

λ^3 -1,3-Diphosphacyclobutadiene-Cobalt Complexes by Cyclodimerization of λ^3 -Phosphaalkynes

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λ^3 -Phosphaalkynes $P\equiv C-R$ [$R = \textit{tert}$ -butyl (**1a**) or isopropyl (**1b**)] react with $(\eta^5\text{-cyclopentadienyl})\text{bis}(\text{ethene})\text{cobalt}$ (**2**) or $\text{bis}(\text{ethene})(\eta^5\text{-indenyl})\text{cobalt}$ (**3**) by displacement of ethene to yield the $(\eta^4\text{-1,3-diphosphacyclobutadiene})\text{cobalt}$ complexes **4a, b** and **5a, b**. These are the first reported syntheses of a λ^3 -1,3-diphosphacyclobutadiene (λ^3 -1,3-diphosphete)^{14,15}. Complex **4** reacts smoothly with the lone pairs of the phosphorus atoms to give the dinuclear or trinuclear cobalt complexes **6a, b** and **7a, b**. The structures of the new complexes **4–7** have been elucidated by spectroscopic methods, especially ¹³C-NMR spectroscopy. The X-ray analyses of **4a** and **5a** confirm these structures.

The parent compound of the phosphaalkynes, phosphacetylene ($HC\equiv P$), was first generated by Gier¹ in 1961. It is a highly reactive compound which, like some of its simple substitution products, is stable only at low temperature². Systematic investigations of their synthetic potential began only after phosphaalkynes with sterically bulky organic substituents, which are stable at room temperature, had been prepared on a laboratory scale³. It was found that λ^3 -phosphaalkynes are ideal partners for reactions with 1,3-dipoles^{3b,c,4} or 1,3-dienes⁵. They thus react very similarly to alkynes.

It was therefore of interest to carry out cycloadditions with λ^3 -phosphaalkynes on transition metal compounds. The likelihood that this idea could be realized was enhanced after it became clear that λ^3 -phosphaalkynes are nearly always bound 'side on' in transition metal complexes. Mononuclear complexes of platinum⁶, dinuclear complexes of cobalt^{6a,7}, molybdenum⁸, and nickel⁹ and trinuclear metal complexes¹⁰ have been described, all having 'side on' complexation, the last mentioned containing a third metal atom bonded to the free electron pair of the phosphorus atom. The only exception is found in a recently reported series of molybdenum complexes in which the phosphaalkyne is η^1 bound, probably for steric reasons¹¹.

In this paper we describe in detail the reactions of the phosphaalkynes $P\equiv C-R$ [$R = \textit{tert}$ -butyl^{3a}) (**1a**) or isopropyl^{3b}) (**1b**)] with $(\eta^5\text{-cyclopentadienyl})\text{bis}(\text{ethene})\text{cobalt}$

λ^3 -1,3-Diphosphacyclobutadien-Cobalt-Komplexe durch Cyclodimerisierung von λ^3 -Phosphaalkinen

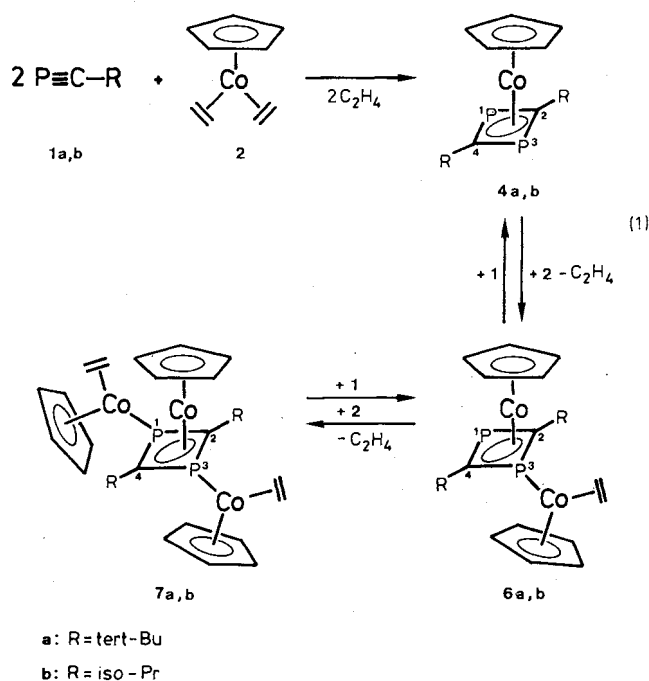
λ^3 -Phosphaalkyne $P\equiv C-R$ [$R = \textit{tert}$ -Butyl (**1a**) oder Isopropyl (**1b**)] reagieren mit $(\eta^5\text{-Cyclopentadienyl})\text{bis}(\text{ethen})\text{cobalt}$ (**2**) oder $\text{Bis}(\text{ethen})(\eta^5\text{-indenyl})\text{cobalt}$ (**3**) unter Verdrängung des Ethens zu den entsprechenden $(\eta^4\text{-1,3-Diphosphacyclobutadien})\text{cobalt}$ -Komplexen **4a, b** und **5a, b**. Damit ist es erstmals gelungen, eine λ^3 -1,3-Diphosphacyclobutadien- $(\lambda^3$ -1,3-Diphosphet)-Struktureinheit aufzubauen^{14,15}. Der Cobaltkomplex **4** geht mit den freien Elektronenpaaren der beiden Phosphoratome bereitwillig Additionsverbindungen ein, wobei die dinuklearen Cobaltverbindungen **6a, b** und die trinuklearen Cobaltverbindungen **7a, b** entstehen. Die Strukturen der neuen Cobaltkomplexe **4–7** wurden durch spektroskopische Methoden, insbesondere die ¹³C-NMR-Spektroskopie bestimmt. Die Kristallstrukturanalysen von **4a** und **5a** bestätigen diese Zuordnung.

(**2**)¹² or $\text{bis}(\text{ethene})(\eta^5\text{-indenyl})\text{cobalt}$ (**3**)^{12,13}, which proceed by smooth cyclodimerization of **1** to form the corresponding $(\lambda^3\text{-1,3-diphosphacyclobutadiene})\text{cobalt}$ complexes. Our results with **1a** and **2** have already been published in a short communication¹⁴, which appeared almost simultaneously with the report by an English research group of the preparation of $\eta^5\text{-cyclopentadienyl-1,3-diphosphacyclobutadiene}$ complexes of cobalt and rhodium from **1**¹⁵.

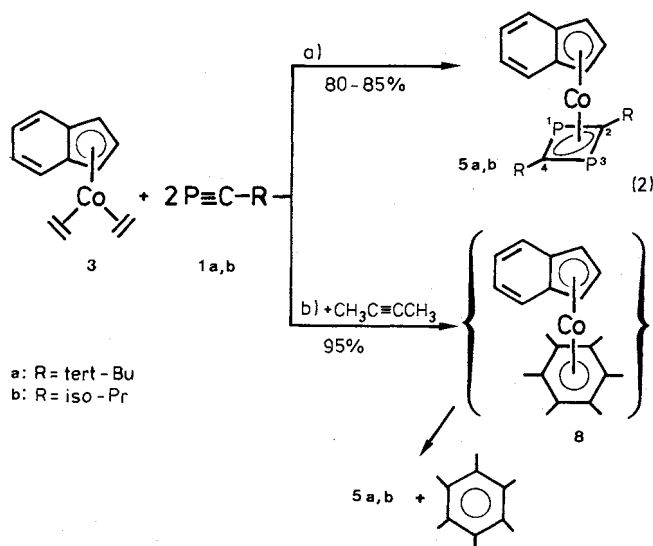
Results

When $(\eta^5\text{-cyclopentadienyl})\text{bis}(\text{ethene})\text{cobalt}$ (**2**) reacts with excess 2-*tert*-butyl-1-phosphaacetylene (**1a**) or 2-isopropyl-1-phosphaacetylene (**1b**) at -30 to -5°C , the corresponding $(1,3\text{-diphosphacyclobutadiene})\text{cobalt}$ complexes **4a** or **4b** are obtained in 67 and 80% yield, respectively. In order to achieve higher yields of **4** it is better to use an excess of **1**, since the free electron pairs of both phosphorus atoms of **4** are able to react with further molecules of **2** by displacement of an ethylene ligand. Depending upon the molar ratio of **1** and **2**, the dinuclear cobalt complexes **6** or the trinuclear complexes **7** are formed. The best way to prepare **6** or **7** is to start with **4** that has been prepared previously and to mix this with **2** in the molar ratio 1:1 or 1:2 to obtain the desired complex in 50–80% yield. **4** can be regained by addition of excess **1** to **6** or **7**.

$\text{Bis}(\text{ethene})(\eta^5\text{-indenyl})\text{cobalt}$ (**3**) reacts with **1a** or **1b** to form the corresponding mononuclear $(\eta^4\text{-1,3-diphosphacyclobutadiene})\text{cobalt}$ complexes.



clobutadiene)cobalt complexes **5a** or **5b**. Further reaction to form di- or trinuclear complexes analogous to **6a,b** or **7a,b** does not take place, probably for steric reasons.



During these experiments, codimerization of **1a** or **1b** with 2-butyne was attempted. However, 2-butyne appears to react considerably faster with **3** than **1a** or **1b**. As a result, in addition to hexamethylbenzene, only **5a** or **5b** is formed, although the yields are significantly higher than when no 2-butyne is present. Very probably the synthesis of **5a,b** proceeds via the 20-electron complex (η^6 -hexamethylbenzene)(η^3 -indenyl) cobalt (**8**)¹⁶, from which the hexamethylbenzene can be displaced by **1a** or **1b** more easily than ethylene from **3**. However, a codimerization with **1a** can be achieved when an alkyne with two bulky residues is selected, for example, bis(trimethylsilyl)acetylene¹⁷.

The new (1,3-diphosphacyclobutadiene)cobalt complexes **4a,b** – **7a,b** are red crystalline materials, with the exception

of **4b**, which is a red oil. The mononuclear compounds **4a** and **5a,b** have defined melting points. **4a,b** and **5a,b** are surprisingly inert compounds which do not decompose when exposed to the air for a long time. They also have a high thermal stability; **5b**, for example, can be sublimed under an inert atmosphere at 170°C without decomposition. They have a correspondingly low reactivity. Up to now it has not been possible to liberate the 1,3-diphosphacyclobutadiene residue in a defined reaction, e. g., with KCN¹⁸ or (NH₄)₂Ce(NO₃)₆¹⁹, nor can the cyclopentadienyl or indenyl ligands be removed by reductive elimination with sodium or potassium. Only the free electron pairs of the two phosphorus atoms of **4a,b** are available to form addition compounds. Examples are **6a,b** and **7a,b** and the reaction of **4a** with bis(1,5-cyclooctadiene)nickel, which liberates the cyclooctadiene quantitatively to yield a red powder with the composition [CpCo(*tert*-Bu₂C₂P₂)]_nNi_m, which is insoluble in organic solvents and obviously polymeric.

All the cobalt complexes described here deliver correct elemental analyses. Their structures were first determined spectroscopically and those of **4a** and **5a** were later confirmed by X-ray crystallography (see below).

In the mass spectra the molecule peaks M⁺ were detected only for the mononuclear complexes **4a,b** and **5a,b**, mostly with high intensities. Furthermore, it is noteworthy that the mass spectra are rather similar and that the characteristic fragments M⁺ – P₂ and M⁺ – C₂R₂ are observed (see Table 1). On the other hand, the di- and trinuclear complexes **6** and **7b** decompose during measurements, so that their spectra are very dependent upon the exact conditions employed (see Table 1).

Table 1. Mass spectra of the (1,3-diphosphacyclobutadiene)cobalt complexes **4a,b** and **5a,b** (for ⁵⁹Co)

Complex	M ⁺ ^{a)}	M ⁺ – P ₂ ^{a)}	M ⁺ – (C ₂ R ₂) ^{a)}	M ⁺ – (P ₂ C ₂ R ₂) ^{a)}
4a	324 (96)	262 (100)	186 (51)	124 (69)
4b	296 (96)	234 (100)	186 (52)	124 (66)
5a	374 (47)	312 (40)	236 (100)	174 (65)
5b	346 (96)	284 (24)	236 (99)	174 (64)

^{a)} Relative intensity in brackets.

NMR Studies

Since the structures of these novel cobalt complexes were determined by NMR despite the lack of suitable comparison data, the spectra and their interpretation will be examined in more detail. The NMR data are collected in Table 2.

In the ³¹P-NMR spectrum of a sample of pure **4a** a singlet was observed at $\delta_p = 38.1$ and in the ¹³C-NMR spectrum the resonance of the diphosphacyclobutadiene carbon atoms was observed as a triplet at 107.55 ppm with an apparent *J*_{PC} coupling of 54.4 Hz. However, since an AA'X spin system with a large P–P coupling constant, such as may be found when the phosphorus atoms are directly bonded,

could also give rise to this multiplet structure²⁰, these spectra did not exclude a wide range of alternative structures such as diphosphacobaltacyclopentadienes or possibly complexes with two "end on"- or "side on"-bonded phosphoacetylene ligands.

Table 2. ¹³C- and ³¹P-NMR data of the (1,3-diphosphacyclobutadiene)cobalt complexes **4a**, **b**, **5a**, **b**, **6a**, and **7a**

Complex		³¹ P		¹³ C			
		P	C-2, C-4	C-(<i>tert</i> -Butyl)	CH ₃	C-(Cp)	C-(Ethene)
4a	δ	38.1	107.55	34.33	31.21	81.53	
	a) J_{PC}^1 , Hz J_{CH}^1 , Hz		54.4	7.1	4.1	125	177
4b	δ	47.4	104.3	31.9	24.0	81.9	
	b) J_{PC}^1 , Hz J_{CH}^1 , Hz		54.4	8.4	5.7 ^{d)}	127	177
5a	δ	38.0	109.6	35.0	30.7	e)	
	b) J_{PC}^1 , Hz J_{CH}^1 , Hz		54.4	6.8	4.8	126	
5b	δ	44.2	104.8	30.5	23.6		
	b) J_{PC}^1 , Hz J_{CH}^1 , Hz		54.2	8.1	8.3, 3.9 ^{f)}	125	126
6a	δ	P-1 134.9 ^{b)} P-3 -32.0	102.82	32.75	30.81	80.31 ^{g)}	26.81
	a) J_{PC}^1 , Hz J_{CH}^1 , Hz		58.7, 19.6	7.1, 3.7	126	177	154
7a	δ	85.9	99.38	33.02	30.65	80.26 ^{h)}	27.08
	c) J_{PC}^1 , Hz J_{CH}^1 , Hz		22.1	4.2	5.0	126	176

^{a)} [D₈]Toluene, -50°C. - ^{b)} [D₆]Benzene, 40°C. - ^{c)} [D₈]Toluene, -30°C. - ^{d)} 0.5 [³J_{PC} + ³J_{PC}] (although this signal should be the X part of an AA'X spin system (cf. **5b**), it was an apparent triplet and unsuitable for simulation). - ^{e)} Indenyl signals: δ_C (Hz): 125.5 (¹J_{CH} 160); 126.6 (¹J_{CH} 164); 102.2 (s); 72.9 (¹J_{CH} 178); 83.3 (¹J_{CH} 176). Compare with Figure 1a for assignment. - ^{f)} ¹³C multiplet is X part of an AA'X spin system. See Figure 1b. - ^{g)} Indenyl Signals; δ_C (Hz): 124.7 (¹J_{CH} 161); 125.2 (¹J_{CH} 164); 100.9 (s); 73.6 (¹J_{CH} 178); 85.2 (¹J_{CH} 176). See Figure 1a for assignment. - ^{h)} ²J_{P-1,P-3} = 5 Hz. - ⁱ⁾ Cp in CpCo(C₂H₄); δ_C = 82.35 (¹J_{PC} = 2.4, ¹J_{CH} = 176 Hz). - ^{j)} Cp in CpCo(C₂H₄); δ_C = 82.67 (¹J_{CH} = 174 Hz).

A second sample containing both **4a** and **6a** in the ratio 1:2 was the key to the structure determination. The ³¹P-NMR spectrum of this sample had three approximately equally intensive signals, one of which was assigned to **4a**. Although the other two singlets at 134.9 and -32.0 ppm seemed to be due to two other compounds, in the ¹³C-NMR spectrum (in addition to the signals from **4a**), just one other signal was observed for the phosphoacetylene carbon (a doublet of doublets at 102.8 ppm), suggesting that there was only one other compound present.

Re-examination of the ³¹P-NMR spectrum of this sample at 121 MHz and -50°C showed that while the signal at

134.9 ppm had a line width of 36 Hz, the narrower resonance at -32.0 ppm was a doublet of ca. 5 Hz that was just resolved. This splitting collapsed when the temperature was raised or lowered by 30°C. A very effective means of establishing whether this barely detectable splitting of the one resonance was due to P-P coupling was to record a ³¹P 2D-COSY NMR spectrum²¹. Observation of crosspeaks between the signals at 134.9 and -32.0 ppm confirmed that the two phosphorus atoms are spin coupled with one another and that they therefore must be part of the same molecule.

If the two phosphorus atoms in **6a** are different (two signals) but the two carbon atoms (C-2 and C-4) are symmetrically equivalent (one signal) then P-1 must now have the same bonding and symmetry relationship to both of these carbon atoms. The same applies to P-3. This is only consistent with a diphosphacyclobutadiene ring being present.

The similarity of the ¹³C NMR chemical shifts and the J_{PC} couplings of ca. 55 Hz for **4a** and **6a** suggested that the structures of these molecules are closely related. Further experiments confirmed that **6a** could be prepared from **4a** and showed that a third complex **7a** could be prepared by complexation of another CpCo(ethylene) moiety to the other phosphorus atom. The broadening of the signal at δ_P = 134.9 in the spectrum of **6a** results from scalar relaxation due to the σ -bonded cobalt atom. At -50°C this phosphorus nucleus does not relax quite fast enough to cause the coupling observed at the other to collapse.

Inspection of the data collected in Table 2 reveals that the chemical shifts of the diphosphacyclobutadiene ring carbons undergo a small regular shift to higher field in the series **4a** → **6a** → **7a**. ¹J_{PC} is approximately 55 Hz and is reduced to about 20 Hz when the phosphorus atom is bonded to a second cobalt fragment by its lone pair. By contrast, the phosphorus chemical shifts are very sensitive to changes in their environment. For example, in the spectrum of **6a** the resonance of P-3 moves 70 ppm to higher field relative to its position in **4a** on complexation of P-1 with a second cobalt atom. Similarly, in **7a** when P-3 is also bound to a CpCo(C₂H₄) group, the resonance of P-1 is shifted to 85.9 ppm, 49 ppm to higher field than its chemical shift in **6a**.

Figure 1a illustrates the ¹³C-NMR spectrum of complex **5b**. The signals for C-2 and C-4 are, as expected, split into triplets due to coupling with the two equivalent phosphorus atoms. However, the resonance of the isopropyl methyl carbon atoms is a multiplet typical of the X part of an AA'X spin system²⁰.

When one of the methyl carbon atoms is ¹³C, then C-5 becomes chiral and the phosphorus atoms in this isotopomer are diastereotopic (Figure 1b). As a result, in the ¹³C-NMR spectrum of this isotopomer these phosphorus atoms are not equivalent and have different coupling constants to the methyl carbon (see Legend, Figure 1). Only one ¹³C-NMR resonance is observed for the methyl carbons because the methyl groups are enantiotopic. Simulation of the methyl resonance (Figure 1c) allows ²J_{P,P} to be calculated (3.5 Hz).

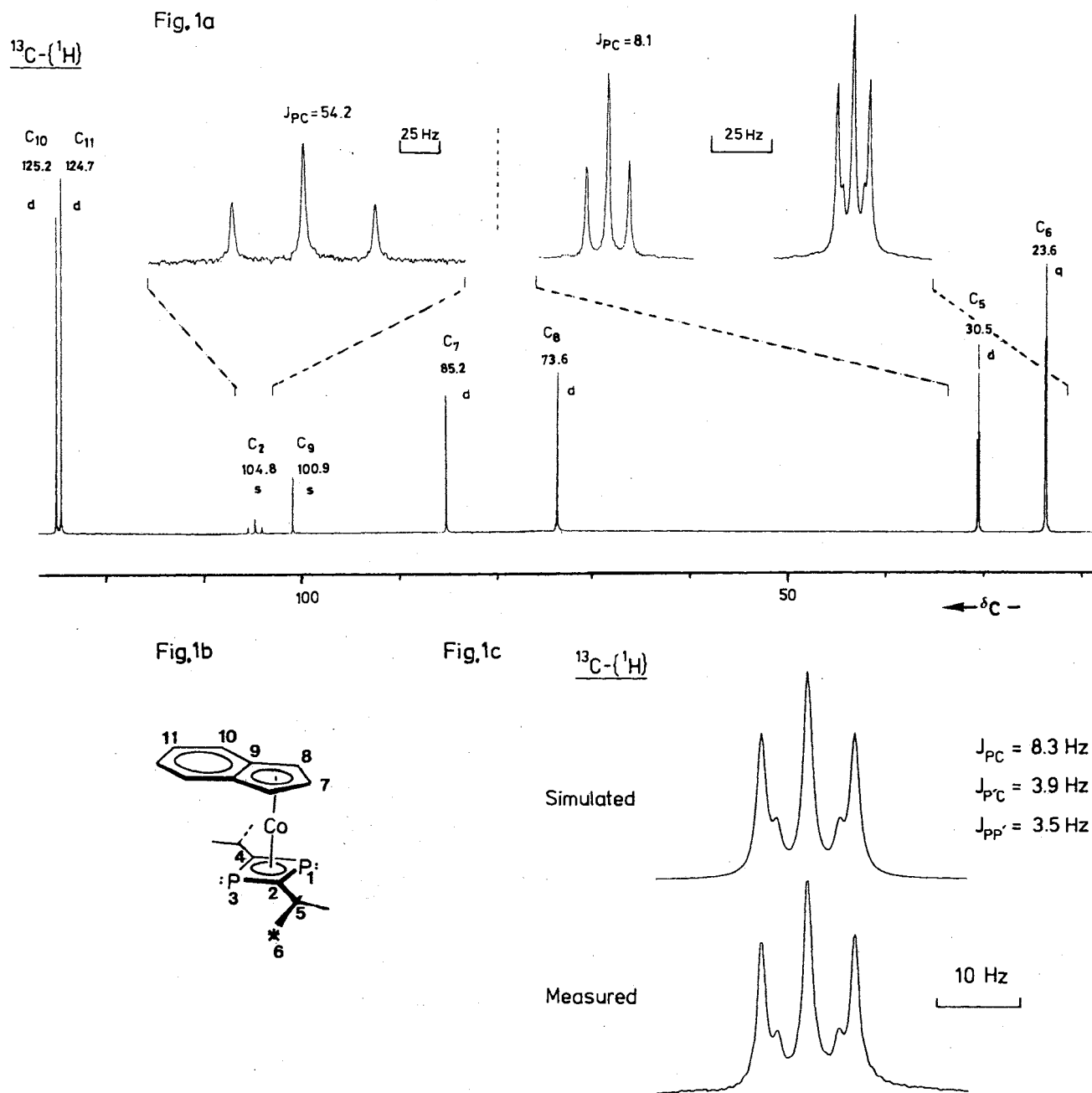


Figure 1. 75.5 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5b** in C_6D_6 at 40°C

Fig. 1a: Spectrum in the region 127 – 18 ppm with expansions of the multiplets from C-2 and the isopropyl carbon atoms C-5 and C-6. — Fig. 1b: Isotopomer with a ^{13}C -methyl group. C-5 is chiral, P-1 and P-3 are diastereotopic. Their ^{31}P chemical shifts will be practically identical but the coupling constants $^3J_{\text{P},1,\text{C}-6}$ and $^3J_{\text{P},3,\text{C}-6}$ should have different weighted averages because the rotamers about the C-2–C-4 axis are not all equally populated. — Fig. 1c): Enlargement of the methyl resonance at 23.6 ppm (lower trace). This is simulated (upper trace) as the X region of an AA'X spin system (A = ^{31}P , X = ^{13}C).

X-Ray Crystallography

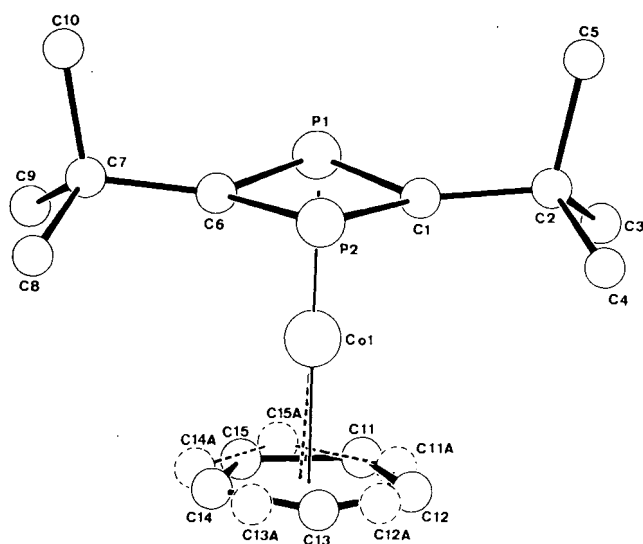
The structure determination of compounds **4**–**7** by NMR has been confirmed by crystal structure analyses of compounds **4a** and **5a**. The experimental details of the structure determinations are given in Table 3. Tables 4–7 list fractional coordinates and selected bond distances and angles. Refinement of **4a** was hampered by disorder of the cyclopentadiene moiety; the latter was included in the final least squares refinement cycles in two orientations with partial

occupancies of the atomic sites (70/30). Figures 2 and 3 represent the molecular structures of **4a** and **5a**, respectively. In both compounds, two coordination sites of the central cobalt atoms are occupied by almost coplanar four- and five-membered ring systems. The metal-to-ring distances Co–P (av. 2.25(1) Å) and Co–C (av. 2.06(2) Å) of the 1,3-diphosphacyclobutadiene are as expected. All cyclic P–C bonds of the hetero-cyclobutadiene rings are equidistant, the P–C distances average to 1.797 Å¹⁵, which is in accordance

Table 3. Crystal structure data of **4a** and **5a***)

	4a	5a
Formula	C ₁₅ H ₂₃ CoP ₂	C ₁₉ H ₂₅ CoP ₂
M _r	324.2	374.3
Crystal Size (mm)	0.32x0.58x0.94	0.14x0.61x0.32
Crystal Colour	dark-red	dark-red
a (Å)	16.587(1)	6.379(1)
b	16.562(3)	9.205(1)
c	12.131(2)	16.818(1)
α (°)	90.	102.12(1)
β	94.94(1)	91.67(1)
γ	90.	102.85(1)
V (Å ³)	3320.2	938.4
d _{calcd} (gcm ⁻³)	1.30	1.32
Z	8	2
Space Group	P2 ₁ /c	P $\bar{1}$
μ (Mo-K α) (cm ⁻¹)	12.04	10.74
Absorption Corr.	empirical	
min.	0.851	
max.	1.112	
Enraf-Nonius CAD4 Diffractometer		
Scan Mode	$\omega - 2\theta$	$\omega - 2\theta$
Refl. Measured	8019 (+h+k+l)	5373 (+h+k+l)
sin θ/λ _{max}	0.64	0.70
Unique Refl.	7499	5372
Observed Refl.	5329 (I > 2 σ (I))	4458 (I > 2 σ (I))
Param. Varied	315	299
R	0.042	0.030
R _w	0.053	0.038
Fin. Diff. Fourier (eÅ ⁻³)	0.55	0.77

*) Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie Physik Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-52608, the names of the authors, and the full citation of the journal.

Figure 2. Molecular structure of **4a**Table 4. Selected distances (Å) and angles (°) of **4a** (averaged for two molecules)

Co - P1	2.245(1)	P1 - C1	1.797(3)
Co - P2	2.241(6)	P1 - C6	1.797(7)
Co - C1	2.060(3)	P2 - C1	1.798(3)
Co - C6	2.054(3)	P2 - C6	1.797(3)
Co - C11	2.059(6)	C1 - C2	1.514(5)
		C6 - C7	1.516(8)
C6 - Co - C1	69.1(2)	C6 - P2 - C1	80.9(3)
C6 - Co - P2	49.3(1)	C2 - C1 - P2	130(1)
C6 - Co - P1	49.2(1)	C2 - C1 - P1	130(1)
C1 - Co - P2	49.2(1)	P2 - C1 - P1	98.9(2)
C1 - Co - P1	49.1(1)	C7 - C6 - P2	130(1)
P2 - Co - P1	75.0(1)	C7 - C6 - P1	130(1)
C6 - P1 - C1	80.9(2)	P2 - C6 - P1	98.9(2)

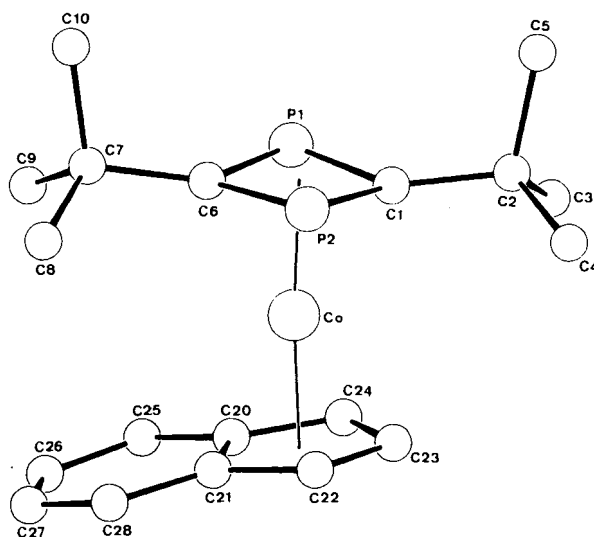
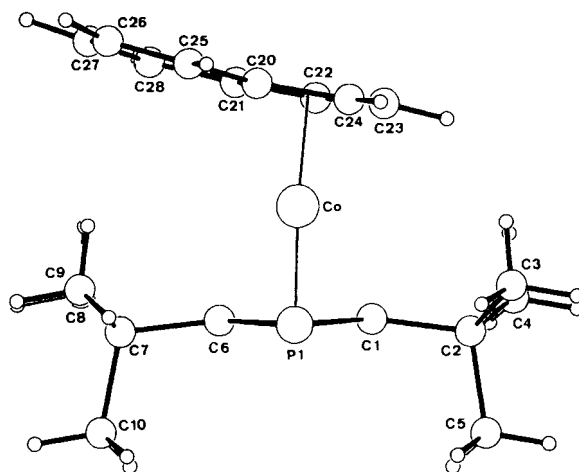
Figure 3. Molecular structure of **5a**Figure 4. Side view of **5a**

Table 5. Atomic fractional coordinates and equivalent isotropic thermal parameters (\AA^2) with standard deviations in parentheses for **4a**

$$U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

Atom	x	y	z	U_{eq}
Co1	0.2598(1)	0.0862(1)	0.1765(1)	0.041
Co2	0.8522(1)	0.0739(1)	0.3162(1)	0.043
P1	0.3337(1)	0.0825(1)	0.0302(1)	0.047
P2	0.3884(1)	0.0889(1)	0.2488(1)	0.045
P3	0.8252(1)	0.1325(1)	0.4758(1)	0.052
P4	0.7913(1)	0.1909(1)	0.2665(1)	0.047
C1	0.3571(2)	0.0153(2)	0.1448(3)	0.042
C2	0.3662(2)	-0.0755(2)	0.1447(3)	0.050
C3	0.3001(2)	-0.1150(2)	0.0678(4)	0.064
C4	0.3612(3)	-0.1089(3)	0.2624(4)	0.079
C5	0.4492(2)	-0.0947(2)	0.1027(4)	0.076
C6	0.3556(2)	0.1562(2)	0.1379(3)	0.043
C7	0.3631(2)	0.2467(2)	0.1283(3)	0.050
C8	0.3560(3)	0.2862(2)	0.2403(3)	0.071
C9	0.2978(3)	0.2794(2)	0.0440(4)	0.077
C10	0.4450(3)	0.2650(3)	0.0868(4)	0.093
C16	0.8730(2)	0.1891(2)	0.3737(3)	0.044
C17	0.9502(2)	0.2392(2)	0.3840(3)	0.053
C18	1.0182(2)	0.1947(3)	0.4534(4)	0.068
C19	0.9779(2)	0.2600(3)	0.2719(4)	0.080
C20	0.9310(2)	0.3183(3)	0.4432(4)	0.080
C21	0.7476(2)	0.1255(2)	0.3634(3)	0.045
C22	0.6626(2)	0.0918(2)	0.3600(3)	0.053
C23	0.6294(2)	0.0750(3)	0.2418(4)	0.074
C24	0.6086(2)	0.1552(3)	0.4109(4)	0.069
C25	0.6611(3)	0.0151(3)	0.4293(4)	0.084
C11	0.1440(4)	0.0453(5)	0.1341(5)	0.053
C11A	0.1506(9)	0.0224(9)	0.163(2)	0.050
C12	0.1697(3)	0.0151(4)	0.2407(6)	0.049
C12A	0.1796(8)	0.038(1)	0.279(1)	0.050
C13	0.1889(4)	0.0826(6)	0.3096(5)	0.064
C13A	0.1840(6)	0.1283(8)	0.291(1)	0.031
C14	0.1749(4)	0.1541(5)	0.2474(9)	0.074
C14A	0.1602(7)	0.1632(7)	0.185(1)	0.036
C15	0.1460(4)	0.1295(5)	0.1418(7)	0.071
C15A	0.1409(7)	0.1024(9)	0.104(1)	0.039
C26	0.9451(5)	0.0340(4)	0.2276(8)	0.061
C26A	0.9594(7)	0.0160(9)	0.284(2)	0.048
C27	0.9493(4)	-0.0047(5)	0.3330(7)	0.055
C27A	0.920(1)	-0.028(1)	0.351(1)	0.060
C28	0.8758(5)	-0.0477(4)	0.3414(6)	0.056
C28A	0.840(1)	-0.0510(9)	0.295(2)	0.057
C29	0.8264(3)	-0.0354(4)	0.2379(7)	0.055
C29A	0.8434(8)	-0.011(1)	0.189(1)	0.043
C30	0.8701(6)	0.0163(5)	0.1701(5)	0.063
C30A	0.914(1)	0.030(1)	0.186(1)	0.061

Table 6. Selected distances (\AA) and angles ($^\circ$) of **5a**

Co - P2	2.248(1)	C1 - C2	1.514(2)
Co - P1	2.251(1)	C6 - C7	1.514(2)
Co - C1	2.045(1)	Co - C20	2.159(2)
Co - C6	2.084(1)	Co - C21	2.166(2)
P2 - C1	1.802(2)	Co - C22	2.063(2)
P2 - C6	1.788(2)	Co - C23	2.048(2)
P1 - C1	1.797(2)	Co - C24	2.046(2)
P1 - C6	1.796(2)		
C6 - Co - C1	68.3(1)	C6 - P1 - C1	80.4(1)
C6 - Co - P1	48.7(1)	C2 - C1 - P1	128.8(1)
C6 - Co - P2	48.6(1)	C2 - C1 - P2	130.2(1)
C1 - Co - P1	49.2(1)	P1 - C1 - P2	99.1(1)
C1 - Co - P2	49.4(1)	C7 - C6 - P1	129.2(1)
P1 - Co - P2	75.0(1)	C7 - C6 - P2	129.7(1)
C6 - P2 - C1	80.5(1)	P1 - C6 - P2	99.7(1)

Angle between best planes defined by C20-C24 and C20, C21, C25-C28 is 174° .

Table 7. Atomic fractional coordinates and equivalent isotropic thermal parameters (\AA^2) with standard deviations in parentheses for **5a**

$$U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

Atom	x	y	z	U_{eq}
Co	0.3234(1)	0.0709(1)	0.2232(1)	0.033
P1	0.0891(1)	0.2228(1)	0.2309(1)	0.040
P2	0.5150(1)	0.3041(1)	0.2876(1)	0.037
C1	0.3504(2)	0.2792(2)	0.1946(1)	0.034
C2	0.4071(3)	0.3314(2)	0.1167(1)	0.042
C3	0.2504(4)	0.2345(3)	0.0443(1)	0.059
C4	0.6404(3)	0.3299(3)	0.0989(1)	0.058
C5	0.3825(4)	0.4980(3)	0.1304(2)	0.067
C6	0.2562(2)	0.2313(2)	0.3203(1)	0.035
C7	0.1919(3)	0.2171(2)	0.4048(1)	0.045
C8	0.3708(4)	0.1774(3)	0.4527(1)	0.064
C9	-0.0199(4)	0.0977(3)	0.3998(1)	0.062
C10	0.1580(5)	0.3736(3)	0.4485(1)	0.073
C20	0.1796(3)	-0.1707(2)	0.2023(1)	0.048
C21	0.3821(3)	-0.1382(2)	0.2488(1)	0.044
C22	0.5431(3)	-0.0643(2)	0.2028(2)	0.060
C23	0.4413(5)	-0.0597(2)	0.1290(1)	0.074
C24	0.2199(5)	-0.1163(2)	0.1294(1)	0.068
C25	-0.0061(4)	-0.2536(2)	0.2326(2)	0.076
C26	0.0202(6)	-0.3038(3)	0.3023(2)	0.104
C27	0.2199(6)	-0.2697(3)	0.3470(2)	0.091
C28	0.3976(4)	-0.1876(2)	0.3224(1)	0.069

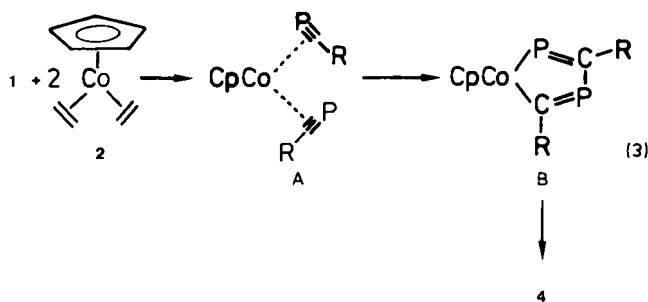
with partial double bond character of these bonds in four-membered ring systems^{5b,22}. The same observation has been made in η^4 -cyclobutadiene metal complexes²³ and is in line with the anticipated bond order. In contrast to cyclobutadiene complexes, both rings are slightly folded (8°), and the cyclic angles are grouped into two categories. Whereas the C-P-C angles are acute (average 80°), the P-C-P angles are 99° . The *tert*-butyl groups, bonded with standard sp^2 - sp^3 bond distances at the cyclic carbon atoms, are bent by $4-6^\circ$ out of the mean cyclobutadiene plane, pointing away from the metal²⁴.

In compound **5a** the cobalt atom is coordinated to the indenyl ligand as in similar indenyl metal compounds²⁵. The Co-C distances to three adjacent carbon atoms (C-22, C-23, and C-24) of the five-membered ring are about 0.1 \AA shorter than to C-20 and C-21 indicating that the bonding of the indenyl residue to cobalt lies between an η^5 - and η^3 -arrangement (Figure 3). Steric interference of a *tert*-butyl group at atom C-6 with the six-membered indenyl ring causes not only an interplanar folding of 6.5° along C-20/C-21, but also a slight deviation from linearity (4.4°) of the cobalt complexation. These distortions from ideal arrangement are evident from the side view of the molecule given in Figure 4.

Discussion

The cyclodimerization of λ^3 -phosphaalkynes to form the (1,3-diphospha-cyclobutadiene)cobalt complexes **4** and **5** in

principle confirms the analogy often mentioned in the literature between the chemical properties of these compounds and alkynes^{3b,26,27}. When examined in more detail, however, there are also significant differences, which result in the products of **2** or **3** with **1** differing from those of their reaction with alkynes. For example, as a rule when dialkylacetylenes undergo coupling reactions on cobalt starting from **2** or **3** no (cyclobutadiene)cobalt complexes are formed. These are produced only when alkynes with bulky groups are used, e.g., bis(trimethylsilyl)acetylene^{13,17,28}. Otherwise, depending upon the reaction conditions, cyclotrimerization to benzene derivatives or co-cyclotrimerization to (1,3-cyclohexadiene)cobalt complexes takes place¹⁶. As far as the formation of (1,3-diphosphacyclobutadiene)cobalt complexes is concerned, it can be assumed that first a di(π -phosphaalkyne)cobalt complex **A** is formed in which coupling occurs to give a 1-cobalta-2,4-diphosphacyclopentadienyl complex **B**, which in turn undergoes reductive elimination to give the product **4** or **5**.



An analogous sequence of reactions is thought to take place when (cyclobutadiene)cobalt complexes or benzene derivatives are formed from alkynes^{16,29}. In contrast to the dimerization of phosphaalkynes, in the cyclization of alkynes the reaction of a third alkyne molecule with the cobalt complex **B** is generally faster than the reductive elimination. (η^5 -Cyclopentadienyl)cobaltacyclopentadienyls have as yet only been isolated in the presence of triphenylphosphane³⁰. On heating with ethylene³¹ or alkynes^{28,30,32}, these compounds can react further to complete the cyclotrimerization, but heating the pure (η^5 -cyclopentadienyl)(triphenylphosphane)cobaltacyclopentadiene affords (η^4 -cyclobutadiene)(η^5 -cyclopentadienyl)cobalt³¹.

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Experimental

All experiments were carried out under argon in dried solvents. — MS³³: Varian CH-5 at 70 eV. — ¹H NMR: Bruker AM 200; WH 400 (internal standard TMS). — ¹³C NMR: Bruker WM 300 (standard TMS). — ³¹P NMR: Bruker WP 80 or WM 300 (external standard H₃PO₄). — Elemental analyses: Dornis and Kolbe, Mülheim a. d. Ruhr.

The following compounds were prepared by literature methods: 2-*tert*-butyl-1-phosphaacetylene [(2,2-dimethylpropylidene)phosphane (**1a**)]^{3a}; 2-isopropyl-1-phosphaacetylene [(2-methylpropylidene)phosphane (**1b**)]^{3b}; (η^5 -cyclopentadienyl)bis(ethylene)cobalt (**2**)¹² and bis(ethylene)(η^5 -indenyl)cobalt (**3**)¹³.

(η^5 -Cyclopentadienyl)(η^4 -2,4-di-*tert*-butyl-1,3-diphosphacyclobutadiene)cobalt (**4a**): 2.0 g (20 mmol) of **1a** dissolved in 10 ml of ether/pentane (1:1) was added dropwise over 1 h to a red-brown solution of 1.4 g (7.8 mmol) of **2** in 20 ml of ether/pentane at -30°C . After stirring for 1 h at -5°C , all volatile materials were removed at 10^{-3} Torr. The crystalline residue was dissolved in 10 ml of pentane, the solution kept at -78°C for 12 h, and the supernatant liquid drawn off the crystals that had precipitated with a glass frit. After drying at 10^{-3} Torr, the yield of wine red crystals of **4a** was 1.7 g (67%), m.p. 54°C . — MS: m/z (%) = 324 (96, M^+ for ⁵⁹Co); 262 (100, $M^+ - P_2$); 186 (51, CpCoP₂); 124 (69, CpCo). — ¹H NMR ([D₈]toluene, 400 MHz): δ = 4.92 (s, 5H); 0.91 (s, 18H). — ³¹P and ¹³C NMR: see Table 2.

C ₁₅ H ₂₃ CoP ₂ (324.2)	Calcd. C 55.57 H 7.15 Co 18.18
	Found C 55.80 H 7.03 Co 18.10

(η^5 -Cyclopentadienyl)(η^4 -2,4-di-isopropyl-1,3-diphosphacyclobutadiene)cobalt (**4b**): A solution of 1.5 g (15 mmol) of **1b** in 10 ml of THF was added dropwise to a solution of 1.0 g (5.56 mmol) of **2** in 20 ml of THF at -5°C over 10 min and stirred for 1 h at the same temperature. All volatile components were removed at 10^{-3} Torr, the red oily residue was dissolved in pentane, and the insoluble components were filtered off in a 5-cm column filled with Florisil. After the pentane had been removed by evaporation followed by pumping at 10^{-3} Torr, **4b** was obtained as a red oil, 1.27 g (80%). — MS: see Table 1. — ¹H NMR (C₆D₆, 400 MHz): δ = 4.92 (s, 5H); 1.21 (m, 2H); 0.82 (d, J = 6.5 Hz, 12H). — ³¹P and ¹³C NMR: see Table 2.

C ₁₃ H ₁₉ CoP ₂ (296.1)	Calcd. C 53.63 H 4.85 Co 20.24
	Found C 53.49 H 4.74 Co 19.89

(η^4 -2,4-Di-*tert*-butyl-1,3-diphosphacyclobutadiene)(η^5 -indenyl)-cobalt (**5a**): 0.54 g (10 mmol) of 2-butyne was added to a solution of 0.50 g (2.17 mmol) of **3** in 25 ml of ether at -30°C . The solution was stirred as 0.40 g (4.0 mmol) of **1a** in 10 ml of ether was added at 0°C over 0.5 h. All volatile components were drawn off the dark red solution at 0.01 Torr, and the red oil that was left was dissolved in 35 ml of pentane and fractionated by chromatography on a 6-cm Al₂O₃ column. The initial eluent was colourless; by evaporation of the solvent from this fraction 0.1 g of hexamethylbenzene was obtained with m.p. 166°C (lit. 166°C); the mass and ¹H-NMR spectra were identical with those of an authentic sample). The following red fraction was cooled to -78°C , causing **5a** to precipitate as feathery red crystals. These were freed of pentane with a glass frit and were dried at 10^{-3} Torr. Yield 0.77 g (95%), m.p. 52°C . — MS: m/z (%) = 374 (47, M^+ for ⁵⁹Co); 312 (40, $M^+ - P_2$); 236 (100, C₉H₇CoP₂); 174 (65, C₉H₇Co); 115 (41). — ¹H NMR (C₆D₆, 400 MHz): δ = 7.36 (m, 2H); 6.81 (m, 2H); 5.70 (d, J = 2.7 Hz, 2H); 4.88 (t, J = 2.7 Hz, 1H); 0.82 (s, 18H). — ³¹P and ¹³C NMR (see Table 2).

C ₁₉ H ₂₅ CoP ₂ (374.3)	Calcd. C 60.97 H 6.73 Co 15.75
	Found C 60.68 H 6.68 Co 15.78

Comments: a) The same results are obtained when 2-butyne is added to **3** at the same time as **1a**. b) When **5a** is prepared as above but without adding 2-butyne, the yield of **5a** is 85%.

(η^4 -2,4-Diisopropyl-1,3-diphosphacyclobutadiene)(η^5 -indenyl)-cobalt (**5b**): 1.5 ml of 2-butyne was added to a solution of 1.0 g (4.35 mmol) of **3** in 15 ml of toluene at -30°C . A solution of 1.0 g (11.63 mmol) of **1b** in diethyl ether cooled to -78°C was then added dropwise to the first solution at 0°C over 10 min. After stirring for 1 h all volatile components were removed at 10^{-3} Torr. The residue was dissolved in 15 ml of pentane/diethyl ether (1:1), the solution filtered over Celit and kept at -78°C for 48 h. The solvent was

drawn off the cubic red crystals which had formed with a long pipette and the crystals were dried in a high vacuum (10^{-3} Torr): Yield 1.15 g (95%), m.p. 42°C . — MS: m/z (%) = 346 (96, M^+ for ^{59}Co); 331 (16); 284 (24, $\text{M}^+ - \text{P}_2$); 236 (100, $\text{C}_9\text{H}_7\text{CoP}_2$); 174 (64 $\text{C}_9\text{H}_7\text{Co}$); 115 (37). — ^1H NMR (C_6D_6 , 400 MHz): δ = 7.17 (m, 2H); 6.77 (m, 2H); 5.93 (d, J = 2.7 Hz, 2H); 4.45 (t, J = 2.7 Hz, 1H); 0.88 (m, 2H); 0.69 (d, J = 9.7 Hz, 12H). — ^{31}P and ^{13}C NMR: see Table 2.

$\text{C}_{17}\text{H}_{21}\text{CoP}_2$ (346.2) Calcd. C 58.97 H 6.11 Co 17.02
Found C 58.78 H 6.03 Co 16.89

Comment: Without 2-butyne this preparation yields 80% **5b**.

(η^5 -Cyclopentadienyl)[(η^5 -cyclopentadienyl)ethenecobalt]- μ -(η^4 -2,4-di-tert-butyl-1,3-diphosphacyclobutadiene)cobalt (**6a**): 0.60 g (3.4 mmol) of **2**, dissolved in 15 ml of diethyl ether/pentane (1:1), was added dropwise over 0.5 h at 0°C to a wine-red solution of 1.1 g (3.4 mmol) of **4a** in 25 ml of diethyl ether/pentane (1:1), producing a darkening of the reaction solution. After stirring for 1 h at 0°C all volatile components were pumped off at 10^{-3} Torr, the residual brown solid was dissolved in diethyl ether, the solution filtered over Florisil and kept at -78°C for 36 h. The supernatant liquid was removed with a glass frit from the fine red needles that had formed, and the product was dried at 10^{-3} Torr, yielding 1.03 g of **6a** (64%), m.p. 125°C (decomp.). — MS: m/z (decomp.) = 391; 324; 262; 186; 124. — ^1H NMR ($[\text{D}_8]$ toluene, 400 MHz): δ = 4.84 (s, 5H); 4.62 (s, 5H); 2.67 (m, J_{HH} = 11.8, J_{PH} = 2.7 Hz, 2 ethene-H); 2.06 (m, J_{HH} = 11.8, J_{PH} = 8.6 Hz, 2 ethene-H); 1.01 (s, 18H). — ^{31}P and ^{13}C NMR: see Table 2.

$\text{C}_{22}\text{H}_{32}\text{Co}_2\text{P}_2$ (476.3) Calcd. C 55.48 H 6.77 Co 24.75
Found C 55.31 H 6.69 Co 24.58

Comment: **6a** can also be prepared directly in ca. 50% yield when the mol ratio of **2** and **1a** in the preparation of **4a** is changed to 1:1. In this case, however, the formation of **4a** cannot be avoided. **4a** and **6a** can be separated by chromatography on an Al_2O_3 column: with toluene as liquid phase **4a** is eluted selectively, and then **6a** can be obtained.

(η^5 -Cyclopentadienyl)bis[(η^5 -cyclopentadienyl)ethenecobalt]- μ -(η^4 -2,4-di-tert-butyl-1,3-diphosphacyclobutadiene)cobalt (**7a**): A wine-red solution of 1.5 g (4.7 mmol) of **4a** in 25 ml of diethyl ether/pentane (1:1) was mixed at 0°C with 1.7 g (9.4 mmol) of **2** dissolved in 20 ml of diethyl ether/pentane (1:1), causing the precipitation of a red-brown solid. All volatile components were pumped off at 10^{-3} Torr, the residue was dissolved in 50 ml of diethyl ether and the solution kept at -78°C for 24 h. After the supernatant liquid had been removed with a glass frit from the red-brown crystals that had precipitated, these were dried at 10^{-3} Torr at room temperature. Yield 1.14 g (50%), m.p. 135°C (decomp.). — MS: m/z (decomp.) = no M^+ ; 572; 472; 324; 262; 189; 124. — ^1H NMR ($[\text{D}_8]$ toluene; 400 MHz): δ = 4.88 (s, 5H); 4.57 (s, 10H); 2.81 (m, 4H); 2.04 (m, 4H); 1.15 (s, 18H). — ^{31}P and ^{13}C NMR: see Table 2.

$\text{C}_{29}\text{H}_{41}\text{Co}_3\text{P}_2$ (628.4) Calcd. C 55.43 H 6.58 Co 28.13
Found C 55.02 H 6.25 Co 27.94

(η^5 -Cyclopentadienyl)bis[(η^5 -cyclopentadienyl)ethenecobalt]- μ -(η^4 -2,4-di-isopropyl-1,3-diphosphacyclobutadiene)cobalt (**7b**): 0.48 g (5.6 mmol) of **1b** in 5 ml of diethyl ether/pentane (1:1) was added dropwise over 10 min to a solution of 1.5 g (8.4 mmol) of **2** in 5 ml of diethyl ether/pentane (1:1) at -5°C . After stirring for another 10 min to allow further reaction, all volatile components were pumped off at 10^{-2} Torr, the residue was dissolved in 10 ml of toluene and the solution filtered over Celit. On addition of 5 ml of pentane **7b** crystallized. After filtration and drying at 10^{-3} Torr brown crystals [1.42 g (85%)] were obtained. M.p. 72°C

(decomp.). — MS: m/z (decomp.) = no M^+ ; 544; 434 ($\text{C}_9\text{Co}_3\text{P}_2$); 296; 243; 189 (C_9Co); 124. — ^1H NMR ($[\text{D}_8]$ toluene, 400 MHz): δ = 4.85 (s, 5H), 4.56 (s, 10H), 1.48 (m, J = 6.8 Hz, 2H); 1.07 (d, J = 6.8 Hz, 12H); 2.02 (m, J_{PH} = 8.2 Hz, 4H); 2.64 (m, J_{PH} = 0, 4H). — ^{31}P NMR (C_6D_6 , 32.4 MHz): δ = 93.2 (s).

$\text{C}_{27}\text{H}_{37}\text{Co}_3\text{P}_2$ (600.3) Calcd. C 54.02 H 6.21 Co 29.45
Found C 53.90 H 6.15 Co 28.94

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1a: 78129-68-7 / **1b**: 101055-68-9 / **2**: 69393-67-5 / **3**: 98704-29-1 / **4a**: 105267-82-1 / **4b**: 111662-48-7 / **5a**: 111662-49-8 / **5b**: 111662-50-1 / **6a**: 109885-86-1 / **6b**: 111662-52-3 / **7a**: 109851-60-7 / **7b**: 111662-51-2

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[268/87]