

Single and double π -alkyne coordination in oxidation–reduction equilibria of low-valent trimethylphosphinecobalt complexes: spontaneous formation of a mixed valence dicobalttetrahedrane core in the structure of $\text{Co}_2\text{Cl}(\mu_2\text{-Me}_3\text{E-C}\equiv\text{C-C}\equiv\text{C-EMe}_3)\text{(PMe}_3)_4$ (E = Si, C)

Hans-Friedrich Klein*, Markus Schwind

Eduard-Zintl-Institut für Anorganische Chemie, Technische Hochschule Darmstadt, Hochschulstrasse 10, D-6100 Darmstadt (Germany)

Ulrich Flörke and Hans-Jürgen Haupt

Anorganische und Analytische Chemie der Universität/GH Paderborn, Warburger Strasse 100, D-4790 Paderborn (Germany)

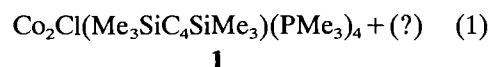
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Abstract

Neutral dicobalttetrahedrane complexes $\text{Co}_2\text{Cl}(\mu_2\text{-Me}_3\text{E-C}\equiv\text{C-C}\equiv\text{C-EMe}_3)\text{(PMe}_3)_4$ (E = Si (1), C (2), Ge (3)) containing cobalt(0) and cobalt(I) have been isolated from oxidation–reduction equilibria. Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.747(2)$, $b = 12.140(4)$, $c = 16.111(5)$ Å, $\alpha = 97.29(2)$, $\beta = 95.72(2)$, $\gamma = 103.70(2)^\circ$, $V = 1820.5$ Å³, $Z = 2$. Final discrepancy indices are $R = 0.064$ and $R_w = 0.044$ for 3110 independent data ($F > 4\sigma(F)$). The structure has a Co_2C_2 tetrahedrane core formed by double π -coordination of one alkyne function to Co–Co connected $\text{Co}(\text{PMe}_3)_3$ and $\text{CoCl}(\text{PMe}_3)$ fragments giving a 33-electron count for the tetrahedrane unit. ESR spectra (toluene solution at 298 K) suggest the unpaired electron to reside at the $\text{Co}(\text{PMe}_3)_3$ site in a metal orbital. Diphenylbutadiyne exclusively forms diamagnetic $\text{CoCl}(\eta^2\text{-PhC}\equiv\text{CC}\equiv\text{CPh})\text{(PMe}_3)_3$ (**4**) while with $\text{Me}_3\text{CC}\equiv\text{CC}\equiv\text{CCMe}_3$ both types of complexes are observed. Under 1 bar carbon monoxide, **1** is transformed to mononuclear carbonyl(trimethylphosphine)cobalt compounds and diyne is liberated.

Introduction

Dimetal tetrahedranes $\text{Co}_2(\text{CR}^1\equiv\text{CR}^2)(\text{CO})_{6-n}\text{L}_n$ ($\text{R}^1, \text{R}^2 = \text{alkyl, aryl, trialkylsilyl}$; $\text{L} = \text{PR}_3, \text{P}(\text{OR})_3, \text{AsR}_3$; $n = 0, 1, 2$) are synthesized from carbonylcobalt(0) compounds and symmetric or asymmetric alkynes $\text{R}^1\text{C}\equiv\text{CR}^2$ preserving an 18-electron count in cobalt valence-shells. Such syntheses have been performed with a great variety of alkyne substituents and donor ligands [1]. By contrast the number of isolated cobalt(I) compounds containing alkyne ligands is restricted because of subsequent cyclotrimerization reactions that usually yield a number of products but no compound with a tetrahedrane core Co_2C_2 [2–4]. Although single-electron oxidation of Co_2C_2 compounds has been demonstrated [5], to our knowledge no cobalt(I) compound with this structural feature has been described. Therefore we were surprised by a spontaneous formation of the title compound **1** from cobalt(I) and a butadiyne according to eqn. (1) but also in different stoichiometries with lower yields.



At first the fate of reduction equivalents or half of the chloride ligands, respectively, remained an open question, because several byproducts were formed as an intractable oil. However, yields of **1** were easily optimized by adjusting the stoichiometry for the average oxidation state of cobalt(+1/2). In this contribution we describe the syntheses and properties of related butadiynecobalt complexes including 18-electron species of cobalt(I) with η^2 -coordinated diyne.

Experimental

All air-sensitive and volatile material was handled in a closed glass apparatus either *in vacuo* or under argon. New compounds were characterized by spectroscopic techniques as described earlier [6]. ESR spectra were recorded on a Varian E3 spectrometer using

*Author to whom correspondence should be addressed.

internal frequency calibration by a Hall probe. Microanalyses (C, H by combustion) were obtained by Dornis & Kolbe, Microanalytical Laboratory, D-4100 Mülheim. Starting materials were prepared by literature methods: $\text{CoCl}(\text{PMe}_3)_3$ [7], $\text{Co}(\text{cyclo-C}_5\text{H}_8)(\text{PMe}_3)_3$ [8], $\text{Me}_3\text{EC}\equiv\text{CC}\equiv\text{CEMe}_3$ (E = C [9], Si [10], Ge [11]), $\text{PhC}\equiv\text{CC}\equiv\text{CPh}$ [12].

Preparations

Chlorotetrakis(trimethylphosphine)

bis(trimethylsilyl)butadiyne-dicobalt (1)

(a) 540 mg $\text{CoCl}(\text{PMe}_3)_3$ (1.67 mmol) in 60 ml of THF were combined at -70°C with 162 mg of bis(trimethylsilyl)butadiyne (0.83 mmol) in 15 ml of THF. Upon warming to 20°C the violet solution turned dark green within 30 min. The volatiles were removed *in vacuo* to give a dark green oil that partly solidified after 30 min at 20°C . The residue was dissolved in 30 ml pentane, filtered and crystallized at -70°C . After 72 h dark green needles were isolated by decantation, washing with cold pentane and drying *in vacuo*. Yield 130 mg (24% based on diyne).

(b) 510 mg $\text{Co}(\text{cyclo-C}_5\text{H}_8)(\text{PMe}_3)_3$ (1.44 mmol) in 80 ml of THF were reacted at -70°C with 62 mg CoCl_2 (0.48 mmol) and 186 mg of bis(trimethylsilyl)butadiyne (0.96 mmol). The dark green mixture was warmed to 20°C and kept stirring for 24 h. The volatiles were removed *in vacuo* and the dark brown residue was extracted with 30 ml pentane over a glass-sinter disc (G 3). Cooling over dry-ice afforded green needles that were dried *in vacuo* at 20°C . A specimen was found suitable for X-ray diffraction. Yield 422 mg (68% based on diyne), m.p. $153\text{--}154^\circ\text{C}$.

Anal. Calc. for $\text{C}_{22}\text{H}_{54}\text{ClCo}_2\text{P}_4\text{Si}_2$ (652.1): C, 40.52; H, 8.35; P, 19.00. Found: C, 40.47; H, 8.17; P, 18.64%.

IR (nujol solution, $4000\text{--}400\text{ cm}^{-1}$): 2090s $\nu\text{C}\equiv\text{C}$; 1245s $\delta_s\text{SiCH}_3$; 840s ρSiCH_3 ; 520w νCoC ; 1295m, 1280m, 940s, 760m, 720s, 700m, 660s (PMe_3).

Chloro(2,2,7,7-tetramethyloctadiyne-

3,5)tetrakis(trimethylphosphine)-dicobalt (2)

(a) 483 mg $\text{CoCl}(\text{PMe}_3)_3$ (1.50 mmol) and 207 mg $\text{Me}_3\text{CC}\equiv\text{CC}\equiv\text{CCMe}_3$ (1.28 mmol) were combined at -70°C in 50 ml of THF. Upon warming to 20°C the dark green solution turned red. After 12 h the volatiles were removed *in vacuo* and the red-brown oil was dissolved in 30 ml pentane. Filtering and cooling to -30°C afforded green needles. Yield 30 mg (3%), m.p. $140\text{--}141^\circ\text{C}$. The major product (610 mg) remained as a red oil.

(b) 598 mg $\text{Co}(\text{cyclo-C}_5\text{H}_8)(\text{PMe}_3)_3$ (1.68 mmol) in 75 ml of THF were combined with 82 mg CoCl_2 (0.63 mmol) and 165 mg $\text{Me}_3\text{CC}\equiv\text{CC}\equiv\text{CCMe}_3$ (1.02 mmol). After 24 h at 20°C workup as above and crystallization from 40 ml pentane gave dark green needles. Yield 320 mg (51% based on diyne), m.p. $140\text{--}141^\circ\text{C}$.

Anal. Calc. for $\text{C}_{24}\text{H}_{54}\text{ClCo}_2\text{P}_4$ (619.9): C, 46.50; H, 8.78. Found: C, 46.29; H, 8.53%.

IR (nujol solution, $2600\text{--}1600\text{ cm}^{-1}$) 2: 2180m $\nu\text{C}\equiv\text{C}(\text{free})$. Red oil: 2180m $\nu\text{C}\equiv\text{C}(\text{free})$; 1730m $\nu\text{C}\equiv\text{C}(\pi\text{-coord.})$. 2,2,7,7-tetramethylbutadiyne-3,5: 2190w, 2150m $\nu\text{C}\equiv\text{C}$.

Chloro(diphenylbutadiyne)tris(trimethylphosphine)-cobalt (4)

595 mg $\text{CoCl}(\text{PMe}_3)_3$ (1.84 mmol) and 374 mg $\text{PhC}\equiv\text{CC}\equiv\text{CPh}$ (1.85 mmol) were combined in 80 ml of THF at -70°C and the violet mixture was allowed to warm to 20°C . After 12 h a red-brown solution was filtered and concentrated to 30 ml *in vacuo*. Crystallization at -20°C after 10 days afforded red-brown needles. Yield 950 mg (98% based on cobalt), decomp. $>89^\circ\text{C}$.

Anal. Calc. for $\text{C}_{25}\text{H}_{37}\text{ClCoP}_3$ (524.9): C, 57.21; H, 7.11; P, 17.70. Found: C, 56.87; H, 6.74; P, 16.93%.

$^1\text{H NMR}$ (300 MHz, $d_8\text{-THF}$, 308 K, TMS external reference, δ): $\delta(\text{PCH}_3)$ 1.1 (d, 27 H, $^2J(\text{PH})$ 6.0 Hz), $\delta(\text{CH})$ 7.3 (m, 10 H).

TABLE 1. Crystal data and details of data collection and structure refinement

	1
Formula	$\text{C}_{22}\text{H}_{54}\text{ClCo}_2\text{P}_4\text{Si}_2$
Formula weight	652.1
Crystal dimensions (mm)	$0.09 \times 0.16 \times 0.75$
Crystal system	triclinic
Space group	$P\bar{1}$
<i>a</i> (Å)	9.747(2)
<i>b</i> (Å)	12.140(4)
<i>c</i> (Å)	16.111(5)
α (°)	97.29(2)
β (°)	95.72(2)
γ (°)	103.70(2)
<i>V</i> (Å ³)	1820.5
<i>Z</i>	2
<i>D</i> _{calc} (g/cm ³)	1.189
$\lambda(\text{Mo K}\alpha)$ (Å)	0.71073
μ (mm ⁻¹)	1.23
<i>F</i> (000)	690
Scan method	$\omega\text{-}2\theta$
Scan velocity (°/min)	2.9
Data collection range (°)	$3 \leq 2\theta \leq 55$ $-12 \leq h \leq 12$ $-15 \leq k \leq 15$ $0 \leq l \leq 20$
No. reflections measured	9309
No. unique data ($F > 4\sigma(F)$)	3110
No. parameters refined	281
<i>R</i>	0.0647
<i>R</i> _w ^a	0.0439
Max. (Δ/σ)	0.001
Residuals min./max. ($e/\text{Å}^3$)	$-0.50/0.61$

^a $1/w = \sigma^2(F) + 0.0001F^2$.

IR (nujol mull, 2600–1600 cm^{-1}): 2130 vs $\nu\text{C}\equiv\text{C}(\text{free})$; 1760 m $\nu\text{C}\equiv\text{C}(\text{coord.})$.

Reaction of 1 with excess carbon monoxide

500 mg **1** (0.77 mmol) in 60 ml of pentane gave a deep green solution that under 1 bar CO within 6 h at 20 °C turned dark red depositing a yellow solid. This was isolated by filtration, washed with refluxing pentane, and dried *in vacuo* to give 224 mg $\text{CoCl}(\text{CO})_2(\text{PMe}_3)_2$ [7] (0.74 mmol, 96%). The filtrate was evaporated to dryness affording 197 mg of red $\text{Co}_2(\text{CO})_4(\text{PMe}_3)_4$ [7] (0.36 mmol, 94%).

Single crystal X-ray analysis

The crystal was sealed in a capillary under argon and mounted on a Nicolet R3m/V diffractometer. Cell dimensions (Table 1) were refined from 25 reflections $10 \leq 2\theta \leq 25^\circ$. A total of 9309 intensities was collected in the range $3 \leq 2\theta \leq 55^\circ$, and Lp and empirical absorption corrections (via ψ -scans) were applied. Merging equivalents gave 8414 independent reflections ($R_{\text{int}} = 0.026$), of which 3110 were considered observed with $F > 4\sigma(F)$. The structure was solved by Patterson and conventional Fourier methods. Full-matrix least-squares refinement with all non-hydrogen atoms an-

TABLE 2. Selected bond lengths (Å) and angles (°)

Co(1)–Co(2)	2.473(1)	Co(1)–P(1)	2.196(2)
Co(1)–P(2)	2.206(2)	Co(1)–P(3)	2.196(2)
Co(1)–C(1)	1.957(6)	Co(1)–C(2)	1.934(6)
Co(2)–Cl	2.213(2)	Co(2)–P(4)	2.316(2)
Co(2)–C(1)	1.985(7)	Co(2)–C(2)	1.951(5)
Si(1)–C(1)	1.838(7)	Si(2)–C(4)	1.808(7)
C(1)–C(2)	1.373(9)	C(2)–C(3)	1.421(9)
C(3)–C(4)	1.199(9)		
Co(2)–Co(1)–P(1)	97.6(1)	Co(2)–Co(1)–P(2)	98.3(1)
Co(2)–Co(1)–P(3)	150.3(1)	Co(2)–Co(1)–C(1)	51.7(2)
Co(2)–Co(1)–C(2)	50.8(2)	P(1)–Co(1)–P(2)	100.8(1)
P(1)–Co(1)–P(3)	100.4(1)	P(1)–Co(1)–C(1)	139.8(2)
P(1)–Co(1)–C(2)	100.5(2)	P(2)–Co(1)–P(3)	101.2(1)
P(2)–Co(1)–C(1)	108.2(2)	P(2)–Co(1)–C(2)	144.4(2)
P(3)–Co(1)–C(1)	100.6(2)	P(3)–Co(1)–C(2)	102.5(2)
C(1)–Co(1)–C(2)	41.3(3)	Co(1)–Co(2)–Cl	118.8(1)
Co(1)–Co(2)–P(4)	137.1(1)	Co(1)–Co(2)–C(1)	50.6(2)
Co(1)–Co(2)–C(2)	50.2(2)	Cl–Co(2)–P(4)	98.4(1)
Cl–Co(2)–C(1)	123.1(2)	Cl–Co(2)–C(2)	163.2(2)
P(4)–Co(2)–C(1)	125.3(2)	P(4)–Co(2)–C(2)	97.1(2)
C(1)–Co(2)–C(2)	40.8(3)	Co(1)–C(1)–Co(2)	77.7(3)
Co(1)–C(1)–Si(1)	154.4(4)	Co(1)–C(1)–C(2)	68.4(4)
Co(2)–C(1)–Si(1)	122.7(3)	Co(2)–C(1)–C(2)	68.2(4)
Si(1)–C(1)–C(2)	130.9(5)	Co(1)–C(2)–Co(2)	79.1(2)
Co(1)–C(2)–C(1)	70.2(4)	Co(1)–C(2)–C(3)	140.6(4)
Co(2)–C(2)–C(1)	70.9(3)	Co(2)–C(2)–C(3)	130.5(5)
C(1)–C(2)–C(3)	137.3(6)	C(2)–C(3)–C(4)	177.4(8)
Si(2)–C(4)–C(3)	175.6(7)		

TABLE 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^3$) for **1**

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Co(1)	2523(1)	1324(1)	2658(1)	43(1)
Co(2)	606(1)	2123(1)	2055(1)	49(1)
Cl	–1609(2)	1042(2)	1830(2)	99(1)
P(1)	3286(2)	802(2)	1469(1)	59(1)
P(2)	1188(3)	–332(2)	2865(2)	83(1)
P(3)	4438(3)	1503(2)	3559(2)	69(1)
P(4)	361(2)	3380(2)	1116(2)	69(1)
Si(1)	1234(3)	3383(2)	4081(2)	69(1)
Si(2)	5568(3)	6035(2)	2096(2)	75(1)
C(1)	1761(7)	2551(6)	3188(5)	45(3)
C(2)	2551(7)	2901(6)	2566(4)	41(3)
C(3)	3480(8)	3927(7)	2414(5)	49(4)
C(4)	4277(8)	4768(7)	2258(5)	57(4)
C(11)	1979(9)	545(8)	528(5)	102(5)
C(12)	3972(9)	–483(7)	1299(5)	89(5)
C(13)	4766(9)	1862(7)	1175(6)	97(5)
C(21)	2002(10)	–1393(8)	3287(8)	160(8)
C(22)	65(10)	–1295(7)	1926(7)	149(6)
C(23)	–153(9)	–278(8)	3566(6)	110(5)
C(31)	4118(11)	1430(10)	4665(5)	156(8)
C(32)	5637(8)	555(7)	3468(5)	87(5)
C(33)	5698(9)	2883(7)	3680(7)	131(6)
C(41)	–1382(8)	3058(8)	493(6)	119(6)
C(42)	627(9)	4882(7)	1571(6)	92(5)
C(43)	1555(9)	3503(8)	304(5)	99(5)
C(51)	19(14)	4165(11)	3703(7)	218(11)
C(52)	2735(12)	4405(11)	4678(9)	261(10)
C(53)	321(15)	2509(10)	4797(7)	228(11)
C(61)	7281(10)	5732(9)	2106(11)	266(13)
C(62)	5044(13)	6463(9)	1061(7)	188(9)
C(63)	5640(12)	7249(8)	2909(7)	152(7)

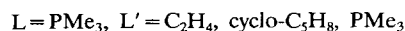
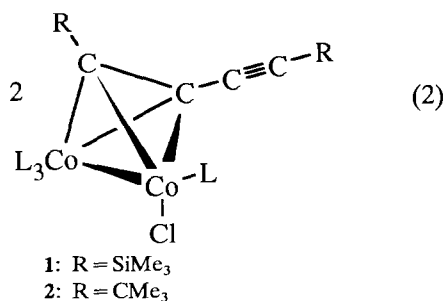
Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

sotropic. Hydrogen atoms were fixed at idealized positions. Anisotropic displacement parameters of methyl groups C21, C22, C33, and C51–C63 indicate some degree of disorder which could not be resolved, however. Refinement converged smoothly at $R = 0.064$, $R_w = 0.044$. Further results are given in Table 1. Bond lengths and angles are given in Table 2; atomic coordinates and equivalent isotropic displacement coefficients in Table 3. Scattering factors and structure refinement were from SHELXTL-Plus (Siemens 1990).

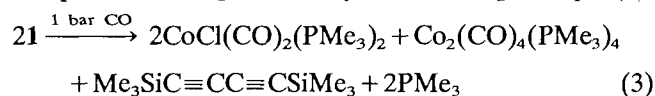
Results

Syntheses and properties

In an optimized synthesis cobalt(0) and cobalt(II) materials in the presence of an alkyne undergo an oxidation–reduction process according to eqn. (2) smoothly affording dinuclear compounds **1** and **2**.

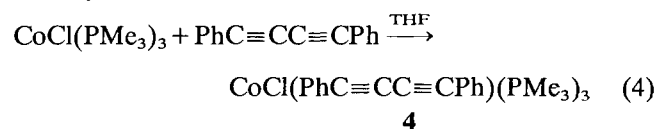


From pentane bunches of dark green needles (**1**) are obtained that melt at 154–155 °C under argon with slow decomposition. At 20 °C in air the crystals retain their shining surface for 10 min before oxidation visibly proceeds that instantaneously occurs in pentane or ether if air is admitted. Under argon in refluxing benzene (or toluene) no decomposition was observed, but under carbon monoxide the cobalt(I) fragment is quantitatively split off the tetrahedrane core of **1** as a mononuclear complex liberating the dialkyne according to eqn. (3).



The dark green crystals of **2** melt at 140–141 °C with slow decomposition. Yields of 50% are achieved in the correct stoichiometry of eqn. (1). In a 1:1 ratio only traces of **2** are isolated while a red oil as main product displays IR bands as expected for complex $\text{CoCl}(\eta^2\text{-Me}_3\text{CC}\equiv\text{CC}\equiv\text{CCMe}_3)(\text{PMe}_3)_3$. Synthesis and properties of the germanium compound **3** closely resemble those of **1**, and no mononuclear cobalt(I) species has been obtained from a 1:1 reaction.

With diphenylbutadiyne this tendency is reversed as no mixed-valence tetrahedrane cluster could be detected. Syntheses in all attempts afforded diamagnetic **4** with optimum yields according to eqn. (4). In a 2:1 reaction no evidence for double π -coordination of the butadiyne was found.



ESR spectra of **1** and **2** (1% in toluene, 298 K) show hyperfine couplings that originate from ⁵⁹Co nuclei ($I=7/2$) coupled to a single electron. Three g values and 24 lines are expected for one ⁵⁹Co nucleus in the absence of ³¹P coupling, but less than 16 lines are resolved in the spectra of **1** and **2** (Fig. 1). The data extracted in a first approximation would be consistent

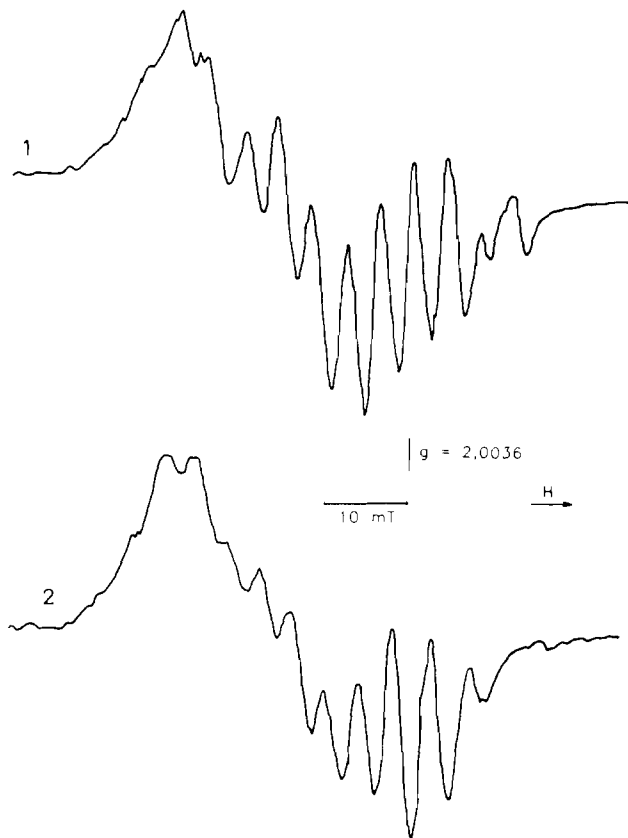


Fig. 1. ESR spectra of **1** and **2** (0.1% in toluene, 298 K). **1**: $g_1=2.022$ ($A_1=4.5$ mT), $g_2=2.029$ ($A_2=3.6$ mT), $g_3=2.116$ ($A_3=4.9$ mT). **2**: $g_1=2.009$ ($A_1=4.3$ mT), $g_2=2.010$ ($A_2=4.5$ mT), $g_3=2.135$ ($A_3=4.8$ mT).

with the unpaired electron residing in a molecular orbital that is centered on the metal at the $\text{Co}(\text{PMe}_3)_3$ site. Accordingly no radical reactions such as hydrogen abstraction from toluene or polymerization of styrene could be initiated by **1** or **2**.

Molecular structure of complex **1**

The paramagnetic valence state of dicobalt compounds **1–3** and the lack of characteristic IR bands of coordinated alkyne functions suggested structural investigation as the most informative method.

A suitable crystal of **1** grown from pentane was subjected to an X-ray crystal structure determination. The crystal structure consists of isolated molecules (Fig. 2) with the Co_2C_2 core of a dicobalttetrahedrane. The metal–metal distance (2.473(1) Å) and the bond length of the tetrahedral C1–C2 edge (1.373(9) Å) do not significantly exceed the narrow range of other dicobalttetrahedranes ($\text{Co–Co}=2.45\text{–}2.49$ Å, $\text{C–C}=1.32\text{–}1.37$ Å [1]). There is no significant difference in Co–C bond lengths for both cobalt atoms and the tetrahedral edges Co–Co and C–C point in perpendicular directions. The C–C edge forms the angles

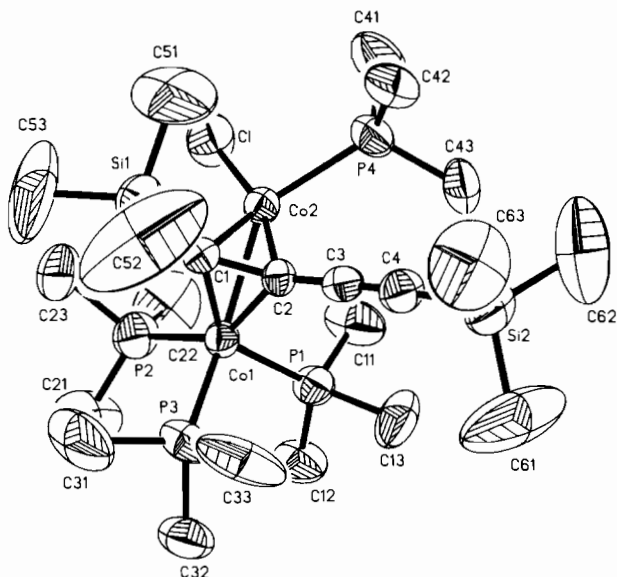


Fig. 2. Molecular structure of **1** (ORTEP plot).

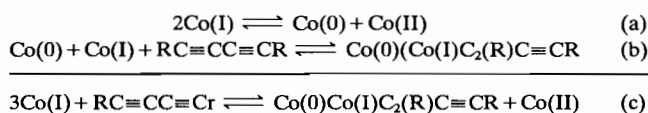
$\text{Si1-C1-C2} = 130.9(5)^\circ$ and $\text{C1-C2-C3} = 137.3(6)^\circ$ that are consistent with sp^2 -carbon atoms as is the typical single bond $\text{C}(\text{sp}^2)\text{-C}(\text{sp})$ distance in **1**: $\text{C2-C3} = 1.421(9) \text{ \AA}$ (vinylacetylene: 1.43 \AA [13]).

The Co1 atom bears three trimethylphosphine ligands at angles P-Co-P of av. $100.8(1)^\circ$ which is close to the expected minimum of the ligand cone-angle under steric congestion [14] at a distance Co-P of av. $2.199(2) \text{ \AA}$, that represents zerovalent cobalt [15]. At Co2 this distance is significantly larger ($\text{Co2-P4} = 2.316(2) \text{ \AA}$), indicating an oxidation state of cobalt(I) and the angle $\text{C1-Co2-P4} = 98.4(1)^\circ$ is smaller without steric crowding while the Co2-Cl bond length ($2.213(2) \text{ \AA}$) is in the usual range for cobalt(I) [16].

A crystallographic study of complex **2** (see 'Supplementary material') shows similar molecular structures for both complexes, the SiMe_3 groups in **1** being replaced by CMe_3 in **2**.

Conclusions

η^2 -Coordination of disubstituted butadiynes by 16-electron cobalt(I) complexes does not always proceed as a simple ligand addition reaction. While $\text{CoCl}(\text{PMe}_3)_3$ smoothly adds diphenylbutadiyne to form the stable 18-electron compound **4**, Me_3E substituents ($\text{E} = \text{C}, \text{Si}, \text{Ge}$) of butadiyne cause a shift of oxidation-reduction equilibria of low-valent cobalt in a new process (c) schematically consisting of two steps (a) and (b).



While the reverse reaction (a) is the basis for the reported synthesis of cobalt(I) halides [7], reaction (b) constitutes a novel property of diynes ($\text{R} = \text{CMe}_3, \text{SiMe}_3, \text{GeMe}_3$): with one of the alkyne functions cobalt(I) and cobalt(0) are tied together in a tetrahedrane structure similar to that formed by dicobalt hexacarbonyl and alkynes or diynes. The absence of carbonyl ligands is essential, because with excess carbon monoxide reaction (b) is completely reversed.

Supplementary material

Hydrogen atom coordinates, anisotropic temperature factors and structure factors listing have been deposited as Supplementary Publications no. CSD 320531 (complex **2**) and no. CSD 320532 (complex **1**). Copies may be obtained through the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen.

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