

Synthesis and structural characterization of cobalt complexes derived from conjugated tetraynes

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Abstract

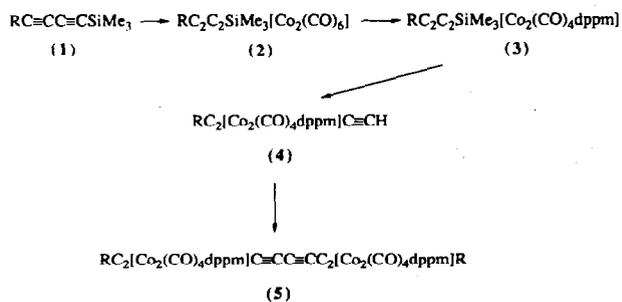
Some novel tetrayne complexes $RC_2[Co_2(CO)_4dppm]C\equiv CC\equiv CC_2[Co_2(CO)_4dppm]R$ (**5**) (where $R = SiMe_3$, **a**; 4-MeC₆H₄, **b**; C₆H₅, **c**; 4-MeOC₆H₄, **d**; 4-FC₆H₄, **e**; dppm = 1,2-bis(diphenylphosphino)methane) have been synthesized either by oxidative coupling of $RC_2[Co_2(CO)_4dppm]C\equiv CH$ (**4**) or by lithiation and subsequent hydrolysis of $RC_2[Co_2(CO)_4dppm]CH=CHCl$ (**8**). An X-ray structure determination of **5a** reveals that the two $Co_2(CO)_4dppm$ units are *trans* to each other. The cobalt units can be removed from **5** by oxidizing reagents.

Keywords: Cobalt; Tetraynes; Crystal structure; Carbonyl; Alkyne

1. Introduction

The highly conjugated polyynes and their transition metal complexes have attracted considerable interest in recent years owing to their potential applications in material science [1]. Acetylenes are important precursors for the molecular carbon rod and cyclo[*n*] species [2]. The construction of a polyyne usually involves stepwise coupling reactions of terminal acetylene units [3]. Despite the various modifications that have been made to improve the yield, these methods suffer from the limited accessibility of the starting compound. The instability of free polyynes has also discouraged development of this approach [4]. The use of cobalt–alkyne complexes in organic synthesis is well established [5,6]. Rubin et al. [7] reported that the cobalt–alkyne complex bearing free terminal alkyne groups can undergo oxidative coupling; the stable μ -dppm (dppm = 1,2-bis(diphenylphosphino)methane) cobalt complexes of carbon cyclo[*n*] ($n = 18, 24$) were obtained by this method. Attempts to remove the cobalt units in these complexes were unsuccessful, owing in part to the strong shielding of the metal atoms by the dppm ligands.

In connection with our interest [8] in the chemistry of organometallic polymers, $[M(L)_x C\equiv C-R-C\equiv C]_n$, we needed a ready route to a class of conjugated polyyne ligands. We describe below the synthesis of cobalt complexes of a linear tetrayne, namely $RC_2[Co_2(CO)_4dppm]C\equiv CC\equiv CC_2[Co_2(CO)_4dppm]R$ (**5**), by modification of two previously described routes to tetrayne ligands. The characterization of the complexes are described along with the X-ray determination of the structure of $Me_3SiC_2[Co_2(CO)_4dppm]C\equiv CC\equiv CC_2[Co_2(CO)_4dppm]SiMe_3$ (**5a**). The decomplexation of species is also described.



a. $R = SiMe_3$; **b.** $R = 4-Me-C_6H_4$; **c.** $R = C_6H_5$;

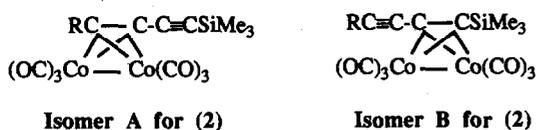
Scheme 1.

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2. Results and discussion

2.1. Synthesis via the complex $RC_2[Co_2(CO)_4dppm]C\equiv CH$

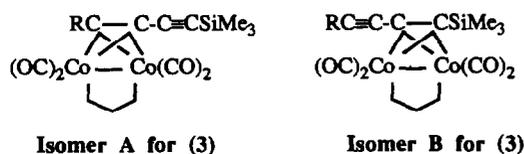
The reaction sequence employed in the synthesis is outlined in Scheme 1. 1-Trimethylsilyl-1,3-diyne (**1**) can be prepared by a published procedure [9]. The reaction of equal molar quantity of **1** with dicobalt octacarbonyl affords the complex **2** as a deep red oil. The cobalt complex of bis(trimethylsilyl)-1,3-butadiyne (**1a**) has been reported previously [10], and so further studies were concentrated on the reactions involving the asymmetric diynes **1b** and **1c**. The 1H NMR spectrum of **2** gives two singlets of equal intensity in the $SiMe_3$ region, suggesting that the two $C\equiv C$ bonds in **1b** and **1c** exhibit equal reactivities towards cobalt carbonyl so that a 1:1 mixture of two isomers **2A** and **2B** is produced.



where $R \neq SiMe_3$.

As the complexed alkynyl bond loses its triple bond character, there is a deshielding effect on the adjacent protons. A larger downfield shift is expected for isomer **2B**, in which the $SiMe_3$ group is directly connected to the coordinated $C\equiv C$ bond, than for isomer **2A**, in which the $SiMe_3$ group is two atoms away.

Attempts to remove the $SiMe_3$ group in complexes **2** with fluoride anion or potassium carbonate led to decomposition of the complex. However, **2** were readily connected into **3**, which are stabilized by the bridging ligand, the latter was introduced by refluxing **2** with equal molar quantity of dppm in benzene, and **3** were obtained as red crystals [11]. The 1H NMR spectra of complexes **3** again exhibit two $SiMe_3$ signals, but with different intensities in case of **3b** and **3c**, indicating that the formation of isomer **3A** (strong $SiMe_3$ peak) is favoured over isomer **3B** (weak $SiMe_3$ peak), possibly due to lower steric repulsion between the $Co_2(CO)_4$ -dppm and $SiMe_3$ groups in the former isomer.



where $R \neq SiMe_3$;



It is difficult to separate the isomers **A** and **B** because of their similar chromatographic properties.

However, when a complex **3** is treated with potassium hydroxide, the isomer **3B** remains unchanged while **3A** is converted into the desired tetrayne precursor **4**. Oxidative coupling of complexes **4** affords **5**, stable cobalt complexes of tetrayne, in ca. 80% yield.

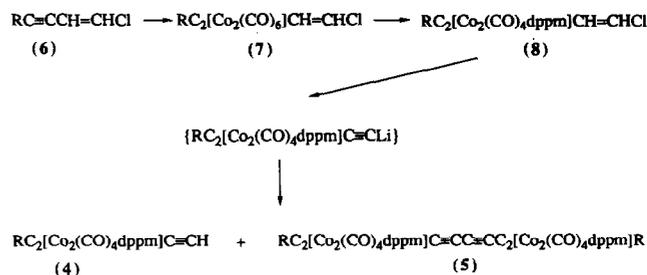
This synthetic procedure was restricted by the difficulty of obtaining terminal acetylenes in high purity, and so an attempt was made to find a milder and more general route to tetraynes.

2.2. Synthesis via the complex $RC_2[Co_2(CO)_4dppm]CH=CHCl$

The reaction sequence employed in the synthesis is outlined in Scheme 2. The 1-Chloro-1-ene-3-yne (**6**) were prepared by the published procedure [12]. The ligands **6** were found to react smoothly with equal molar quantity of dicobalt octacarbonyl at room temperature, to afford the complexes **7** as red crystals. Attempts to bring about *trans* elimination of HCl from **7** by use of tetra-butylammonium fluoride (TBAF) as base were unsuccessful, and use of a stronger base, e.g. potassium hydroxide or lithium diisopropylamide (LDA), led to decomposition. The ligand dppm was introduced as described above to give complexes **8**. The *cis*-configurations of complexes **7** and **8** are confirmed by the proton coupling pattern (doublet) and coupling constant $^3J(^1H-^1H) = 7.2$ Hz in the 1H NMR spectrum. Attempted dehalogenation of **8** by use of TBAF was unsuccessful, but treatment of complexes **8** with an excess of LDA and subsequent hydrolysis gave complexed **5** (major product) along with **4** as a minor product. A lithium acetylide cobalt complex has been suggested to be an intermediate in a similar system [6a].

2.3. Characterization of the complex $RC_2[Co_2(CO)_4dppm]C\equiv CC\equiv CC_2[Co_2(CO)_4dppm]R$ (**5**)

The IR spectra of complexes **5** are identical to those reported previously [5a]. The $C\equiv C$ stretching absorp-



a. $R=SiMe_3$; b. $R=4-Me-C_6H_4$; c. $R=C_6H_5$; d. $R=4-MeO-C_6H_4$; e. $R=4-F-C_6H_4$;

Scheme 2.

Table 1
NMR data^a for complex **5**^b

	5a	5b	5c	5d	5e
¹ H NMR					
CH ₂ (dppm)	3.31 (m, 1H)	3.21 (m, 1H)	3.22 (m, 1H)	3.22 (m, 1H)	3.23 (m, 1H)
	4.01 (m, 1H)	3.80 (m, 1H)	3.81 (m, 1H)	3.82 (m, 1H)	3.82 (m, 1H)
CH ₃	0.43 (s, 9H)	2.38 (s, 3H)	–	3.86 (s, 3H)	–
³¹ P NMR					
	–104.4	–101.7	–101.7	–101.6	–101.6
¹³ C NMR					
CO	206.8	206.3	206.2	206.3	206.5
	201.7	201.1	201.1	201.3	201.5
C(1)	91.6	98.5	98.2	98.3	97.0
C(2)	76.5	63.9	64.0	66.9	65.8
C(3)	86.6	86.8	86.8	86.6	86.9
C(4)	83.0	84.4	84.5	84.1	84.8
CH ₂ (dppm)	39.8	37.6	37.9	37.0	37.7
CH ₃	0.55	21.5	–	29.5	–

^a In ppm.^b Same numbering scheme as in Fig. 1.

tion is obscured by the strong CO absorptions. The EI mass spectra show the parent ions for **5**, followed by the fragments from successive loss of eight carbonyl groups.

Compounds **5a–f** have been fully characterized by ¹H, ³¹P and ¹³C NMR spectroscopy (see Table 1). The methylene protons of the dppm ligand appear as an unresolved ABX₂ (X = ³¹P) multiplets in the ¹H NMR. The ³¹P NMR spectrum shows a singlet, as observed for analogous μ -dppm cobalt-alkyne complexes [11]. Two CO signals are observed in the 210–200 ppm region in the ¹³C NMR spectra. The assignment of ¹³C chemical shifts of tetrayne carbons is based on two observations: (i) broadening of the C(1) and C(2) signals because of unresolved ³¹P–¹³C coupling and (ii) the increase in the anisotropic effect as the length of the polyyne chain increases, causes an upfield shift of the alkyne carbon signals.

2.4. X-ray structure of Me₃SiC₂[Co₂(CO)₄dppm]C≡CC≡CC₂[Co₂(CO)₄dppm]SiMe₃ (**5a**)

Bending of the linear alkyne bond on formation of the cobalt-alkyne complex has been employed to stabilize strained carbon cyclo[*n*] systems [7]. To investigate the effect of complexation on the linearity and rigidity of polyyne, a single crystal X-ray diffraction study of **5a** was carried out. Selected bond lengths and angles for **5a** are listed in Table 2.

The molecular structure of **5a** (Fig. 1) showed some important features. The molecule lies on a crystallographic centre of symmetry located at the midpoint of the C(4)–C(4a) bond. The overall structure resembles that of dimeric cobalt-diyne complexes with the two Co₂C₂ units linked through four alkyne carbons in a *trans* configuration [13]. In each Co₂C₂ unit, the 'al-

kyne' C≡C vector is perpendicular to the Co–Co vector and the four Co–C (alkyne) distances are equal within experimental error. The Co–Co separation (2.478(3) Å) is in the region expected for cobalt-alkyne complexes, indicating the presence of a metal–metal bond [13]. The C(1)–C(2) distance, 1.343(11) Å, is lengthened owing to the loss of triple bond character after complexation, and the Si(1)–C(1)–C(2) bond angle, 147.0(7)°, and C(1)–C(2)–C(3), 144.4(9)°, are greatly reduced from the angle of 180° expected for a linear alkyne. The Co–P distances of 2.237(3) and 2.219(3) Å are comparable with the values found for the complex C₆H₅C₂[Co₂(CO)₄dppm]C₆H₅ (2.210 and 2.215 Å) [11] and other μ -dppm cobalt systems [14]. The –C≡CC≡C– linkage is not strictly linear; the angles C(2)–C(3)–C(4) and C(3)–C(4)–C(4a) being 171.1(11)° and 178.8(8)°, respectively. The bond lengths, C(2)–C(3) = 1.386(9) Å, C(3)–C(4) = 1.210(10) Å and C(4)–C(4a) = 1.372(14) Å, are in the range normally observed for sp-hybridized carbon–carbon distances for C≡C and C–C bonds. Similar bond length distributions have been reported for two free octatetraynes, namely 1,8-

Table 2
Selected bond lengths (Å) and bond angles (°) for **5a**

Co(1)–Co(2)	2.478(3)	Si(1)–C(1)	1.864(10)
Co(1)–C(1)	1.971(10)	C(1)–C(2)	1.343(11)
Co(1)–C(2)	1.965(8)	C(2)–C(3)	1.386(9)
Co(2)–C(1)	1.953(9)	C(3)–C(4)	1.210(10)
Co(2)–C(2)	1.955(8)	C(4)–C(4a)	1.372(14)
Co(1)–P(1)	2.237(3)		
Co(2)–P(2)	2.219(3)		
Si(1)–C(1)–C(2)	147.0(7)		
C(1)–C(2)–C(3)	144.4(9)		
C(2)–C(3)–C(4)	171.1(11)		
C(3)–C(4)–C(4a)	178.8(8)		

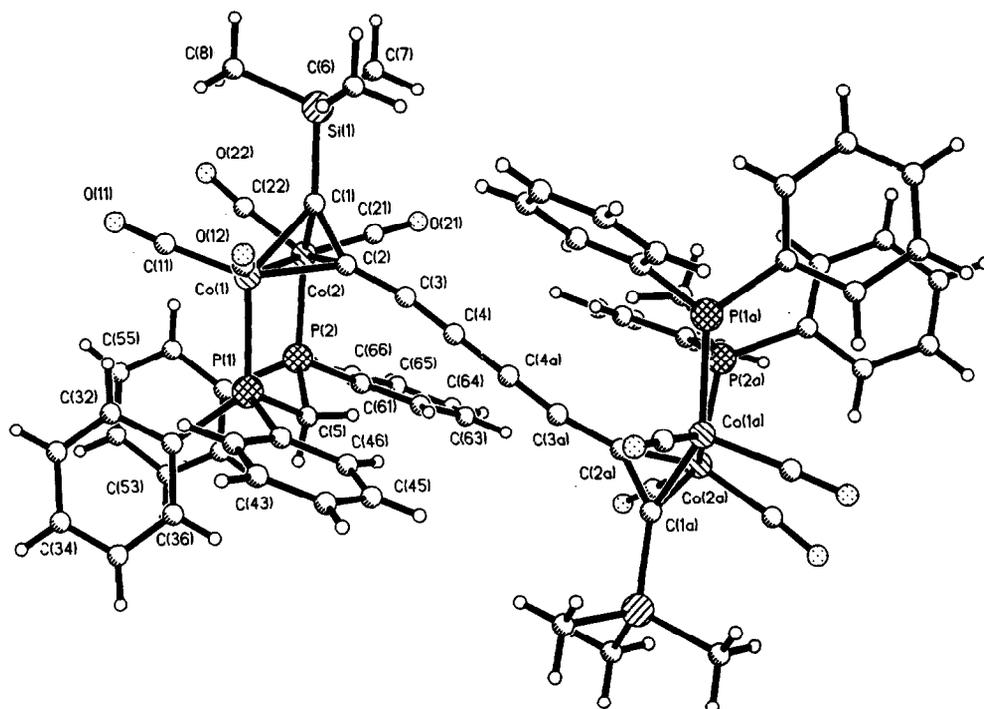


Fig. 1. The molecular structure of **5a** showing the atom numbering scheme.

bis(phenyl)octatetrayne and 1,8-bis(trimethylsilyl)-octatetrayne [15].

2.5. Decomplexation

Several oxidizing reagents have been shown to remove the cobalt unit from cobalt-alkyne complexes by attacking the cobalt atoms (Ce^{IV} and Fe^{III} ions) or oxidizing the CO ligands (amine N-oxide) [16]. As noted in the discussion of the syntheses, replacement of the CO ligands by dppm strengthens the bonds between the cobalt atoms and alkyne ligand, so that the degradation of the complex is expected to be more difficult.

The cobalt unit is known to be removed from the complex $\text{Me}_3\text{SiC}_2[\text{Co}_2(\text{CO})_4\text{dppm}]\text{C}\equiv\text{CSiMe}_3$ is by use of ferric nitrate or trimethylamine N-oxide; the diyne $\text{Me}_3\text{SiC}\equiv\text{CC}\equiv\text{CSiMe}_3$ being recovered in 70% yield. Removal of the $\text{Co}_2(\text{CO})_4\text{dppm}$ groups from the complexes **5** was similarly brought about by use of equivalents of $\text{Fe}(\text{NO}_3)_3$ in MeOH at room temperature. After work-up, the free tetraynes were isolated as pale yellow oily solids by TLC. The IR and UV spectra show the characteristic features of conjugated polyynes [17].

3. Conclusion

The applicability of cobalt-alkyne complexes in acetylene synthesis has been demonstrated by the

preparation of $\text{Co}_2(\text{CO})_4\text{dppm}$ complexes of various tetraynes. The approach used, via the choroenyne intermediate, is very promising and can, in principle, be extended to the preparation of higher polyynes analogues [18]. The X-ray structure of **5a** shows that there is a *trans*-configuration of two cobalt-containing moieties, which reinforces the rigid nature of carbon backbone and allows the regular extension of the polyynes chains. Decomplexation of the complexes **5** is facilitated by the *trans* structure and the absence of sensitive functional groups in the system.

4. Experimental details

4.1. General

All reactions were carried out under nitrogen by use of standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. Column chromatography was carried out on column of Merck silica gel 230–400 mesh. Thin layer chromatography (TLC) was performed on glass plates (20 cm × 20 cm) coated with ca. 2 mm silica gel (type 60 GF254 Merck). The reagents $n\text{BuLi}$ (2.5 M in hexane) and dppm were obtained from Aldrich and used as received. The following compounds were prepared by minor modification of published methods: 4-MeO- $\text{C}_6\text{H}_4\text{C}\equiv\text{CH}$, 4-F- $\text{C}_6\text{H}_4\text{C}\equiv\text{CH}$ [19], $\text{Co}_2(\text{CO})_8$ [20], $\text{RC}\equiv\text{CC}\equiv\text{CSiMe}_3$ [9], $\text{RC}\equiv\text{CCH}=\text{CHCl}$ [12].

Infrared spectra were recorded in NaCl cell (0.5 mm

path length) on a Perkin-Elmer 1710 Fourier Transform spectrometer. UV spectra were recorded for dichloromethane solutions on a PU 8730 UV/VIS spectrophotometer. EI mass spectra were recorded on a Kratos MS 902 spectrometer. NMR spectra were recorded on Bruker WH 400 Fourier Transform spectrometers. The chemical shifts were referenced to residual protons in CDCl_3 (7.25 ppm) for ^1H , to CDCl_3 (77.0 ppm) for ^{13}C , and to external $\text{P}(\text{OMe})_3$ for ^{31}P .

4.2. Preparation of $\text{RC}_2\text{C}_2\text{SiMe}_3[\text{Co}_2(\text{CO})_4\text{dppm}]$

In a typical procedure, a solution of $\text{Co}_2(\text{CO})_8$ (778 mg, 2.27 mmol) and $\text{C}_6\text{H}_5\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3$ (**1c**) (430 mg, 2.17 mmol) in hexane (75 ml) was stirred at 25°C . The IR spectrum showed that the bridging carbonyl bands from $\text{Co}_2(\text{CO})_8$ has disappeared completely after 30 min. The solvent was removed and the residue was chromatographed with hexane as eluant. The only red band was collected, and kept at 0°C to yield a red solid. The spectral data suggested that it was a 1:1 mixture of $\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_2[\text{Co}_2(\text{CO})_6]\text{SiMe}_3$ and $\text{C}_6\text{H}_5\text{C}_2[\text{Co}_2(\text{CO})_6]\text{C}\equiv\text{CSiMe}_3$, denoted by $\text{C}_6\text{H}_5\text{C}_2\text{C}_2\text{SiMe}_3[\text{Co}_2(\text{CO})_6]$ (**2c**). A solution of **2c** (970 mg, 2 mmol) and dppm (770 mg, 2 mmol) in benzene (30 ml) was refluxed at 80°C for 16 h. The solvent was removed under reduced pressure and the residue was chromatographed with hexane as eluant. The deep red band was collected and kept at 0°C to yield red crystals. The spectral data indicated that it was a mixture of $\text{C}_6\text{H}_5\text{C}_2[\text{Co}_2(\text{CO})_4\text{dppm}]\text{C}\equiv\text{CSiMe}_3$ and $\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_2[\text{Co}_2(\text{CO})_4\text{dppm}]\text{SiMe}_3$, in more than 1:1 ratio denoted by $\text{C}_6\text{H}_5\text{C}_2\text{C}_2\text{SiMe}_3[\text{Co}_2(\text{CO})_4\text{dppm}]$ (**3c**); 74% overall yield based on diyne (**1c**). IR (CH_2Cl_2 , cm^{-1}): ν_{CO} 2027s, 2004s, 1976s. Anal. Found: C, 61.96; H, 4.52; M⁺, 813. Calcd for $\text{C}_{42}\text{H}_{36}\text{O}_4\text{P}_2\text{SiCo}_2$: C, 62.07; H, 4.47; M, 813.

Other complexes of the type $\text{RC}_2\text{C}_2\text{SiMe}_3[\text{Co}_2(\text{CO})_4\text{dppm}]$ were prepared by the same general procedure.

3a 82% overall yield based on diyne **1a**. IR (CH_2Cl_2 , cm^{-1}): ν_{CO} 2026s, 2003s, 1974s. Anal. Found: C, 57.66; H, 4.97; M⁺, 808. Calcd for $\text{C}_{39}\text{H}_{40}\text{O}_4\text{P}_2\text{Si}_2\text{Co}_2$: C, 57.91; H, 5.00; M, 809.

3b: 69% overall yield based on diyne **1b**. IR (CH_2Cl_2 , cm^{-1}): ν_{CO} 2027s, 2004s, 1975s. Anal. Found: C, 62.39; H, 4.86; M⁺, 826. Calcd for $\text{C}_{43}\text{H}_{38}\text{O}_4\text{P}_2\text{SiCo}_2$: C, 62.47; H, 4.64; M, 827.

4.3. Preparation of $\text{RC}_2[\text{Co}_2(\text{CO})_4\text{dppm}]\text{CH}=\text{CHCl}$

In a typical procedure, a solution of $\text{Co}_2(\text{CO})_8$ (2.05 g, 5.8 mmol) and $\text{C}_6\text{H}_5\text{C}\equiv\text{CCH}=\text{CHCl}$ (**6c**) (950 mg, 5.8 mmol) in hexane (25 ml) was stirred at 25°C . The IR spectrum showed that the bridging carbonyl bands from $\text{Co}_2(\text{CO})_8$ had disappeared completely after 30

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for **5a**

	x	y	z	U_{eq}^a
Co(1)	3400(1)	1222(1)	623(1)	60(1)
Co(2)	3574(1)	-525(1)	475(1)	61(1)
P(1)	3287(1)	1076(2)	1595(1)	59(1)
P(2)	3360(1)	-1042(2)	1303(1)	63(1)
Si(1)	4015(1)	969(3)	-474(2)	95(2)
C(1)	3869(3)	656(6)	276(4)	61(4)
C(2)	4048(3)	524(6)	965(4)	55(4)
C(3)	4478(3)	553(7)	1586(4)	63(4)
C(4)	4811(3)	535(7)	2169(4)	71(4)
C(5)	3534(3)	-114(6)	1988(4)	61(4)
C(6)	4448(4)	2030(9)	-249(6)	133(8)
C(7)	4329(5)	-65(10)	-671(7)	173(11)
C(8)	3447(5)	1224(9)	-1242(5)	146(8)
C(11)	2803(4)	1269(8)	-113(5)	79(5)
O(11)	2433(3)	1276(6)	-592(3)	115(4)
C(12)	3581(4)	2482(10)	704(5)	89(6)
O(12)	3717(3)	3277(6)	750(4)	121(5)
C(21)	4013(4)	-1459(9)	557(5)	87(6)
O(21)	4305(3)	-2038(7)	620(5)	126(5)
C(22)	3090(4)	-799(7)	-356(5)	73(5)
O(22)	2793(3)	-940(6)	-912(3)	110(4)
C(31)	2677(3)	1107(7)	1624(4)	67(4)
C(32)	2229(4)	1123(8)	1020(5)	84(5)
C(33)	1766(4)	1085(8)	1046(6)	101(6)
C(34)	1743(4)	1080(8)	1678(6)	95(6)
C(35)	2170(4)	1075(8)	2278(5)	87(6)
C(36)	2630(4)	1089(7)	2242(4)	79(5)
C(41)	3642(3)	1973(7)	2267(4)	65(5)
C(42)	3456(4)	2917(8)	2183(5)	82(5)
C(43)	3714(6)	3636(9)	2643(7)	101(7)
C(44)	4147(6)	3447(11)	3184(8)	121(9)
C(45)	4340(5)	2525(12)	3283(6)	131(7)
C(46)	4083(4)	1795(8)	2825(5)	94(6)
C(51)	2702(3)	-1311(6)	1118(5)	64(4)
C(52)	2567(4)	-1605(7)	1626(5)	80(5)
C(53)	2087(5)	-1784(8)	1510(6)	96(7)
C(54)	1709(5)	-1680(8)	849(7)	102(7)
C(55)	1833(4)	-1422(9)	325(6)	104(6)
C(56)	2326(4)	-1213(8)	458(5)	86(5)
C(61)	3698(4)	-2154(8)	1768(5)	78(5)
C(62)	4160(4)	-2120(9)	2323(5)	104(5)
C(63)	4416(5)	-2970(12)	2610(6)	147(9)
C(64)	4207(7)	-3832(12)	2362(9)	132(11)
C(65)	3749(6)	-3904(10)	1815(7)	117(8)
C(66)	3491(4)	-3064(9)	1532(6)	94(6)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonally analyzed U_{ij} tensor.

min. The solvent was removed and the residue was chromatographed on a silica column with hexane as eluant. The only red band was collected and kept at 0°C to yield $\text{C}_6\text{H}_5\text{C}_2[\text{Co}_2(\text{CO})_6]\text{CH}=\text{CHCHCl}$ (**7c**) as a red solid (2.35 g, 89%). A solution of **7c** (2.02 g, 4.5 mmol) and dppm (1.73 g, 4.5 mmol) in benzene (75 ml) was refluxed at 80°C for 16 h. The solvent was removed under reduced pressure and the residue was chromatographed with hexane as eluant. The deep red band was collected and kept at 0°C to yield

$C_6H_5C_2[Co_2(CO)_4dppm]CH=CHCl$ (**8c**) (3.50 g, 93%) as red crystals. IR (CH_2Cl_2 , cm^{-1}): ν_{CO} 2026s, 1999s, 1972m. Anal. Found: C, 59.73; H, 4.00; M^+ , 766. Calcd for $C_{39}H_{29}O_4ClP_2Co_2$: C, 60.29; H, 3.77; M , 766.

Complexes of the type $RC_2[Co_2(CO)_4dppm]CH=CHCl$ were prepared by the same general procedure.

8a: IR (CH_2Cl_2 , cm^{-1}): ν_{CO} 2020s, 1992vs, 1964m. Anal. Found: C, 55.58; H, 4.46; M^+ , 772. Calcd for $C_{36}H_{33}O_4ClP_2SiCo_2$: C, 55.93; H, 4.31; M , 773.

8b: IR (CH_2Cl_2 , cm^{-1}): ν_{CO} 2025s, 1998vs, 1972m. Anal. Found: C, 60.47; H, 3.99; M^+ , 791. Calcd for $C_{40}H_{31}O_4ClP_2Co_2$: C, 60.73; H, 3.96; M , 791.

8d: IR (CH_2Cl_2 , cm^{-1}): ν_{CO} 2024s, 1997s, 1978m. Anal. Found: C, 59.01; H, 3.82; M^+ , 807. Calcd for $C_{40}H_{51}O_5ClP_2Co_2$: C, 59.53; H, 3.88; M , 807.

8e: IR (CH_2Cl_2 , cm^{-1}): ν_{CO} 2026s, 2000vs, 1972m. Anal. Found: C, 59.03; H, 3.50; M^+ , 794. Calcd for $C_{39}H_{28}O_4ClP_2Co_2$: C, 59.00; H, 3.56; M , 794.

4.4. Preparation of $RC_2[Co_2(CO)_4dppm]C\equiv CC\equiv CC_2-[Co_2(CO)_4dppm]R$

Method A. In a typical procedure $C_6H_5C_2C_2SiMe_3-[Co_2(CO)_4dppm]$ (**3c**) (1.40 g, 1.8 mmol) was treated with KOH (150 mg, 2.6 mmol) in methanol at 25°C and the reaction was monitored by IR spectroscopy. The terminal acetylenic absorption appeared after 20 min and reached its maximum intensity after 4 h, after which the solvent was removed and the residue was subjected to TLC with dichloromethane/hexane (1:2 by vol.) as eluant. The first red band from the top was shown to contain as $C_6H_5C_2[Co_2(CO)_4dppm]C\equiv CH$ (**4c**) (813 mg) and the second $C_6H_5C\equiv CC_2[Co_2(CO)_4dppm]SiMe_3$. A solution of **4c** (120 mg, 0.16 mmol) in dry pyridine (20 ml) was stirred with $Cu(OAc)_2$ (20 mg) at room temperature for 24 h. The solution was then filtered through Celite, the solvent was removed under reduced pressure, and the residue was subjected to column chromatography with dichloromethane/hexane (1:1) as eluant. The solid from the main red band was crystallized from hexane at 0°C to give $C_6H_5C_2[Co_2(CO)_4dppm]C\equiv CC\equiv CC_2[Co_2(CO)_4dppm]C_6H_5$ (**5c**) (95 mg, 80%) as deep red crystals.

Method B. In a typical procedure to a hexane solution of 2.5 M n -BuLi (0.6 ml, 1.5 mmol) was added dropwise a THF solution of 1Pr_2NH (0.20 ml, 1.5 mmol) at -78°C. After 10 min, a THF solution of $C_6H_5C_2[Co_2(CO)_4dppm]CH=CHCl$ (**8c**) (100 mg, 0.13 mmol) was added at the same temperature and the mixture was stirred for a further 30 min then allowed to warm slowly to 25°C. The solvent was removed at reduced pressure and the residue was subjected to TLC with dichloromethane/hexane (1:2 by vol.) as eluant. The solid from the first red band from the top showed spectroscopic features identical with those of an au-

thentic sample of $C_6H_5C_2[Co_2(CO)_4dppm]C\equiv CH$ (**4c**). The second deep red band yielded the tetrayne complex $C_6H_5C_2[Co_2(CO)_4dppm]C\equiv CC\equiv CC_2[Co_2(CO)_4dppm]C_6H_5$ (**5c**) (98 mg, 52%).

Other complexes of the type $RC_2[Co_2(CO)_4dppm]C\equiv CC\equiv CC_2[Co_2(CO)_4dppm]R$ were prepared by one or both of the above, as follows:

5a from methods A and B: IR (CH_2Cl_2 , cm^{-1}): ν_{CO} 2022s, 2001vs, 1971 m, Anal. Found: C, 58.78; H, 4.26; M^+ , 1471. Calcd for $C_{72}H_{62}O_8P_4Si_2Co_4$: C, 58.84; H, 4.41; M , 1471.

5b from methods A and B: IR (CH_2Cl_2 , cm^{-1}): ν_{CO} 2026s, 2006vs, 1977m. Anal. Found: C, 64.00; H, 4.03; M^+ , 1506. Calcd for $C_{80}H_{58}O_8P_4Co_4$: C, 63.76; H, 3.89; M , 1506.

5c from methods A and B: IR (CH_2Cl_2 , cm^{-1}): ν_{CO} 2024s, 2004vs, 1975m. Anal. Found: C, 63.52; H, 3.69; M^+ , 1479. Calcd for $C_{78}H_{54}O_8P_4Co_4$: C, 63.34; H, 3.69; M , 1479.

5d from method B: IR (CH_2Cl_2 , cm^{-1}): ν_{CO} 2025s, 2005vs, 1976m. Anal. Found: C, 62.70; H, 4.33; M^+ , 1538. Calcd for $C_{80}H_{58}O_{10}P_4Co_4$: C, 62.43; H, 3.81; M , 1539.

5e from method B: IR (CH_2Cl_2 , cm^{-1}): ν_{CO} 2027s, 2007s, 1978m. Anal. Found: C, 61.95; H, 3.54; M^+ , 1515. Calcd for $C_{78}H_{52}O_8F_2P_4Co_4$: C, 61.84; H, 3.47; M , 1515.

4.5. Decomplexation

This was carried out on a small scale involving ca. 0.02 mmol of the tetrayne complex and 0.08 mmol of $Fe(NO_3)_3 \cdot 9H_2O$ in 10 ml of methanol at 25°C. After 24 h, the solvent was removed and the residue subjected to TLC with hexane as eluant. The free tetrayne was obtained as an oily solid and characterised by IR and UV spectroscopy.

4.6. Crystal structure determination for **5a**

Diffusion of hexane into a dichloromethane solution of **5a** at 0°C produced crystals suitable for X-ray analysis. Crystal data: dark red block, $C_{72}H_{62}O_8P_4Si_2Co_4$; $M = 1471.0$; monoclinic, space group $C2/c$; $a = 29.26(2)$, $b = 13.608(9)$, $c = 21.268(13)$ Å; $\beta = 115.08(5)^\circ$; $V = 7670(9)$ Å³; $Z = 4$; $D_{calcd} = 1.274$ g cm^{-3} ; $F(000) = 3016$; $T = 298$ K; $\lambda(MoK\alpha) = 0.71073$ Å.

A crystal of dimensions 0.42 mm \times 0.21 mm \times 0.27 mm was mounted on glass fiber on a Siemens R3m/V diffractometer. Data were collected by the ω - 2θ scan mode ($5 < 2\theta < 45^\circ$). From a total of 5587 reflections (5041 unique), 2891 with $F > 4.0\sigma(F)$ were used in the structural solution and refinement. The structure was solved by Patterson methods and refined by full-matrix

least-squares to $R = 0.0569$ and $R_w = 0.0648$. Hydrogen atoms were placed in calculated positions riding on the relevant carbon atoms. The final atomic coordinates for the non-hydrogen atoms and the equivalent isotropic displacement parameters are listed in Table 3. Full lists of bond lengths, and angles and tables of thermal parameters have been deposited with the Cambridge Crystallographic Data Centre.

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References

- [1] (a) G.J. Ashwell and D. Bloor (eds.), *Organic Materials for Non-linear Optics III*, Sec. Publ. No. 137, R. Soc. Chem., London, 1992. (b) J.L. Bredas and R.R. Chance (eds.), *Conjugated Polymer Materials: Opportunities in Electronic, Optoelectronic and Molecular Electronics*, NATO ASI Series, Vol. 182, Kluwer, Dordrecht, 1990. (c) J.E. Sheets, C.E. Carraher, Jr. and C.U. Pittman, Jr. (eds.), *Metal-Containing Polymeric Systems*, Plenum, New York, 1985.
- [2] F. Diederich and Y. Rubin, *Angew. Chem., Int. Ed. Engl.*, **31** (1992) 1101.
- [3] T.X. Neeman and G.M. Whitesides, *J. Org. Chem.*, **53** (1988) 2489.
- [4] L. Brandsma, *Preparative Acetylenic Chemistry*, Elsevier, New York, 1971.
- [5] (a) R.S. Dickson and P.J. Fraser, *Adv. Organomet. Chem.*, **12** (1974) 323. (b) P.L. Pauson, *Tetrahedron*, **41** (1985) 5855.
- [6] For examples of polyene polymers containing $\text{Co}_2(\text{CO})_6$ moieties, see (a) P. Magnus and D.P. Becker, *J. Chem. Soc., Chem. Commun.*, (1985) 640. (b) N.M. Agh-Atabay, W.E. Lindsell, P.N. Preston, P.J. Tomb, A.D. Lloyd, R. Raugel-Rojo, G. Spruce and B.S. Wherrett, *J. Mater. Chem.*, **2** (1992) 1241. (c) W.E. Lindsell, P.N. Preston and P.J. Tomb, *J. Organomet. Chem.*, **439** (1992) 201. (d) T. Matsumoto, S. Kotani, K. Shiina and K. Sonogashira, *Appl. Organomet. Chem.*, **7** (1993) 613.
- [7] Y. Rubin, C.B. Knobler and F. Diederich, *J. Am. Chem. Soc.*, **112** (1990) 4966.
- [8] (a) M.S. Khan, S.J. Davies, A.K. Kakkar, D.J. Schwartz, B. Lin, B.F.G. Johnson and J. Lewis, *J. Organomet. Chem.*, **424** (1992) 87. (b) J. Lewis, M.S. Khan, A.K. Kakkar, B.F.G. Johnson, T.B. Marder, H.B. Fyfe, F. Wittmann, R.H. Friend and A.E. Dray, *J. Organomet. Chem.*, **425** (1992) 165. (c) Z. Atherton, C.W. Faulkner, S.L. Ingham, A.K. Kakkar, M.S. Khan, J. Lewis, N.J. Long and P.R. Raithby, *J. Organomet. Chem.*, **462** (1993) 265.
- [9] J.A. Miller and G. Zweifel, *Synthesis*, (1983) 128.
- [10] (a) K.H. Pannell and G.M. Crawford, *J. Coord. Chem.*, **2** (1973) 251. (b) Ref. [7].
- [11] B.E. Hanson and J.S. Mancini, *Organometallics*, **2** (1983) 126.
- [12] A.K. Kende and C.A. Smith, *J. Org. Chem.*, **53** (1988) 2655.
- [13] (a) Ref. 6a. (b) B.F.G. Johnson, J. Lewis, P.R. Raithby and D.A. Wilkinson, *J. Organomet. Chem.*, **408** (1991) C9. (c) C.E. Housercroft, B.F.G. Johnson, M.S. Khan, J. Lewis, P.R. Raithby, M.E. Robson and D.A. Wilkinson, *J. Chem. Soc., Dalton Trans.*, (1992) 3171.
- [14] O. Heyke, G. Beuter and I.-P. Lorenz, *J. Chem. Soc., Dalton Trans.*, (1992) 2405.
- [15] (a) I. Nitta, *Acta Crystallogr.*, **13** (1960) 1035. (b) B.F. Coles, P.B. Hitchcock and D.M. Walton, *J. Chem. Soc., Dalton Trans.*, (1975) 443.
- [16] (a) K.M. Nicholas and R. Pettit, *Tetrahedron Lett.*, (1971) 3457. (b) Y. Shvo and E. Nazum, *J. Chem. Soc., Chem. Commun.*, (1974) 336. (c) D. Seyferth, M.O. Nestle and A.T. Wehman, *J. Am. Chem. Soc.*, **97** (1975) 7417.
- [17] (a) R. Eastmond, T.R. Johnson and D.R.M. Walton, *Tetrahedron*, **28** (1972) 4601. (b) R. Eastmond and D.R.M. Walton, *Tetrahedron*, **28** (1972) 4591.
- [18] For a recent example see: Z. Yuan, G. Stringer, I.R. Jobe, D. Kreller, K. Scott, L. Koch, N.J. Taylor and T.B. Marder, *J. Organomet. Chem.*, **452** (1993) 115.
- [19] (a) S. Takahashi, Y. Knroyama, K. Sonogashira and N. Hagi-hara, *Synthesis*, (1980) 627. (b) W.B. Austin, N. Bilow, W. Kellaghan and K.S.Y. Lau, *J. Org. Chem.*, **46** (1981) 2280.
- [20] I. Wender, H.W. Sternberg, S. Metlin and M. Orchin, *Inorg. Synth.*, **5** (1957) 190.