—Ph), 1380 [m, $C(CH_3)_2$], 1360 [m, $C(CH_3)_2$], 1326 (w), 1308 (w), 1269 (w), 1244 (w), 1229 (w), 1183 (w), 1146 (w), 1117 (m), 1090 (m), 1070 (w), 1045 (m), 1036 (m), 1027 (m), 999 (m), 928 (m), 877 (w), 827 (m, Cp-R), 761 (s, Ph), 743 (s, Ph), 697 (s, Ph), 552 (m), 537 (m), 501 (m), 465 (m). — ^{1}H NMR (200 MHz, [D$_8$]THF): δ = 1.34 [d, 6H, 7(8)-H, $^3J_{P,H}$ = 12.3 Hz], 5.6 [AA'BB' line system, 4H, 2(5)-, 3(4)-H, $\Sigma J_{2(5),3(4)}$ = 4.6 Hz], 7.16 (m, 10H, arom. H). — ^{13}C NMR (50.3 MHz, [D$_8$]THF): δ = 29.3 [dq, C-7(8), $^2J_{P,C}$ = 15.3 Hz], 36.9 (d, C-6, $^1J_{P,C}$ = 16.2 Hz), 103.3 [d, C-3(4)], 103.4 [d, C-2(5)], 125.8 (d, C-1, $^2J_{P,C}$ = 9.7 Hz), 127.8 (dd, C-11 or C-12, $^3J_{P,C}$ = 6.5 Hz), 128.0 (d, C-11 or C-12), 135.9 (dd, C-10, $^2J_{P,C}$ = 19.5 Hz), 140.6 (d, C-9, $^1J_{P,C}$ = 26.0 Hz). — ^{31}P NMR (81 MHz, [D$_8$]THF): δ = 21.2.

Lithium [1-(Diisopropylphosphanyl)-1-methylethyl]cyclopentadienide (**3**): 2.43 g (21.9 mmol) of 6,6-dimethylfulvene (**1**)[24] is added to a solution of 2.71 g (21.9 mmol) of lithium diisopropylphosphide[25] in 200 ml of THF at 20°C, the colour of the mixture changing from red to pale yellow. The mixture is stirred at 20°C for 3 h and then refluxed for 14 h. The THF is evaporated into a cold trap, the residue is taken up in 200 ml of diethyl ether and the mixture filtered through a P4 frit. The residue is dried at 0.001 mbar for 8 h, yield 0.75 g (6.7 mmol, 31%) of **4** (grey powder, identified by ^{1}H NMR). The solvent is evaporated from the filtrate into a cold trap and the residue dried at 0.001 mbar for 8 h. Filtration yield 2.55 g, consisting of 5% of **4**, 30% of lithium [1-(diisopropyloxophosphoranyl)-1-methylethyl]cyclopentadienide, and 65% of **3** (^{1}H, ^{31}P NMR). — ^{1}H NMR (**3**, 400 MHz, [D$_8$]THF): δ = 0.78 (dd, 6H, 10-H, $^3J_{9,10}$ = 7.0, $^3J_{P,H}$ = 8.9 Hz), 0.99 (dd, 6H, 11-H, $^3J_{9,11}$ = 7.2, $^3J_{P,H}$ = 13.3 Hz), 1.43 [d, 6H, 7(8)-H, $^3J_{P,H}$ = 11.3 Hz], 1.56 (dsept, 2H, 9-H, $^2J_{P,H}$ = 4.0 Hz), 5.37 + 5.40 [AA'BB' line system, 4H, 2(5)-, 3(4)-H, $\Sigma J_{2(5),3(4)}$ = 6.2 Hz]. — ^{13}C NMR (50.3 MHz, [D$_8$]-THF): δ = 20.5 [dq, C-10 or C-11, $^2J_{P,C}$ = 8.7 Hz], 23.1 (dd, C-9, $^1J_{P,C}$ = 23.5 Hz), 23.8 [dq, C-10 or C-11, $^2J_{P,C}$ = 21.8 Hz], 29.9 [dq, C-7(8), $^2J_{P,C}$ = 19.2 Hz], 35.6 (d, C-6, $^1J_{P,C}$ = 19.2 Hz), 102.8 [d, C-2(5), -3(4)], 127.0 (d, C-1, $^2J_{P,C}$ = 3.5 Hz). — ^{31}P NMR (81 MHz, [D$_8$]THF): δ = 39.7.

Preparation of Lithium [2-(Phosphanyl)ethyl]cyclopentadienides

Procedure 1: An equimolar amount of spiro[2.4]hepta-4,6-diene (**5**)[26] is added to a solution of the lithium dialkyl- or diarylphosphide in THF. The mixture is refluxed for 5 h. The solvent is evaporated into a cold trap, and pentane is added to the residue. The solid product is isolated by filtration of the mixture through a P4 frit and subsequent drying of the residue at 0.001 mbar for 8 h.

Lithium [2-(Diphenylphosphanyl)ethyl]cyclopentadienide[9] (**6**): Procedure 1; 2.29 g (11.9 mmol) of lithium diphenylphosphide[25] in 200 ml of THF, 1.10 g (11.9 mmol) of **5**[26]. Yield 2.14 g (7.5 mmol, 63%) of **6**, colourless powder, m.p. >250°C, purity 95% (^{1}H, ^{31}P NMR). — IR (KBr): $\tilde{\nu}$ = 3069 cm^{-1} (m), 3053 (m, Cp, Ph), 3027 (m), 3014 (w), 2848 (w), 1953 (w), 1883 (w), 1585 (m, Ph), 1480 (m, Ph), 1446 (m, Ph), 1432 (s, P—Ph), 1356 (w), 1309 (w), 1274 (w), 1093 (m), 1049 (w), 1027 (w, Cp—R), 1017 (w), 999 (w), 971 (w), 825 (s, Cp—R), 763 (s, Ph), 748 (s, Ph), 697 (s, Ph). — ^{1}H NMR (200 MHz, [D$_8$]THF): δ = 2.35 (m, 2H, 7-H), 2.59 (m, 2H, 6-H), 5.51 [AA'BB' line system, 4H, 2(5)-, 3(4)-H), $\Sigma J_{2(5),3(4)}$ = 4.0 Hz], 7.26 (m, 6H, *m*-, *p*-H), 7.44 (m, 4H, *o*-H). — ^{13}C NMR (50.3 MHz, [D$_8$]THF): δ = 27.2 (dt, C-6 or C-7, $^1J_{C,H}$ = 127, $J_{P,C}$ = 17.2 Hz), 31.9 (dt, C-6 or C-7, $^1J_{C,H}$ = 130, $J_{P,C}$ = 10.4 Hz), 102.9 [d, C-2(5), -3(4), $^1J_{C,H}$ = 159 Hz], 120.3 (d, C-1, $^3J_{P,C}$ = 14.0 Hz), 128.9 (d, C-10 or C-11, $^1J_{C,H}$ = 160 Hz), 129.0 (dd, C-10 or C-11, $^1J_{C,H}$ = 161 Hz), 133.5 (dd, C-9, $^1J_{C,H}$ = 160, $^2J_{P,C}$ = 18.3 Hz), 140.9 (d, C-8, $^1J_{P,C}$ = 15 Hz). — ^{31}P NMR (81 MHz, [D$_8$]THF): δ = −15.7.

Lithium [2-(Diisopropylphosphanyl)ethyl]cyclopentadienide (**7**): Procedure 1; 4.05 g (32.6 mmol) of lithium diisopropylphosphide[25] in 250 ml of THF, 3.0 g (32.6 mmol) of **5**[26]. Yield 5.82 g [26.9 mmol, 83%, purity 95% (^{1}H, ^{31}P NMR)] of **7**, colourless powder. — IR (KBr): $\tilde{\nu}$ = 3084 cm^{-1} (m), 3068 (m, Cp, Ph), 1636 (w), 1626 (w), 1613 (w), 1524 (w), 1461 (m), 1412 (w), 1382 (m, *i*Pr), 1364 (m, *i*Pr), 1250 (w), 1230 (m), 1152 (w), 1101 (w), 1060 (w), 1041 (m, Cp—R), 1027 (m, Cp—R), 950 (w), 932 (m), 897 (m), 881 (m), 864 (w), 831 (m), 753 (s, Cp—R), 676 (m), 637 (m), 602 (w), 581 (w). — ^{1}H NMR (200 MHz, [D$_8$]THF): δ = 1.09 (dd, 6H, 9-H, $^3J_{8,9}$ = 7.2, $^3J_{P,H}$ = 13.0 Hz), 1.10 (dd, 6H, 10-H, $^3J_{8,10}$ = 7.2, $^3J_{P,H}$ = 10.8 Hz), 1.64 (m, 2H, 7-H, $^2J_{P,H}$ = 5.3, $^3J_{6,7}$ = 7.4 Hz), 1.73 (dsept, 2H, 8-H, $^2J_{P,H}$ = 3.0 Hz), 2.53 (m, 2H, 6-H, $^3J_{P,H}$ = 8.4 Hz), 5.32 + 5.36 [AA'BB' line system, 4H, 2(5)-, 3(4)-H, $\Sigma J_{2(5),3(4)}$ = 4.9 Hz]. — ^{13}C NMR (50.3 MHz, [D$_8$]THF): δ = 19.4 (dq, C-9 or C-10, $^2J_{P,C}$ = 10.5 Hz), 20.7 (dq, C-9 or C-10, $^2J_{P,C}$ = 15.6 Hz), 24.1 (dd, C-8, $^1J_{P,C}$ = 13.1 Hz), 25.7 (dt, C-6 or C-7, $J_{P,C}$ = 15.7 Hz), 29.1 (dt, C-6 or C-7, $J_{P,C}$ = 19.1 Hz), 102.6 [d, C-2(5) or C-3(4)], 102.7 [d, C-2(5) or C-3(4)], 121.1 (d, C-1, $^3J_{P,C}$ = 13.1 Hz). — ^{13}P NMR (81 MHz, [D$_8$]THF): δ = 2.7.

Lithium [2-(Di-tert-butylphosphanyl)ethyl]cyclopentadienide (**8**): Procedure 1; 6.52 g (42.9 mmol) of lithium di-*tert*-butylphosphide[25] in 250 ml of THF, 3.95 g (42.9 mmol) of **5**[26]. Yield 9.62 g [39.0 mmol, 92%, purity 95% (^{1}H, ^{31}P NMR)] of **8**, colourless powder. — IR (KBr): $\tilde{\nu}$ = 3065 cm^{-1} (m, Cp), 2949 (s, CH_2, CH_3), 2898 (m, CH_2, CH_3), 2866 (m, CH_2, CH_3), 1698 (w), 1685 (w), 1617 (w), 1473 (m), 1389 (m, *t*Bu), 1365 (m, *t*Bu), 1152 (m), 1043 (w), 1023 (w), 983 (w), 933 (w), 896 (w), 818 (m), 755 (m, Cp—R), 674 (w), 640 (w). — ^{1}H NMR (200 MHz, [D$_8$]THF): δ = 1.16 (d, 18H, CH_3, $^3J_{P,H}$ = 10.5 Hz), 1.68 (m, 2H, 7-H, $^2J_{P,H}$ = 4.4, $^3J_{6,7}$ = 17.5 Hz), 2.56 (m, 2H, 6-H, $^3J_{P,H}$ = 6.0 Hz), 5.34 + 5.36 [m, 4H, 2(5)-, 3(4)-H, $\Sigma J_{2(5),3(4)}$ = 4.0 Hz). — ^{13}C NMR (50.3 MHz, [D$_8$]THF): δ = 25.3 (dt, C-6 or C-7, $^1J_{C,H}$ = 126, $J_{P,C}$ = 19.8 Hz), 30.3 (dq, CH_3, $^1J_{C,H}$ = 126, $^3J_{P,C}$ = 13.6 Hz), 31.7 (dt, C-6 or C-7, $^1J_{C,H}$ = 126, $J_{P,C}$ = 22.8 Hz), 31.8 (d, C-8, $^1J_{P,C}$ = 26.6 Hz), 102.7 (d, C-2(5), -3(4), $^1J_{C,H}$ = 158 Hz), 121.5 (d, C-1, $^3J_{P,C}$ = 15.7 Hz). — ^{31}P NMR (81 MHz, [D$_8$]THF): δ = 28.1.

Lithium [3-(Diphenylphosphanyl)propyl]cyclopentadienide[11] (**10**): A solution of 22.64 g (257 mmol) of sodium cyclopentadienide in 100 ml of THF is added to a solution of 7.43 g (28.3 mmol) of (3-chloropropyl)diphenylphosphane[10]. After refluxing for 14 h the solvent is evaporated into a cold trap. The residue is taken up in diethyl ether and hydrolysed with argon-saturated water. The organic layer is washed three times with 50 ml of water each, and the aqueous layer is washed with 100 ml of diethyl ether. The collected organic layers are dried with $MgSO_4$, and the diethyl ether is evaporated into a cold trap. The residue is taken up in pentane, and at 0°C 18.3 ml of a 1.6 M solution of *n*-butyllithium in hexane is added. The precipitated product is collected by filtration through a P4 frit, washed three times with 50 ml of pentane and dried at 0.001 mbar. Yield 4.48 g [15.1 mmol, 51%, purity 95% (^{1}H, ^{31}P NMR)] of **10**, beige powder. — IR (KBr): $\tilde{\nu}$ = 3677 cm^{-1} (m), 3069 (m, Cp, Ph), 2929 (m, CH_2), 2890 (m, CH_2), 2858 (w, CH_2), 2840 (w, CH_2), 1951 (w), 1882 (w), 1810 (w), 1585 (w, Ph), 1571 (w), 1480 (m, Ph), 1454 (w), 1433 (m, P—Ph), 1373 (w), 1328 (w), 1304 (w), 1272 (w), 1181 (w), 1157 (w), 1121 (w), 1096 (w), 1069 (w), 1026 (m, Cp—R), 998 (w), 949 (w), 898 (w), 824 (m, Cp—R), 809 (m, Cp—R), 738 (s, Ph), 695 (s, Ph). — ^{1}H NMR (200 MHz, [D$_8$]THF): δ = 1.69 (m, 2H, 7-H), 2.12 (m, 2H, 8-H), 2.57 (m, 2H, 6-H, $^3J_{6,7}$ = 7.7 Hz), 5.41 [AA'BB' line system, 4H, 2(5)-, 3(4)-H, $\Sigma J_{2(5),3(4)}$ = 4.6 Hz], 7.24 (m, 6H, *m*-, *p*-H), 7.37 (m, 4H, *o*-H). — ^{13}C NMR (50.3 MHz, [D$_8$]THF): δ = 28.9 (dt, C-6 or C-7, $J_{P,C}$ = 15.7 Hz), 29.7 (dt, C-6 or C-7, $J_{P,C}$ = 11.7 Hz), 32.8 (dt, C-8, $^1J_{C,H}$ = 123, $J_{P,C}$ = 13.4 Hz), 102.5 [d, C-2(5) or C-3(4), $^1J_{C,H}$ = 159 Hz], 103.2 [d, C-2(5) or C-3(4), $^1J_{C,H}$ = 158 Hz], 119.4 (s, C-1), 128.8 (d, C-11 or C-12, $^1J_{C,H}$ = 160 Hz), 128.9

(dd, C-11 or C-12, $^1J_{C,H} = 160$, $J_{P,C} = 6.1$ Hz), 133.4 (dd, C-10, $^1J_{C,H} = 160$, $^2J_{P,C} = 18.4$ Hz), 140.8 (d, C-9, $^1J_{P,C} = 14.9$ Hz). – ^{31}P NMR (81 MHz, [D$_8$]THF): δ = –15.2.

Lithium [3-(Diisopropylphosphanyl)propyl]cyclopentadienide (**11**): A solution of 13.2 g (150 mmol) of sodium cyclopentadienide in 250 ml of THF is added to a solution of 2.2 g (11.5 mmol) of (3-chloropropyl)diisopropylphosphane[10] in 250 ml of THF. After stirring for 3 h at 25°C the mixture is refluxed for another 3 h. The THF is evaporated into a cold trap at –25°C/0.001 mbar, the residue is taken up in 300 ml of diethyl ether. The solution is washed three times with 150 ml of argon-saturated water, then the organic layer is dried with $MgSO_4$. After filtration through a P3 frit the solvent is evaporated into a cold trap at –25°C/0.001 mbar, and the residue is taken up in pentane, and 7.2 ml of a 1.6 M solution of *n*-butyllithium in hexane is added. After 30 min the precipitated lithium salt is isolated by filtration through a P4 frit, washed three times with 50 ml of pentane, and dried at 25°C/0.001 mbar. Yield 1.7 g [7.4 mmol, 65%, purity 89% (^{1}H, ^{31}P NMR)] of **11**, ochre powder. – IR (KBr): $\tilde{\nu}$ = 3678 cm^{-1} (w), 3067 (w, Cp), 2948 (m, CH_2, CH_3), 2931 (m, CH_2, CH_3), 2872 (w, CH_2, CH_3), 1697 (w), 1614 (w), 1460 (m), 1413 (w), 1382 (m, *i*Pr), 1364 (m, *i*Pr), 1231 (w), 1040, 1027 (m, Cp–R), 821 (w), 751 (m, Cp–R), 676 (m), 600 (m). – ^{1}H NMR (200 MHz, [D$_8$]THF): 1.06 (dd, 6H, 10-H, $^3J_{9,10} = 6.9$, $^3J_{P,H} = 10.7$ Hz), 1.08 (dd, 6H, 11-H, $^3J_{9,11} = 7.1$, $^3J_{P,H} = 13.2$ Hz), 1.40 (m, 2H, 8-H, $^2J_{P,H} = 2.1$, $^3J_{7,8} = 8.0$ Hz), 1.67 (m, 2H, 7-H, $^3J_{6,7} = 7.7$ Hz), 1.69 (m, 2H, 9-H, $^1J_{P,H} = 2.5$ Hz), 2.45 (t, 2H, 6-H), 5.30 + 5.32 [AA′BB′ line system, 4H, 2(5)-, 3(4)-H, $\Sigma J_{2(5),3(4)} = 4.2$ Hz]. – ^{13}C NMR (50.3 MHz, [D$_8$]THF): δ = 19.4 (dq, C-10 or C-11, $^2J_{P,C} = 10.4$ Hz), 20.7 (dq, C-10 or C-11, $^2J_{P,C} = 16.5$ Hz), 23.2 (dt, C-6 or C-7, $J_{P,C} = 18.5$ Hz), 24.3 (dd, C-9, $^1J_{P,C} = 14.9$ Hz), 31.6 (dt, C-6 or C-7, $J_{P,C} = 17.4$ Hz), 33.2 (dt, C-8, $^1J_{P,C} = 10.5$ Hz), 102.4 [d, C-2(5) or C-3(4)], 103.0 [d, C-2(5) or C-3(4)], 119.9 (s, C-1). – ^{31}P NMR (81 MHz, [D$_8$]THF): δ = 3.8.

Preparation of Bis{[ω-(phosphanyl)alkyl]cyclopentadienyl}iron(II) Derivatives

Procedure 2: A suspension of $FeCl_2 \cdot 2$ THF in THF is added to a solution of the lithium salt of the ligand in THF. The yellow solution becomes dark brown, and the mixture is refluxed for 14 h. After evaporation of the THF into a cold trap the residue is taken up in diethyl ether and the mixture then filtered through a P4 frit covered with a 2.5 cm high layer of alumina. Finally, the solvent is condensed into a cold trap and the residue dried at 0.001 mbar for 4 h. If necessary, the product is purified by column chromatography.

Bis{[1-(diphenylphosphino)-1-methylethyl]-η^5-cyclopentadienyl}iron(II) (**12**): 20.0 ml of a 1.5 M solution of *n*-butyllithium in hexane is slowly added to a cold stirred solution (0°C) of 5.6 g (30.0 mmol) of diphenylphosphane in 250 ml of THF. The orange-red solution is stirred for 1 h at 20°C. 3.2 ml (30.0 mmol) of 6,6-dimethylfulvene[24] is added at 20°C, and the mixture is refluxed for 48 h, the colour of the mixture becoming brown. The THF is evaporated into a cold trap, and the black-brown residue is taken up in diethyl ether. The ethereal solution is filtered through a P4 frit. Then a suspension of 4.1 g (15.1 mmol) of $FeCl_2 \cdot 2$ THF in 100 ml of THF is added. The mixture is stirred for 16 h at 20°C. After evaporation of the solvent into a cold trap the residue is taken up in 250 ml of diethyl ether. The ethereal suspension is filtered through a P4 frit covered with a 3 cm high layer of alumina. The alumina is eluted with diethyl ether until the eluted solution remains colourless. The solvent is evaporated from the deep red filtrate into a cold trap, and the residue is chromatographed on silica gel [column 15 × 2 cm, pentane/diethyl ether (10:1)]. Yield 2.48 g [3.9 mmol, 26%, purity 95% (^{1}H, ^{31}P NMR)] of **12**, brown-yellow crystals, m.p. 129°C. – IR (KBr): $\tilde{\nu}$ = 3105 cm^{-1} (w), 3074 (w, Cp, Ph), 3052 (w, Cp, Ph), 2958 (w, Cp, Ph), 2922 (w, CH_2, CH_3), 2862 (w, CH_2, CH_3), 1585 (w), 1568 (w, Ph), 1479 (m, Ph), 1460 (w), 1432 (m, Ph), 1387 (w), 1373 [w, $C(CH_3)_2$], 1357 [w, $C(CH_3)_2$], 1324 (w), 1306 (w), 1270 (w), 1249 (w), 1181 (w), 1157 (w), 1141 (w), 1114 (w), 1094 (w), 1068 (w), 1029 (w), 998 (w), 919 (w), 871 (w), 840 (w), 816 (m, Cp–R), 740 (s, Ph), 696 (s, Ph), 631 (w), 553 (w), 515 (m). – ^{1}H NMR (200 MHz, [D$_8$]THF): δ = 1.43 (d, 12H, 7(8)-H, $^3J_{P,H} = 13.8$ Hz), 3.66 + 3.98 [AA′BB′ line system, 8H, 2(5)-, 3(4)-H, $\Sigma J_{2(5),3(4)} = 3.6$ Hz], 7.18 (m, 12H, *m*-, *p*-H), 7.29 (m, 8H, *o*-H). – ^{13}C NMR (50.3 MHz, [D$_8$]THF): δ = 26.9 [dq, C-7(8), $^2J_{P,C} = 19.3$ Hz], 35.5 (d, C-6, $^1J_{P,C} = 20.2$ Hz), 67.5 [d, C-2(5) or C-3(4)], 67.6 [d, C-2(5) or C-3(4)], 97.7 (d, C-1, $^2J_{P,C} = 6.2$ Hz), 127.5 (d, C-11 or C-12, $J_{P,C} = 7.6$ Hz), 128.6 (d, C-11 or C-12), 135.3 (dd, C-10, $^2J_{P,C} = 21.4$ Hz), 136.4 (d, C-9, $^1J_{P,C} = 22.5$ Hz). – ^{31}P NMR (81 MHz, [D$_8$]toluene): δ = 26.8. – MS (70 eV), *m/z* (%): 638 (5) [M$^+$], 469 (15), 347 (34) [$C_{20}H_{20}PFe^+$], 268 (100) [$C_{20}H_{20}P^+$], 183 (20), 160 (15), 121 (18), 56 (11) [Fe$^+$].

Bis{[2-(diphenylphosphanyl)ethyl]-η^5-cyclopentadenyl}iron(II) (**13**): Procedure 2; 1.0 g (3.5 mmol) of **6**[9], 0.408 g (1.7 mmol) of $FeCl_2 \cdot 1.5$ THF in 200 ml of THF. Reaction time 35 h. Yield 0.775 g (1.3 mmol, 73%) of **13**, yellow crystals from pentane, m.p. 105°C. – UV (THF): λ_{max} (lg ε) = 438 nm (2.15). – IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1} (m), 2943 (w, Cp, Ph), 2927 (w, Cp, Ph), 2910 (w, CH_2), 1583 (w, Ph), 1480 (m, Ph), 1435 (s, P–Ph), 1178 (m), 1096 (m), 1070 (m), 1037 (m, Cp–R), 1026 (m), 1019 (m), 923 (w), 825 (m, Cp–R), 751 (m), 728 (m), 693 (s, Ph). – ^{1}H NMR (200 MHz, [D$_6$]benzene): δ = 2.25 (m, 4H, 7-H), 2.48 (m, 4H, 6-H), 3.84 [s, 8H, 2(5)-, 3(4)-H], 7.1 (m, 12H, *m*-, *p*-H), 7.47 (m, 8H, *o*-H). – ^{13}C NMR (75 MHz, [D$_8$]THF): δ = 26.7 (dt, C-6 or C-7, $^1J_{C,H} = 130$, $J_{P,C} = 19.5$ Hz), 30.3 (dt, C-6 or C-7, $^1J_{C,H} = 131$, $J_{P,C} = 13.4$ Hz), 68.5 [d, C-3(4), $^1J_{C,H} = 173$ Hz], 69.1 [d, C-2(5), $^1J_{C,H} = 173$ Hz], 90.3 (d, C-1, $^3J_{P,C} = 15.2$ Hz), 129.10 (dd, C-10, $^1J_{C,H} = 159$, $^3J_{P,C} = 5.9$ Hz), 129.14 (d, C-11, $^1J_{C,H} = 159$ Hz), 133.5 (dd, C-9, $^1J_{C,H} = 158$, $^2J_{P,C} = 18.8$ Hz), 140.2 (d, C-8, $^1J_{P,C} = 14.9$ Hz). – ^{31}P NMR (81 MHz, [D$_8$]THF): δ = 14.8. – MS (70 eV), *m/z* (%): 610 (28) [M$^+$], 518 (17), 425 (15), 333 (100) [$C_{19}H_{18}PFe^+$], 277 (15) [$C_{19}H_{18}P^+$]. – $C_{38}H_{36}FeP_2$ (610.5): calcd. C 74.76, H 5.94, Fe 9.15, P 10.15; found C 74.61, H 6.03, Fe 9.22, P 10.06.

Bis{[2-(di-tert-butylphosphanyl)ethyl]-η^5-cyclopentadienyl}iron(II) (**14**): Procedure 2; 1.46 g (6.0 mmol) of **8** in 100 ml of THF, 0.89 g (3.3 mmol) of $FeCl_2 \cdot 2$ THF. Yield 1.2 g (2.3 mmol, 75%) of **14**, yellow crystals from pentane, m.p. 64°C. – IR (KBr): $\tilde{\nu}$ = 3099 cm^{-1} (w, Cp), 3089 (w, Cp), 3076 (w, Cp), 2952 (s, CH_2, CH_3), 2941 (s, CH_2, CH_3), 2860 (s, CH_2, CH_3), 1468 (s), 1441 (m), 1386 (s, *t*Bu), 1364 (s, *t*Bu), 1311 (m), 1182 (m, *t*Bu), 1127 (w), 1048 (m, Cp–R), 1020 (m), 925 (m), 812 (s, Cp–R), 708 (m), 659 (m). – ^{1}H NMR (200 MHz, [D$_8$]THF): δ = 1.13 (d, 36H, CH_3, $^3J_{P,H} = 10.5$ Hz), 1.59 (m, 4H, 7-H, $^2J_{P,H} = 5.0$ Hz), 2.51 (m, 4H, 6-H, $^3J_{P,H} = 8.7$ Hz), 3.96 + 4.01 [AA′BB′ line system, 2(5)-, 3(4)-H, $\Sigma J_{2(5),3(4)} = 3.6$ Hz]. – ^{13}C NMR (75 MHz, [D$_8$]THF): δ = 24.3 (dt, C-6 or C-7, $^1J_{C,H} = 127$, $J_{P,C} = 23.6$ Hz), 30.1 (dq, C-9, $^1J_{C,H} = 125$, $^2J_{P,C} = 14.0$ Hz), 31.5 (dt, C-6 or C-7, $^1J_{C,H} = 128$, $J_{P,C} = 29.9$ Hz), 31.8 (d, C-8, $^1J_{P,C} = 23.2$ Hz), 68.4 [d, C-3(4), $^1J_{C,H} = 173$ Hz], 69.1 [d, C-2(5), $^1J_{C,H} = 173$ Hz], 91.2 (d, C-1, $^3J_{P,C} = 15.9$ Hz). – ^{31}P NMR (81 MHz, [D$_8$]THF): δ = 30.4. – MS (70 eV), *m/z* (%): 530 (28) [M$^+$], 385 (30), 293 (25) [$C_{15}H_{26}PFe^+$], 237 (100) [$C_{15}H_{26}P^+$], 57 (22) [$C_4H_9^+$]. – $C_{30}H_{52}FeP_2$ (530.5): calcd. C 67.92, H 9.88, Fe 10.53, P 11.68; found C 67.84, H 9.95, Fe 10.59, P 11.56.

Bis{[3-(diphenylphosphanyl)propyl]-η^5-cyclopentadienyl}iron(II) (**15**): Procedure 2; 4.48 g (15.0 mmol) of **10** in 200 ml of THF,

2.44 g (9.0 mmol) of $FeCl_2 \cdot 2$ THF in 100 ml of THF. Yield 1.07 g (1.7 mmol, 23%) of **15**, yellow-brown crystals from pentane, m.p. 104°C. – IR (KBr): $\tilde{\nu} = 3063$ cm^{-1} (m, Cp, Ph), 2923 (m, CH_2), 2858 (w, CH_2), 1585 (w), 1484 (m, Ph), 1431 (s, P–Ph), 1301 (w), 1283 (w), 1098 (w), 1066 (w), 1049 (w), 1021 (m, Cp–R), 992 (m), 921 (m), 851 (m), 818 (m, Cp–R), 747 (m), 739 (m), 727 (m, Ph), 693 (s, Ph). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.62 (m, 4H, 7-H), 2.05 (t, 4H, 8-H, $^3J_{7,8} = 7.2$ Hz), 2.38 (t, 4H, 6-H, $^3J_{6,7} = 7.8$ Hz), 3.85 + 3.87 [AA′BB′ line system, 8H, 2(5)-, 3(4)-H], 7.30 (m, 12H, *m*-, *p*-H), 7.38 (m, 8H, *o*-H). – ^{13}C NMR (50.3 MHz, [D$_8$]THF): δ = 28.4 (dt, C-6 or C-7 or C-8, $^1J_{C,H} = 128$, $J_{P,C} = 16.6$ Hz), 28.7 (dt, C-6 or C-7 or C-8, $^1J_{C,H} = 127$, $J_{P,C} = 12.5$ Hz), 31.5 (dt, C-6 or C-7 or C-8, $^1J_{C,H} = 127$, $^1J_{P,C} = 13.1$ Hz), 68.4 [d, C-3(4), $^1J_{C,H} = 174$ Hz], 69.3 [d, C-2(5), $^1J_{C,H} = 172$ Hz], 89.3 (s, C-1), 129.04 (dd, C-11, $J_{C,H} = 160$, $^3J_{P,C} = 6.5$ Hz), 129.06 (d, C-12, $^1J_{C,H} = 160$ Hz), 133.5 (dd, C-10, $^1J_{C,H} = 157$, $^2J_{P,C} = 18.8$ Hz), 140.3 (d, C-9, $^1J_{P,C} = 14.9$ Hz). – ^{31}P NMR (81 MHz, [D$_8$]THF): δ = –16.0. – MS (70 eV), *m/z* (%): 638 (52) [M$^+$], 347 (63) [$C_{20}H_{20}PFe^+$], 291 (100) [$C_{20}H_{20}P^+$], 161 (27), 56 (4) [Fe^+]. – $C_{40}H_{40}FeP_2$ (638.6): calcd. C 75.24, H 6.31, Fe 8.75, P 9.70; found C 75.36, H 6.54, Fe 8.26, P 9.28; Mol. mass calcd. 638.19547; found 638.19028 (HRMS).

Treatment of **13** *with* $Fe_2(CO)_9$: 150 ml of THF is filled into a three-necked round-bottom flask equipped with a reflux condenser, two 50-ml dropping funnels, and an argon bubbler on top of the reflux condenser. One dropping funnel is filled with a solution of 744 mg (1.2 mmol) of **13** in 50 ml of THF, the other with a solution of 399 mg (1.1 mmol) of $Fe_2(CO)_9$ in 50 ml of THF. Both solutions are added into the reaction flask simultaneously over 3 h at 20°C with magnetic stirring. The complex reaction mixture is stirred for 121 h at 20°C and then refluxed for another 4 h. After cooling to 20°C the THF is evaporated into a cold trap, and the residue is taken up in 200 ml of diethyl ether. The mixture is filtered through a P4 frit covered with a 2.5 cm thick layer of Celite. Finally the diethyl ether is evaporated into a cold trap. The residue is taken up in 20 ml of diethyl ether and stored at –78°C for 8 h. After removal of the solvent 534 mg of a mixture of **13** and **16** (ca. 80:20, ^{1}H, ^{31}P NMR) is obtained. – IR (mixture **13**/**16**, KBr): $\tilde{\nu} = 1883$ (s, CO), 1872 cm^{-1} (s, CO). – MS (**16**, 70 eV), *m/z* (%): 750 (4) [M$^+$], 666 (46) [M$^+$ – 3 CO], 610 (37) [M$^+$ – $Fe(CO)_3$], 518 (17), 425 (17), 333 (100) [$C_{19}H_{18}PFe^+$], 277 (15) [$C_{19}H_{18}P^+$].

Preparation of Bis[ω-(phosphanyl)alkyl]cyclopentadienyl]dichlorozirconium(IV) Derivatives

Procedure 3: A suspension of $ZrCl_4 \cdot 2$ THF in toluene is added to a suspension of the [ω-(phosphanyl)alkyl]cyclopentadienide in toluene, the mixture becoming orange. After stirring for 4 h at 20°C the mixture is stirred for further 4 h at 80°C, then filtered through a P4 frit covered with a 2.5 cm thick layer of Celite. The solvent is evaporated into a cold trap, and the residue is washed three times with hexane and then dried at 20°C/0.001 mbar for 8 h.

Dichlorobis{[2-(diphenylphosphanyl)ethyl]-η^5-cyclopentadienyl}zirconium(IV) (**17**): Procedure 3; 2.07 g (7.3 mmol) of **6** in 15 ml of toluene, 1.32 g (3.5 mmol) of $ZrCl_4 \cdot 2$ THF in 15 ml of toluene. Yield 2.02 g [2.8 mmol, 81%, purity 95% (^{1}H, ^{31}P NMR)] of **17**, yellow oil. – IR (KBr): $\tilde{\nu} = 3110$ cm^{-1} (m), 3066 (w, Cp, Ph), 2948 (w, CH_2), 2927 (w, CH_2), 2899 (w, CH_2), 1584 (w), 1494 (w), 1480 (w, Ph), 1448 (w), 1432 (m, P–Ph), 1097 (w), 1050 (w), 1039 (m), 1025 (w), 999 (w), 931 (w), 887 (w), 832 (s, Cp–R), 751 (s), 741 (m), 729 (s), 697 (s, Ph). – ^{1}H NMR (200 MHz, [D$_8$]THF): δ = 2.34 (m, 4H, 7-H, $^2J_{P,H} = 5.7$, $^3J_{6,7} = 8.2$ Hz), 2.77 (m, 4H, 6-H, $^3J_{P,H} = 8.8$ Hz), 6.22 + 6.29 [AA′BB′ line system, 8H, 2(5)-, 3(4)-H, $\Sigma J_{2(5),3(4)} = 5.4$ Hz], 7.27 (m, 12H, *m*-, *p*-H), 7.42 (m, 8H, *o*-H). – ^{13}C NMR (50.3 MHz, [D$_8$]THF): δ = 27.4 (dt, C-6 or C-7, $J_{P,C} = 19.7$ Hz), 29.3 (dt, C-6 or C-7, $J_{P,C} = 13.6$ Hz), 113.2 [d, C-2(5) or C-3(4)], 117.1 [d, C-2(5) or C-3(4)], 129.1 (d, C-10 or C-11), 129.2 (d, C-10 or C-11), 133.5 (dd, C-9, $^2J_{P,C} = 18.6$ Hz), 135.3 (d, C-1, $^3J_{P,C} = 14.5$ Hz), 139.6 (dd, C-8, $^1J_{P,C} = 14.4$ Hz). – ^{31}P NMR (81 MHz, [D$_8$]THF): δ = 17.1. – MS (70 eV), *m/z* (%): 531 (4), 439 (34) [M$^+$ – $C_{19}H_{18}P$], 277 (100) [$C_{19}H_{18}P^+$], 250 (12), 199 (10), 183 (22), 211 (23), 36 (14).

Dichlorobis{[2-(di-tert-butylphosphanyl)ethyl]-η^5-cyclopentadienyl}zirconium(IV) (**18**): Procedure 3; 2.71 g (11.1 mmol) of **8** in 24 ml of toluene, 2.09 g (5.6 mmol) of $ZrCl_4 \cdot 2$ THF in 24 ml of toluene. Yield 3.25 g (5.1 mmol, 92%) of **18**, yellow solid, m.p. 115°C. – CV [THF, 0.1 M N(*n*Bu)$_4$ClO$_4$, 20°C, 100 mV/s, vs. SCE]: –0.27 V (ox.), –1.68 (ox.), –1.95 (red.), –2.54 (red.). – IR (KBr): $\tilde{\nu} = 3101$ cm^{-1} (m, Cp), 2939 (s, CH_2, CH_3), 2894 (s, CH_2, CH_3), 2860 (s, CH_2, CH_3), 1490 (m), 1466 (s), 1447 (s), 1425 (m), 1384 (s, *t*Bu), 1361 (s, *t*Bu), 1175 (m), 1107 (w), 1502 (m), 1040 (m), 1018 (m), 934 (w), 877 (w), 827 (s, Cp–R), 809 (s), 768 (m), 725 (m), 663 (w), 592 (w), 441 (w). – ^{1}H NMR (200 MHz, [D$_8$]THF): δ = 1.10 (d, 36H, CH_3, $^3J_{P,H} = 10.7$ Hz), 1.67 (m, 4H, 7-H, $^2J_{P,H} = 5.2$, $^3J_{6,7} = 7.9$ Hz), 2.82 (m, 4H, 6-H, $^3J_{P,H} = 8.4$ Hz), 6.27 + 6.37 [AA′BB′ line system, 8H, 2(5)-, 3(4)-H, $\Sigma J_{2(5),3(4)} = 5.4$ Hz]. – ^{13}C NMR (50.3 MHz, [D$_8$]THF): δ = 22.9 (dt, C-6 or C-7, $J_{P,C} = 23.6$ Hz), 30.2 (dq, C-9, $^2J_{P,C} = 14.5$ Hz), 31.8 (dt, C-6 or C-7, $J_{P,C} = 30.9$ Hz), 31.9 (d, C-8, $^1J_{P,C} = 22.6$ Hz), 112.9 [d, C-2(5) or C-3(4)], 117.5 [d, C-2(5) or C-3(4)], 136.0 (d, C-1, $^3J_{P,C} = 15.7$ Hz). – ^{31}P NMR (81 MHz, [D$_8$]-THF): δ = 29.5. – MS (70 eV), *m/z* (%): 397 (2) [M$^+$ – $C_{15}H_{26}P$], 341 (3) [M$^+$ – $C_{15}H_{26}P$ – C_4H_8], 285 (3) [M$^+$ – $C_{15}H_{26}P$ – 2 (C_4H_8)], 237 (100) [$C_{15}H_{26}P^+$], 57 (47) [$C_4H_9^+$]. – $C_{30}H_{52}Cl_2P_2Zr$ (636.8): calcd. C 56.58, H 8.23, Cl 11.13, P 9.73, Zr 14.32; found C 56.67, H 8.30, Cl 11.08, P 9.84, Zr 14.19.

Dichlorobis{[3-(diphenylphosphanyl)propyl]-η^5-cyclopentadienyl}zirconium(IV) (**19**): Procedure 3; 4.29 g (14.4 mmol) of **10** in 50 ml of toluene, 2.72 g (7.7 mmol) of $ZrCl_4 \cdot 2$ THF in 55 ml of toluene. Yield 3.76 g [5.0 mmol, 66%, purity 95% (^{1}H, ^{31}P NMR)] of **19**, bright yellow oil. – IR (KBr): $\tilde{\nu} = 3070$ cm^{-1}, 3053 (w, Cp, Ph), 2938 (m, CH_2), 2862 (w, CH_2), 1585 (w, Ph), 1482 (m, Cp), 1433 (s, P–Ph), 1096 (w), 1027 (m), 1000 (w), 827 (m, Cp–R), 743 (s, Ph), 698 (s, Ph). – ^{1}H NMR (200 MHz, [D$_8$]THF): δ = 1.70 (m, 4H, 7-H), 2.06 (m, 4H, 8-H), 2.74 (t, 4H, 6-H, $^3J_{6,7} = 7.5$ Hz), 6.10 + 6.32 [AA′BB′ line system, 8H, 2(5)-, 3(4)-H, $\Sigma J_{2(5),3(4)} = 5.4$ Hz], 7.27 (m, 12H, *m*-, *p*-H), 7.42 (m, 8H, *o*-H). – ^{13}C NMR (75.5 MHz, [D$_8$]THF): δ = 28.0 (dt, C-6 or C-7 or C-8, $^1J_{C,H} = 128$, $J_{P,C} = 17.4$ Hz), 28.5 (dt, C-6 or C-7 or C-8, $^1J_{C,H} = 128$, $J_{P,C} = 12.7$ Hz), 32.3 (dt, C-6 or C-7 or C-8, $^1J_{C,H} = 128$, $J_{P,C} = 13.4$ Hz), 113.5 [d, C-3(4), $^1J_{C,H} = 175$ Hz], 117.3 [d, C-2(5), $^1J_{C,H} = 173$ Hz], 129.06 (dd, C-11, $^1J_{C,H} = 160$, $^3J_{P,C} = 6.1$ Hz), 129.10 (d, C-12, $^1J_{C,H} = 161$ Hz), 133.5 (dd, C-10, $^1J_{C,H} = 159$, $^2J_{P,C} = 18.8$ Hz), 134.7 (s, C-1), 140.1 (d, C-9, $^1J_{P,C} = 14.8$ Hz). – ^{31}P NMR (81 MHz, [D$_8$]THF): δ = –16.0. – MS (70 eV), *m/z*: 451 (3) [M$^+$ – $C_{20}H_{20}P$], 291 (100) [$C_{20}H_{20}P^+$], 199 (22), 183 (24), 121 (5), 108 (7).

Preparation of {[ω-(Phosphanyl-P)alkyl]η^5-cyclopentadienyl}cobalt(I) Complexes

Procedure 4: Until the workup all operations are carried out in the dark. *Solution A:* A solution of the lithium [ω-(phosphanyl)alkyl]cyclopentadienide in THF is cooled to –78°C. – *Solution B*[14]: At 20°C $Co_2(CO)_8$, which has been recrystallised from pentane, is dissolved in THF and the solution is cooled to –78°C. A cold solution (–78°C) of iodine in THF is added to the $Co_2(CO)_8$ solution, and the mixture is stirred for 1 h at –78°C. – At –78°C solution B is added to solution A. The mixture is stirred for 16 h and allowed to reach 20°C. The volume is reduced to 30 ml by evaporation of the solvent into a cold trap. 200 ml of diethyl ether is added, and the mixture is filtered through a P4 frit covered with

a 2.5 cm thick layer of alumina (act. 1). The solvent is evaporated from the filtrate into a cold trap, and the residue is taken up in hexane and the solution filtered through a P4 frit. The hexane solution is successively (+5, −10, −30 °C) cooled to −78 °C. The crystallized product is isolated by decanting, washed three times with 20 ml of cold pentane (−78 °C) and finally dried at 20 °C/0.001 mbar for 4 h.

Observation of Dicarbonyl{[2-(diphenylphosphanyl)ethyl]-η⁵-cyclopentadienyl}cobalt(I) (**20**): Procedure 4; solution A: 2.93 g (12.0 mmol) of **6** in 250 ml of THF, solution B: 2.05 g (6.0 mmol) of $Co_2(CO)_8$ in 125 ml of THF, 1.66 g (6.0 mmol) of iodine in 125 ml of THF. The mixture of solutions A and B at −78 °C was allowed to reach −25 °C and stirred at this temp. for 5 d. All following operations are performed at −25 °C. An IR spectrum of the ethereal solution is recorded at −25 °C. — IR (Et_2O, −25 °C): $\tilde{\nu}$ = 1957 cm^{-1} (s, CO), 2019 (s, CO).

Carbonyl{[2-(diphenylphosphanyl-P)ethyl]-η⁵-cyclopentadienyl}cobalt(I) [4a] (**23**): Procedure 4; solution A: 9.64 g (39.5 mmol) of **6** in 200 ml of THF, solution B: 8.67 g (25.3 mmol) of $Co_2(CO)_8$ in 125 ml of THF, 6.42 g (25.3 mmol) of iodine in 250 ml of THF. Yield 3.45 g (9.5 mmol, 24%) of **23**, red crystals from pentane, m.p. 89 °C. — IR (KBr): $\tilde{\nu}$ = 3046 cm^{-1} (w, Cp, Ph), 2963 (w, CH_2), 2933 (w, CH_2), 2913 (w, CH_2), 1897 (s, C=O), 1432 (m, P–Ph), 1092 (m, Cp–R), 746 (w), 701 (m, Ph). — ^{1}H NMR (200 MHz, [D$_6$]benzene): δ = 1.64 (dt, 2H, 6-H, $^3J_{6,7}$ = 7.2, $^3J_{P,H}$ = 27.4 Hz), 2.62 (dt, 2H, 7-H, $^2J_{P,H}$ = 9.2 Hz), 4.94 + 4.98 [AA′BB′ line system, 4H, 2(5)-, 3(4)-H, $\Sigma J_{2(5),3(4)}$ = 4.4, $^3J_{P,H}$ = 0.8, $^3J_{5,P}$ = 1.4 Hz], 7.02 (m, 6H, *m*-, *p*-H), 7.76 (m, 4H, *o*-H, $^3J_{P,H}$ = 11.1 Hz). — ^{13}C NMR (75 MHz, [D$_8$]toluene): δ = 23.6 (dt, C-6, $^1J_{C,H}$ = 130, $^2J_{P,C}$ = 7.9 Hz), 47.6 (dt, C-7, $^1J_{C,H}$ = 131, $^1J_{P,C}$ = 28.7 Hz), 80.2 [d, C-2(5) or C-3(4), $^1J_{C,H}$ = 165 Hz], 82.4 [d, C-2(5) or C-3(4), $^1J_{C,H}$ = 168 Hz], 108.8 (d, C-1, $^3J_{P,C}$ = 7.2 Hz), 128.5 (dd, C-10, $^1J_{C,H}$ = 162, $^3J_{P,C}$ = 10.1 Hz), 129.8 (dd, C-11, $^1J_{C,H}$ = 160, $^4J_{P,C}$ = 2.3 Hz), 132.6 (dd, C-9, $^1J_{C,H}$ = 160, $^2J_{C,P}$ = 11.3 Hz), 137.0 (d, C-8, $^1J_{P,C}$ = 41.0 Hz), 206.6 (s, C-12). — ^{31}P NMR (32 MHz, [D$_6$]benzene): δ = 85.2. — MS (70 eV), *m/z* (%): 364 (21) [M^+], 336 (100) [M^+ − CO], 183 (15) [$C_7H_9PCo^+$], 59 (20) [Co^+]. — $C_{20}H_{18}CoOP$ (364.3): calcd. C 65.95, H 4.98, Co 16.18, P 8.50; found C 66.01, H 5.01, Co 16.04, P 8.48.

Carbonyl{[2-(diisopropylphosphanyl-P)ethyl]-η⁵-cyclopentadienyl}cobalt(I) (**24**): Procedure 4; solution A: 5.3 g (24.6 mmol) of **7** in 250 ml of THF, solution B: 5.46 g (16.0 mmol) of $Co_2(CO)_8$ in 80 ml of THF, 4.05 g (16.0 mmol) of iodine in 160 ml of THF. The residue is chromatographed on silica gel (column 18 × 2 cm, pentane/diethyl ether 10:1). Yield 3.14 g (10.6 mmol, 43%) of **24**, red crystals from pentane/diethyl ether (10:1), m.p. 83 °C. — UV (THF): λ_{max} (lg ε) = 312 nm (3.48). — IR (KBr): $\tilde{\nu}$ = 3748 cm^{-1} (m), 3106 (m), 3086 (m), 2972 (m), 2955 (m, CH_2, CH_3), 2924 (m, CH_2, CH_3), 2909 (m, CH_2, CH_3), 2865 (m, CH_2, CH_3), 1885 (s, CO), 1840 (m), 1462 (m), 1414 (w), 1378 (w, *i*Pr), 1359 (w, *i*Pr), 1240 (w), 1028 (w, Cp–R), 1021 (w), 883 (w), 828 (w), 796 (m, Cp–R), 698 (w), 672 (w), 638 (w), 631 (w), 621 (w), 564 (m), 507 (w). — ^{1}H NMR (200 MHz, [D$_8$]toluene): δ = 0.90 (dd, 6H, 9-H, $^3J_{8,9}$ = 6.9, $^3J_{P,H}$ = 14.0 Hz), 1.05 (dd, 6H, 10-H, $^3J_{8,10}$ = 7.1, $^3J_{P,H}$ = 15.9 Hz), 1.62 (dsept, 2H, 8-H, $^2J_{P,H}$ = 8.9 Hz), 1.66 (m, 2H, 7-H, $^3J_{6,7}$ = 7.6 Hz), 1.94 (m, 2H, 6-H, $^2J_{P,H}$ = 8.2 Hz), 4.85 [s, 4H, 2(5)-, 3(4)-H]. — ^{13}C NMR (50.3 MHz, [D$_8$]THF): δ = 18.4 (q, C-9 or C-10, $^1J_{C,H}$ = 126 Hz), 19.4 (dq, C-9 or C-10, $^1J_{C,H}$ = 127, $^3J_{P,C}$ = 3.2 Hz), 25.3 (dt, C-6, $^1J_{C,H}$ = 128, $^2J_{P,C}$ = 5.9 Hz), 26.9 (dd, C-8, $^1J_{C,H}$ = 127, $^1J_{P,C}$ = 24.4 Hz), 39.8 (dt, C-7, $^1J_{C,H}$ = 128, $^1J_{P,C}$ = 22.7 Hz), 79.6 [dd, C-3(4), $^1J_{C,H}$ = 174, $^2J_{P,C}$ = 3.2 Hz], 81.6 [d, C-2(5), $^1J_{C,H}$ = 175 Hz], 110.5 (d, C-1, $^2J_{P,C}$ = 7.9 Hz), 206.6 (s, C-11). — ^{31}P NMR (81 MHz, [D$_8$]toluene): δ = 113.2. — MS (70 eV), *m/z* (%): 296 (16) [M^+], 268 (18) [M^+ − CO], 226 (38) [M^+ − C_3H_6 − CO], 184 (100) [M^+ − 2 (C_3H_6) − CO], 137 (12), 59 (10) [Co^+]. — $C_{14}H_{22}CoOP$ (296.2): calcd. C 56.76, H 7.49, Co 19.89, P 10.46; found C 56.87, H 7.39, Co 19.82, P 10.37.

Carbonyl{[2-(di-tert-butylphosphanyl-P)ethyl]-η⁵-cyclopentadienyl}cobalt(I) (**25**): Procedure 4; solution A: 3.51 g (14.4 mmol) of **8** in 250 ml of THF, solution B: 3.20 g (9.4 mmol) of $Co_2(CO)_8$ in 50 ml of THF, 2.37 g (9.4 mmol) of iodine in 100 ml of THF. Yield 2.63 g (8.1 mmol, 56%) of **25**, red crystals from diethyl ether, m.p. 119 °C. — UV (cyclohexane): λ_{max} (lg ε) = 221 nm (4.15), 319 (3.44). — IR (KBr): $\tilde{\nu}$ = 3771 cm^{-1} (w), 3104 (w, Cp), 3089 (w, Cp), 3076 (w), 3023 (w), 2986 (w), 2976 (w), 2960 (m, CH_2, CH_3), 2943 (m, CH_2, CH_3), 2925 (m, CH_2, CH_3), 2898 (m, CH_2, CH_3), 2860 (m, CH_2, CH_3), 1898 (s, CO), 1473 (w), 1459 (w), 1413 (w), 1388 (w, *t*Bu), 1368 (w, *t*Bu), 1355 (w), 1303 (w), 1179 (w), 1170 (w), 1033 (w), 1020 (w, Cp–R), 819 (w), 800 (m), 675 (w), 603 (m), 578 (m), 560 (m), 503 (m), 491 (m), 466 (m). — ^{1}H NMR (200 MHz, [D$_8$]THF): δ = 1.33 (d, 18H, CH_3, $^3J_{P,H}$ = 12.7 Hz), 2.07 (dt, 2H, 6-H, $^3J_{6,7}$ = 7.4, $^3J_{P,H}$ = 20.1 Hz), 2.64 (dt, 2H, 7-H, $^2J_{P,H}$ = 8.2 Hz), 4.76 + 4.94 [AA′BB′ line system, 4H, 2(5)-, 3(4)-H, $\Sigma J_{2(5),3(4)}$ = 4.0 Hz]. — ^{13}C NMR (50.3 MHz, [D$_8$]THF): δ = 26.0 (dt, C-6, $^1J_{C,H}$ = 127, $^2J_{P,C}$ = 5.9 Hz), 29.8 (dq, CH_3, $^1J_{C,H}$ = 126, $^2J_{P,C}$ = 4.0 Hz), 36.4 [d, C-8(12), $^1J_{P,C}$ = 17.0 Hz], 40.4 (dt, C-7, $^1J_{C,H}$ = 128, $^1J_{P,C}$ = 19.8 Hz), 78.8 [dd, C-2(5) or C-3(4), $^1J_{C,H}$ = 174, $J_{P,C}$ = 3.4 Hz], 83.1 [dd, C-2(5) or C-3(4), $^1J_{C,H}$ = 175, $J_{P,C}$ = 1.7 Hz], 111.4 (d, C-1, $^3J_{P,C}$ = 7.8 Hz), 208 (s, C-16). — ^{31}P NMR (81 MHz, [D$_8$]THF): δ = 128.9. — MS (70 eV), *m/z* (%): 324 (57) [M^+], 296 (100) [M^+ − CO], 240 (72) [M^+ − C_4H_8 − CO], 184 (97) [M^+ − 2 (C_4H_8) − CO], 137 (27), 59 (18) [Co^+]. — $C_{16}H_{26}CoOP$ (324.3): calcd. C 59.26, H 8.08, Co 18.17, P 9.55; found C 59.19, H 8.10, Co 18.09, P 9.61; Mol. mass calcd. 324.1053; found 324.1064 (HRMS).

Crystal Structure Analysis of **25**[27]: See Tables 3, 4.

Table 3. Details for the crystal structure analysis of **25**

$C_{16}H_{26}CoOP$, crystal size 0.18 x 0.29 x 0.36 mm, colour dark red, a = 10.837(1), b = 12.245(1), c = 12.471(1) Å, β = 97.01(1)°, Z = 4, V = 1642.5 Å^3, d_{cal} = 1.31 gcm^{-1}, Mo–K$_\alpha$ radiation, λ = 0.71069 Å, F(000) = 688, crystal system monoclinic, space group $P2_1/n$ [14], Enraf–Nonius CAD4 diffractometer, scan mode ω–2θ, (sin θ/λ)$_{max}$ = 0.70, 5186 measured reflections (±h,+k,+l), 4781 independent reflections, 3350 observed reflections (I>2σ(I)) for 172 refined parameters, structure solved by heavy atom method, R = 0.043, R_w = 0.043 (w = 1/σ^2(Fo)), EOF = 1.71, residual electron density 0.54 eÅ^{-3}

Carbonyl{[3-(diphenylphosphanyl-P)propyl]-η⁵-cyclopentadienyl}cobalt(I) (**28**): Procedure 4; solution A: 5.00 g (16.0 mmol) of **10** in 250 ml of THF, solution B: 3.73 g (10.9 mmol) of $Co_2(CO)_8$ in 60 ml of THF, 2.64 g (10.9 mmol) of iodine in 100 ml of THF. The residue is chromatographed on silica gel (column 20 × 2 cm, pentane/diethyl ether, 10:1). Yield 2.30 g [6.1 mmol, 39%, purity 95% (^{1}H, ^{31}P NMR)] of **28**, red crystals from hexane, m.p. 72 °C. — IR (KBr): $\tilde{\nu}$ = 3782 cm^{-1} (m), 3074 (m, Cp, Ph), 3051 (w, Cp, Ph), 2936 (m, CH_2, CH_3), 2905 (w, CH_2, CH_3), 2859 (w, CH_2, CH_3), 1899 (s, CO), 1858 (m), 1472 (m), 1435 (m, P–Ph), 1400 (w), 1361 (w), 1338 (w), 1307 (w), 1280 (w), 1260 (w), 1229 (w), 1214 (w), 1181 (w), 1158 (w), 1096 (m), 1040 (w), 1027 (w), 988 (m), 933 (w), 914 (w), 893 (w), 806 (m, Cp–R), 747 (m), 702 (m), 692 (m), 644 (w), 603 (w), 589 (m), 561 (m), 523 (m), 499 (m), 485 (m), 449 (w). — ^{1}H NMR (400 MHz,

Table 4. Atomic coordinates and equivalent isotropic thermal parameters [Å^2] for **25**

$$U_{eq} = 1/3 \sum_i \sum_j U_{ij}\, a_i^* a_j^*\, \bar{a}_i \cdot \bar{a}_j$$

Atom	x	y	z	U_{eq}
Co	0.4904(1)	0.5850(1)	0.1998(1)	0.034
P	0.4936(1)	0.7455(1)	0.2702(1)	0.031
O	0.2381(2)	0.5906(2)	0.1010(2)	0.075
C1	0.6790(2)	0.5810(2)	0.2434(2)	0.044
C2	0.6219(3)	0.5075(2)	0.3109(2)	0.048
C3	0.5573(3)	0.4289(2)	0.2455(3)	0.056
C4	0.5752(3)	0.4514(2)	0.1362(2)	0.055
C5	0.6535(3)	0.5422(3)	0.1353(2)	0.052
C6	0.7433(2)	0.6861(2)	0.2807(2)	0.050
C7	0.6554(2)	0.7592(2)	0.3376(2)	0.046
C8	0.3970(2)	0.7652(2)	0.3854(2)	0.043
C9	0.4053(4)	0.6583(3)	0.4496(2)	0.070
C10	0.4421(3)	0.8583(3)	0.4625(2)	0.063
C11	0.2603(3)	0.7841(3)	0.3419(3)	0.060
C12	0.4714(3)	0.8641(2)	0.1725(2)	0.043
C13	0.5763(3)	0.8554(3)	0.1015(3)	0.066
C14	0.4807(3)	0.9768(3)	0.2265(3)	0.067
C15	0.3492(3)	0.8554(3)	0.0990(3)	0.067
C16	0.3400(2)	0.5872(2)	0.1417(2)	0.045

[D$_6$]benzene): δ = 1.20 (m, 2H, 7-H, $^3J_{6,7}$ = 11.5, $^3J_{7,8}$ = 12.1, $^3J_{P,H}$ = 24.3 Hz), 1.60 (m, 2H, 8-H, $^2J_{P,H}$ = 10.0 Hz), 1.81 (m, 2H, 6-H), 4.65 + 4.97 [AA'BB' line system, 4H, 2(5)-, 3(4)-H, $\Sigma J_{2(5),3(4)}$ = 4.2, $^3J_{P,H}$ = 2.2, $^3J_{P,H}$ = 1.3 Hz], 7.07 (m, 6H, *m*-, *p*-H), 7.70 (m, 4H, *o*-H, $^3J_{P,H}$ = 10.7 Hz). – ^{13}C NMR (75 MHz, [D$_6$]benzene): δ = 23.6 (dt, C-6 or C-7, $J_{P,C}$ = 5.1 Hz), 26.1 (dt, C-6 or C-7, $J_{P,C}$ = 3.6 Hz), 26.2 (dt, C-8, $^1J_{P,C}$ = 26.5 Hz), 80.7 [dd, C-3(4) or C-6(7), $^2J_{P,C}$ = 3.4 Hz], 83.0 [d, C-2(5)], 94.6 (d, C-1, $^2J_{P,C}$ = 2.3 Hz), 128.3 (dd, C-11, $^3J_{P,C}$ = 9.8 Hz), 129.6 (dd, C-12, $^4J_{P,C}$ = 2.3 Hz), 132.9 (dd, C-10, $^2J_{P,C}$ = 11.1 Hz), 138.5 (d, C-9, $^1J_{P,C}$ = 44.0 Hz). – ^{31}P NMR (81 MHz, [D$_6$]benzene): δ = 62.0. – MS (70 eV), *m/z* (%): 378 (24) [M$^+$], 350 (100) [M$^+$ – CO], 242 (11), 183 (17) [$C_7H_9PCo^+$], 138 (5), 107 (4), 59 (11) [Co$^+$]. – $C_{21}H_{20}CoOP$: calcd. 378.05838; found 378.05184 (HRMS).

Carbonyl{[3-(diisopropylphosphanyl-P)propyl]-η^5-cyclopentadienyl}cobalt(I) (**29**): Procedure 4; solution A: 1.30 g (5.8 mmol) of **11** in 200 ml of THF, solution B: 1.29 g (3.8 mmol) of $Co_2(CO)_8$ in 40 ml of THF, 0.96 g of iodine in 60 ml of THF. Yield 0.523 g [1.7 mmol, 27%, purity 95% (^{1}H, ^{31}P NMR)] of **29**, red crystals from hexane, m.p. 68°C. – IR (Film): $\tilde{\nu}$ = 3093 cm^{-1} (w, Cp, Ph), 2956 (s, CH_2, CH_3), 2936 (s, CH_2, CH_3), 2905 (s, CH_2, CH_3), 2869 (s, CH_2, CH_3), 1964 (m), 1914 (s, CO), 1863 (m), 1567 (w), 1461 (s), 1407 (w), 1382 (m, *i*Pr), 1362 (m, *i*Pr), 1340 (w), 1331 (w), 1295 (w), 1283 (w), 1239 (m), 1171 (m), 1159 (w), 1109 (w), 1099 (w), 1078 (w), 1028 (s), 988 (w), 935 (w), 883 (s), 798 (s, Cp–R), 691 (s), 651 (s), 625 (s), 604 (w), 591 (w), 558 (s), 504 (s). – ^{1}H NMR (200 MHz, [D$_8$]THF): δ = 1.28 (dd, 12H, 10-, 11-H, $^3J_{9,10}$ = $^3J_{9,11}$ = 7.1, $^3J_{P,H}$ = 14.8 Hz), 1.92 (m, 4H, 9-, 7-H or 8-H), 2.24 (m, 2H, 7-H or 8-H), 2.43 (m, 2H, 6-H), 4.98 + 5.14 [AA'BB' line system, 2(5)-, 3(4)-H, $\Sigma J_{2(5),3(4)}$ = 4.2 Hz]. – ^{31}P NMR (81 MHz, [D$_8$]THF): δ = 78.6. – MS (70 eV), *m/z* (%): 310 (44) [M$^+$], 282 (62) [M$^+$ – CO], 240 (98) [M$^+$ – C_3H_6 – CO], 198 (100) [M$^+$ – 2 (C_3H_6) – CO], 164 (17), 137 (19), 59 (14) [Co$^+$].

Treatment of **25** *with Lithium Sand:* In a 20-ml Schlenk flask equipped with a magnetic stirring bar 50 mg (7.2 mmol) of lithium sand is activated at the surface by intensive stirring. A cold solution (–78°C) of 200 mg (0.6 mmol) of **25** in 4 ml of [D$_8$]THF is added, and the mixture is stirred for 16 h at –78°C, the colour changing to brown-black. Excess lithium sand is removed by filtration through a P4 frit at –78°C. ^{1}H-, ^{13}C-, ^{31}P-NMR measurements at –80, –60, –40, –10, 0, 10, 20, and 30°C indicate the ligand anion **8**.

Treatment of **23** *with Diphenylethyne under Photochemical Conditions:* In a 150-ml immersion photochemical reactor (Duran glass, high-pressure mercury lamp Philips HPK 125 W) a solution of 400 mg (1.1 mmol) of **23** and 586 mg (3.3 mmol) of diphenylethyne in 150 ml of toluene is irradiated for 50 h. The solvent is evaporated into a cold trap, and excess diphenylethyne is removed by sublimation at 0.001 mbar/25°C. The residue is dissolved in diethyl ether, the solution filtered through a P4 frit and the filtrate cooled to –78°C. Yield 50 mg [0.1 mmol, 9%, purity 95% (^{1}H, ^{31}P NMR)] of *(η^2-diphenylethyne){[2-(diphenylphosphanyl-P)ethyl]-η^5-cyclopentadienyl}cobalt(I)* (**30**), black crystals, m.p. 127°C. – IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1} (m, Cp, Ph), 3058 (m, Cp, Ph), 3020 (w), 2940 (w, CH_2), 2905 (w, CH_2), 2850 (w, CH_2), 1818 (s, coord. C≡C), 1587 (m), 1480 (m), 1433 (m, P–Ph), 1370 (w), 1305 (w), 1155 (w), 1095 (m), 1065 (w), 998 (w), 838 (m), 802 (m, Cp–R), 741 (m), 690 (s, Ph), 637 (m), 580 (m), 552 (w), 520 (s). – ^{1}H NMR (400 MHz, [D$_8$]toluene): δ = 1.85 (dt, 2H, 6-H, $^3J_{6,7}$ = 7.1, $^3J_{P,H}$ = 25.6 Hz), 2.68 (m, 2H, 7-H, $^1J_{P,H}$ = 8.8 Hz), 4.18 [m, 2H, 2(5)-H or 3(4)-H, $\Sigma J_{2(5),3(4)}$ = 4.2, $J_{P,H}$ = 2.9 Hz], 5.66 [m, 2H, 2(5)-H or 3(4)-H], 6.85 [m, 6H, 10(11)-H], 6.96 (m, 2H, 16-H), 7.11 (m, 2H, 15-H), 7.29 (m, 4H, 9-H), 7.83 (m, 2H, 14-H). – ^{13}C NMR (50.3 MHz, [D$_8$]THF): δ = 23.6 (dt, C-6, $^2J_{P,C}$ = 7.8 Hz), 45.9 (dt, C-7, $^1J_{P,C}$ = 28.8 Hz), 79.3 [d, C-2(5) or C-3(4)], 81.3 [dd, C-2(5) or C-3(4), $J_{P,C}$ = 9.6 Hz], 90.4 (d, C-12, $J_{P,C}$ = 10.5 Hz), 110.6 (d, C-1, $^3J_{P,C}$ = 7.0 Hz), 125.3 (d, C-16), 128.1 (d, C-15), 128.2 (dd, C-10, $^3J_{P,C}$ = 8.7 Hz), 129.6 (dd, C-11, $J_{P,C}$ = 2.6 Hz), 131.4 (d, C-14), 133.1 (dd, C-9, $^2J_{P,C}$ = 9.6 Hz), 135.2 (d, C-13, $J_{P,C}$ = 1.8 Hz), 136.0 (d, C-8, $^1J_{P,C}$ = 32.3 Hz). – ^{31}P NMR (81 MHz, [D$_8$]toluene): δ = 69.5. – MS (70 eV), *m/z* (%): 514 (10) [M$^+$], 336 (62) [M$^+$ – C_2Ph_2], 278 (7), 183 (8), 178 (100) [$C_2Ph_3^+$], 152 (11), 89 (9), 76 (8), 59 (3) [Co$^+$]. – $C_{33}H_{28}CoP$ (514.1): calcd. 514.12606; found 514.12554 (HRMS).

Treatment of **25** *with Diphenylethyne under Photochemical Conditions:* In a 150-ml immersion photochemical reactor (Duran glass, high-pressure mercury lamp Philips HPK 125 W) a solution of 212 mg (0.70 mmol) of **25** and 460 mg (2.6 mmol) of diphenylethyne in 150 ml of toluene is irradiated for 91 h. The solvent is evaporated into a cold trap, and excess diphenylethyne is removed by sublimation at 0.001 mbar/25°C. The residue is dissolved in 200 ml of diethyl ether, the solution filtered through a P4 frit and the filtrate cooled to –78°C for 5 d. Yield 120 mg (0.3 mmol, 39%) of *{[2-(di-tert-butylphosphanyl-P)ethyl]-η^5-cyclopentadienyl}(η^2-diphenylethyne)cobalt(I)* (**31**), black crystals, m.p. 218°C (DSC). – IR (KBr): $\tilde{\nu}$ = 3082 cm^{-1}, 3070 (w, Cp, Ph), 3018 (w), 3001 (w), 2986 (w, CH_2, CH_3), 2891 (w, CH_2, CH_3), 2858 (w, CH_2, CH_3), 1795 (m, coord. C≡C), 1586 (m), 1563 (w), 1479 (m), 1437 (w), 1387 (w), 1367 (w, *t*Bu), 1356 (w, *t*Bu), 1310 (w), 1271 (w), 1255 (w), 1174 (w), 1151 (w), 1106 (w), 1069 (w), 1040 (w), 1021 (m), 903 (w), 820 (w), 809 (w), 793 (m, Cp–R), 753 (m), 739 (w), 692 (m, Ph), 675 (w), 623 (w), 573 (w), 509 (w). – ^{1}H NMR (200 MHz, [D$_8$]toluene): δ = 0.98 (d, 18H, CH_3, $^3J_{P,H}$ = 11.8 Hz), 1.80 (m, 4H, 6-, 7-H), 4.10 [m, 2H, 2(5)-H or 3(4)-H, $\Sigma J_{2(5),3(4)}$ = 4.1, $J_{P,H}$ = 2.8 Hz], 5.58 [m, 2H, 2(5)-H or 3(4)-H], 7.10 (m, 2H, *p*-H), 7.31 (m, 4H, *m*-H), 8.14 (m, 4H, *o*-H). – ^{13}C NMR (50.3 MHz, [D$_8$]THF): δ = 25.9 (dt, C-6, $^2J_{P,C}$ = 7.0 Hz), 30.0 (dq, C-9, $^2J_{P,C}$ = 3.7 Hz), 35.5 (d, C-8, $^1J_{P,C}$ = 7.3 Hz), 38.6 (dt, C-7, $^1J_{P,C}$ = 19.8 Hz), 79.3 [dd, C-2(5) or C-3(4), $J_{P,C}$ = 8.8 Hz], 79.8 [d, C-2(5) or C-3(4)], 90.8 (d, C-10, $^2J_{P,C}$ = 9.6 Hz), 112.4 (d, C-1, $^3J_{P,C}$ = 7.0 Hz), 125.2 (d, C-14), 128.3 (d, C-13), 131.0 (d, C-12), 136.0

(s, C-11). – ^{31}P NMR (81 MHz, [D$_8$]toluene): δ = 94.9. – MS (70 eV), *m/z* (%): 474 (10) [M$^+$], 296 (100) [M$^+$ – C_2Ph_2], 254 (12), 240 (48) [M$^+$ – C_2Ph_2 – C_4H_8], 184 (53) [M$^+$ – C_2Ph_2 – 2 (C_4H_8)], 181 (13), 178 (25) [$C_2Ph_2^+$], 59 (6) [Co$^+$], 57 (5) [$C_4H_9^+$]. – $C_{29}H_{36}CoP$ (474.5): calcd. C 73.41, H 7.65, Co 12.42, P 6.53; found C 73.50, H 7.56, Co 12.35, P 6.64.

Treatment of **23** *with 2-Butyne under Photochemical Conditions:* A cold solution (–30°C) of 20 µl (0.3 mmol) of 2-butyne and 40 mg (0.1 mmol) of **23** in 0.8 ml of [D$_8$]toluene is transferred to an NMR tube and subjected to three thaw-pump-freeze cycles with liquid nitrogen. The tube is irradiated (Duran, mercury high-pressure lamp Philips HPK 125 W) for 16 h. Then it is sealed under vacuum. ^{1}H- and ^{31}P-NMR spectroscopy indicate a 30% conversion to *(η^2-2-butyne){[2-(diphenylphosphanyl-P)ethyl]-η^5-cyclopentadienyl}cobalt(I)* (**32**) and the presence of traces of hexamethylbenzene (**33**, MS, ^{1}H NMR). – ^{1}H NMR (**32**, 200 MHz, [D$_8$]toluene): δ = 2.05 (d, 6H, 13-H, $^4J_{P,H}$ = 1.6 Hz), 2.51 (q, 2H, 7-H, $^2J_{P,H}$ = 8.6, $^3J_{6,7}$ = 7.2 Hz), 4.08 [m, 2H, 2(5)-H or 3(4)-H, $\Sigma J_{2(5),3(4)}$ = 4.0 Hz], 5.57 [m, 2H, 2(5)-H or 3(4)-H]. – ^{31}P NMR (81 MHz, [D$_8$]toluene): δ = 79.5.

Treatment of **25** *with 2-Butyne under Photochemical Conditions:* A cold solution (–30°C) of 20 µl (0.3 mmol) of 2-butyne and 36 mg (0.1 mmol) of **25** in 0.8 ml of [D$_8$]toluene is transferred to an NMR tube and subjected to three thaw-pump-freeze cycles with liquid nitrogen. The tube is irradiated (Duran, mercury high-pressure lamp Philips HPK 125 W) for 16 h. Then it is sealed under vacuum. ^{1}H- and ^{31}P-NMR spectroscopy indicate a 30% conversion to *(η^2-2-butyne){[2-(di-tert-butylphoshanyl-P)ethyl]-η^5-cyclopentadienyl}cobalt(I)* (**34**) and the presence of traces of hexamethylbenzene (**33**, MS, ^{1}H NMR). – ^{1}H NMR (**34**, 200 MHz, [D$_8$]toluene): δ = 1.15 [d, 18H, C(CH_3)$_3$, $^3J_{P,H}$ = 11.4 Hz), 2.29 (d, 6H, 11-H, $^4J_{P,H}$ = 1.3 Hz), 3.73 [m, 2H, 2(5)-H or 3(4)-H, $\Sigma J_{2(5),3(4)}$ = 4.2 Hz], 5.40 [m, 2(5)-H or 3(4)-H]. – ^{31}P NMR (81 MHz, [D$_8$]THF): δ = 97.3.

(η^4-1,5-Cyclooctadiene){η^5-[2-(di-tert-butylphosphanyl)ethyl]-cyclopentadienyl}cobalt(I) (**35**): In a 150-ml immersion photochemical reactor (Duran glass, high-pressure mercury lamp Philips HPK 125 W) a solution of 355 mg (1.1 mmol) of **25** in 150 ml of 1,5-cyclooctadiene (1,5-COD) is irradiated for 72 h. The solvent is evaporated at 40°C/0.1 mbar into a cold trap, and the residue is taken up in hexane and the solution filtered through a P4 frit covered with a 2.5 cm thick layer of silica gel. After washing with hexane fourfold elution with diethyl ether yields 180 mg (0.50 mmol, 41%) of **35** as red crystals, m.p. 62°C (DSC) (from diethyl ether). – IR (film): $\tilde{\nu}$ = 3086 cm^{-1} (w, Cp), 2937 (s, CH_2), 2864 (s, coord. 1,5-COD), 2822 (m, coord. 1,5-COD), 1470 (m), 1448 (m), 1387 (w, *t*Bu), 1365 (w, *t*Bu, coord. 1,5-COD), 1321 (w, coord. 1,5-COD), 1175 (w, *t*Bu), 1148 (w, coord. 1,5-COD), 1094 (w), 1018 (w, Cp–R), 855 (w, coord. 1,5-COD), 810 (m, Cp–R). – ^{1}H NMR (200 MHz, [D$_8$]-THF): δ = 1.14 (d, 18H, CH_3, $^3J_{P,H}$ = 10.6 Hz), 1.62 (m, 6H, 6-H or 7-H, 11-H), 2.24 (m, 2H, 6-H or 7-H), 2.39 (m, 4H, 12-H), 3.31 (m, 4H, 10-H), 4.45 [m, 4H, 2(5)-H, 3(4)-H]. – ^{13}C NMR (50.3 MHz, [D$_8$]THF): δ = 23.3 (dt, C-6 or C-7, $J_{P,C}$ = 23.1 Hz), 29.6 (dt, C-6 or C-7, $J_{P,C}$ = 20.9 Hz), 30.1 (dq, CH_3, $^3J_{P,C}$ = 14.0 Hz), 31.6 (d, C-8, $^1J_{P,C}$ = 22.7 Hz), 32.9 (t, C-11), 65.0 (d, C-10), 83.5 [d, C-2(5) or C-3(4)], 84.5 [d, C-2(5) or C-3(4)], 103.7 (d, C-1, $^3J_{P,C}$ = 16.1 Hz). – ^{31}P NMR (81 MHz, [D$_8$]THF): δ = 30.7. – MS (70 eV), *m/z* (%): 404 (6) [M$^+$], 296 (100) [M$^+$ – 1,5-COD], 254 (14), 240 (56) [M$^+$ – 1,5-COD – C_4H_8], 184 (55) [M$^+$ – 1,5-COD – 2 (C_4H_8)], 137 (18), 59 (12) [Co$^+$], 57 (25) [$C_4H_9^+$]. – $C_{23}H_{38}CoP$ (404.5): calcd. C 68.30, H 9.47, Co 14.57, P 7.66; found C 68.19, H 9.42, Co 14.74, P 7.89.

(η^5-[2-(Di-tert-butylphosphanyl)ethyl]cyclopentadienyl}-(η^4-tetraphenylcyclobutadiene)cobalt(I) (**36**): A solution of 3.50 g (19.6 mmol) of diphenylethyne in 200 ml of *ortho*-xylene is refluxed. A solution of 341 mg (0.8 mmol) of **35** in 50 ml of *ortho*-xylene is added dropwise to the boiling solution. After complete addition the mixture is refluxed for 6 d. The solvent is condensed into a cold trap, and excess diphenylethyne (3.4 g, 19.1 mmol) is removed by sublimation at 0.001 mbar. 660 mg of a red oil is obtained, which is taken up in diethyl ether and then stored at –78°C. Yield 330 mg (0.5 mmol, 64%) of **36**, yellow crystals, m.p. 86°C (from diethyl ether). – IR (KBr): $\tilde{\nu}$ = 3079 cm^{-1} (m), 3056 (m), 3027 (m), 2944 (s, CH_2), 2893 (s, CH_2), 2859 (s, CH_2), 1596 (m), 1574 (w), 1536 (w), 1499 (s), 1470 (m), 1446 (m), 1387 (w, *t*Bu), 1364 (w, *t*Bu), 1176 (w, *t*Bu), 1067 (w), 1038, 812 (m, Cp–R), 779 (m), 744 (m, Ph), 699 (s, Ph), 617 (w), 588 (m), 562 (m), 544 (m). – ^{1}H NMR (200 MHz, [D$_8$]THF): δ = 1.00 (d, 18H, CH_3, $^3J_{P,H}$ = 10.6 Hz), 1.40 (m, 2H, 7-H, $^3J_{6,7}$ = 14.2, $^2J_{P,H}$ = 5.8 Hz), 2.09 (m, 2H, 6-H, $^3J_{P,H}$ = 10.6 Hz), 4.49 + 4.56 [AA'BB' line system, 4H, 2(5)-H, 3(4)-H, $\Sigma J_{2(5),3(4)}$ = 4.0 Hz], 7.17 (m, 12H, *m*-, *p*-H), 7.44 (m, 8H, *o*-H). – ^{13}C NMR (50.3 MHz, [D$_8$]THF): δ = 24.7 (dt, C-6 or C-7, $J_{P,C}$ = 24.4 Hz), 28.4 (dt, C-6 or C-7, $J_{P,C}$ = 28.8 Hz), 30.1 (dq, C-9, $^2J_{P,C}$ = 14.0 Hz), 31.7 (d, C-8, $^1J_{P,C}$ = 23.5 Hz), 74.4 (s, C-10), 83.3 [d, C-2(5) or C-3(4)], 83.8 [d, C-2(5) or C-3(4)], 101.3 (d, C-1, $^3J_{P,C}$ = 14.8 Hz), 126.8 (d, C-14), 128.7 (d, C-13), 129.6 (d, C-12), 137.5 (s, C-11). – ^{31}P NMR (81 MHz, [D$_8$]THF): δ = 29.8. – MS (70 eV), *m/z* (%): 652 (100) [M$^+$], 595 (8) [M$^+$ – C_4H_9], 534 (13), 506 (30), 415 (55) [$C_4Ph_4Co^+$], 296 (18) [M$^+$ – C_4Ph_4], 237 (22) [M$^+$ – C_4Ph_4Co], 178 (17) [$C_2Ph_2^+$], 59 (13) [Co$^+$], 57 (19) [$C_4H_9^+$]. – $C_{43}H_{46}CoP$ (652.8): calcd. C 79.12, H 7.10, Co 9.03, P 4.75; found C 79.25, H 7.36, Co 8.75, P 4.68.

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* Dedicated to Professor *Carl Krüger* on the occasion of his 60th birthday.

[1] T. J. Kealy, P. J. Pauson, *Nature (London)* **1951**, *168*, 1039–1040.
[2] J. M. O'Connor, C. P. Casey, *Chem. Rev.* **1987**, *87*, 307–318.
[3] [3a] H. Butenschön, *Angew. Chem.* **1990**, *102*, 1058–1059; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1057–1059. – [3b] K. P. Angermund, P. Betz, H. Butenschön, *Chem. Ber.* **1993**, *126*, 713–724.
[4] [4a] R. T. Kettenbach, H. Butenschön, *New. J. Chem.* **1990**, *14*, 559–601. – [4b] R. T. Kettenbach, H. Butenschön, XXVIII International Conference on Coordination Chemistry, Gera (GDR), 13.–18.8.90, Abstracts of Posters, vol. 1, p. 4–19.
[5] [5a] N. E. Schore, *J. Am. Chem. Soc.* **1979**, *101*, 7410–7412. – [5b] C. Charrier, F. Mathey, *J. Organomet. Chem.* **1979**, *170*, C41–C43. – [5c] F. Mathey, C. Charrier, A. Maisonnat, R. Poilblanc, J. C. Leblanc, C. Moise, *J. Organomet. Chem.* **1982**, *231*, C43–C48. – [5d] T. Kauffmann, J. Olbrich, *Tetrahedron Lett.* **1984**, *25*, 1967–1970. – [5e] D. M. Bensley, Jr., E. A. Mintz, *J. Organomet. Chem.* **1988**, *353*, 93–102. – [5f] N. E. Schore, B. E. LaBelle, *J. Org. Chem.* **1981**, *46*, 2306–2310. – [5g] G. Marr, T. M. White, *J. Chem. Soc., Perkin Trans. 1*, **1973**, 1955–1958.
[6] S. O. Grim, R. C. Barth, *J. Organomet. Chem.* **1975**, *94*, 327–332.
[7] J. Szymoniak, J. Besançon, A. Dormond, C. Moise, *J. Org. Chem.* **1990**, *55*, 1429–1432.
[8] F. Edelmann, Dissertation, Univ. Hamburg, **1983**.
[9] 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*, 328–329.
[10] R. Uriate, T. J. Mazanec, K. D. Tau, D. W. Meek, *Inorg. Chem.* **1980**, *19*, 79–85.
[11] J. Olbrich, Dissertation, Univ. Münster, **1983**.
[12] [12a] B. E. Mann, *Adv. Organomet. Chem.* **1974**, *12*, 135–213. – [12b] See also P. W. Jolly, R. Mynott, *Adv. Organomet. Chem.* **1981**, *19*, 257–304.
[13] [13a] M. D. Rausch, W. P. Hart in *Organometallic Synthesis* (Eds.: R. B. King, J. J. Eisch), Elsevier, Oxford, **1986**, vol. 3, p. 50ff. – [13b] B. G. Conway, M. D. Rausch, *Organomet.* **1985**, *4*, 688–693.

[14] M. Tasi, T. Ranga, G. Pályi in *Organometallic Synthesis* (Eds.: R. B. King, J. J. Eisch), Elsevier, New York, **1988**, vol. 4, p. 262.
[15] [15a] J. Okuda, K. H. Zimmermann, *Chem. Ber.* **1989**, *122*, 1645–1647. – [15b] J. Okuda, E. Herdtweck, K. H. Zimmermann in *Organic Synthesis via Organometallics* (Eds.: K. H. Dötz, R. W. Hoffmann), Vieweg, Braunschweig, **1991**, p. 207–221.
[16] R. B. King, *Inorg.Chem.* **1966**, *5*, 82–87.
[17] A. M. Z. Slawin, D. J. Williams, J. Crosby, J. A. Ramsden, C. White, *J. Chem. Soc., Dalton Trans.* **1988**, 2491–2494.
[18] H. G. Wey, H. Butenschön, *Angew. Chem.* **1990**, *102*, 1469–1471; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1444–1445.
[19] B. Schrader, W. Meier in *Raman/IR-Atlas organischer Verbindungen* (Ed.: Institut für Spektrochemie und angewandte Spektroskopie, Dortmund), Verlag Chemie, Weinheim, **1974**, vol. II.
[20] [20a] H. Bönnemann, *Angew. Chem.* **1985**, *97*, 264–279; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 248–262, and literature cited. – [20b] cf. K. P. C. Vollhardt, *Angew. Chem.* **1984**, *96*, 525–541; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 539–556, and literature cited.
[21] cf. R. Benn, H. Günther, *Angew. Chem.* **1983**, *95*, 381–411; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 350–380.
[22] H.-O. Kalinowski, S. Berger, S. Braun, *^{13}C-NMR-Spektroskopie*, Georg Thieme Verlag, Stuttgart, **1984**, p. 74.
[23] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923.
[24] K. J. Stone, R. D. Little, *J. Org. Chem.* **1984**, *49*, 1849–1853.
[25] H. Priemer, Dissertation, Ruhr-Universität Bochum, **1987**.
[26] C. F. Wilcox, Jr., R. R. Craig, *J. Am. Chem. Soc.* **1961**, *83*, 3866–3871.
[27] Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (FRG), on quoting the depository number CSD-57096, the names of the authors, and the journal citation.

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