

Synthesis and structure of diamine-substituted butene-2-olide-4-ylidene-4-cobalt carbonyl complexes [☆]

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Abstract

Several diamine-substituted cobalt carbonyl butenolide complexes of the type $\text{Co}_2(\text{H,R,C}_4\text{O}_2)(\mu_2\text{-CO})(\text{CO})_4(\text{L-L})$ [$\text{R} = \text{H}$ or ⁿBu; (L-L) = *N,N,N',N'*-tetramethylethylenediamine (tmeda), 1,2-diamino cyclohexane (dach) *cis*- and *trans*-isomers, *o*-phenylene diamine (opda), 1,10-phenanthroline (phen), or 2,2'-dipyridyl (dipy)] have been prepared. The structures of three representatives [$\text{R} = \text{H}$, (L-L) = tmeda (**1**); $\text{R} = \text{ⁿBu}$, (L-L) = phen (**8b**) and dipy (**9**)] have been determined. Complexes **1**, **8b** and **9** crystallise in triclinic $P\bar{1}$ ($a = 7.442(2)$, $b = 9.159(2)$, $c = 14.182(3)$ Å, $\alpha = 79.34(3)$, $\beta = 82.34(3)$, $\gamma = 70.07(3)^\circ$), monoclinic $P2_1/c$ ($a = 10.953(2)$, $b = 16.464(4)$, $c = 14.537(3)$ Å, $\beta = 110.47(2)^\circ$) and monoclinic $P2_1/n$ ($a = 9.698(6)$, $b = 15.508(6)$, $c = 15.966(8)$ Å, $\beta = 79.30(4)^\circ$) space groups, respectively. The complexes with tmeda and *trans*-dach are the first stable cobalt carbonyl derivatives containing saturated aliphatic amines as ligands.

Keywords: Cobalt carbonyl diamine complexes; Structure; Butenolide complexes

1. Introduction

Few cobalt carbonyl derivatives with ligands containing only nitrogen as donor atoms have been described until now. If dicobalt octacarbonyl reacts with amines disproportionation usually takes place and $[\text{CoL}_6]$ - $[\text{Co}(\text{CO})_4]_2$ -type products are obtained; the substituted derivatives $\text{Co}_2(\text{CO})_6(\text{L-L})$ and $\text{Co}_2(\text{CO})_4(\text{L-L})_2$ may be prepared directly from $\text{Co}_2(\text{CO})_8$ only with 1,4-diazabutenes ((L-L) = $\text{RN}=\text{CHCH}=\text{NR}$; ($\text{R} = \text{iPr}$, aryl) [1]. The analogous complexes containing 1,10-phenanthroline or 2,2'-dipyridyl were obtained either from $\text{Co}_2(\text{CO})_4(\text{nbd})_2$ (nbd = norbornadiene) and the appropriate heterocyclic ligand [2] or by reducing $\text{CoCl}_6 \cdot 6\text{H}_2\text{O}$ in the presence of this ligand [3]. Structures for these complexes have been suggested based on spectroscopic data but none has been confirmed by X-ray diffraction.

It should be mentioned in this context, however, that the structures of two cobalt carbonyls that contain N-P-type chelating ligands are known; in these cases the phosphorus donor atoms obviously contribute significantly to the stability of the molecules. These complexes are the mononuclear $\{\text{Co}(\text{CO})[\text{N}(\text{CH}_2\text{CH}_2\text{-PPh}_2)_3]\}(\text{BPh}_4) \cdot \text{Me}_2\text{CO}$ [4] and the dinuclear $\text{Co}_2(\mu\text{-Ph}_2\text{Ppy})_2(\text{CO})_2\text{Cl}$ (PhPpy = 2-diphenylphosphinopyridine) [5]. Even with ligands of this type, however, it is observed in several cases that the nitrogen atom does not coordinate to the metal and they only act as tertiary phosphines without additional donor groups [6].

2. Results and discussion

2.1. Synthesis of the complexes

We have now found that the 2-butenolide cobalt carbonyl ("lactone") complexes $\text{Co}_2(\text{H,R,C}_4\text{O}_2)(\mu_2\text{-CO})(\text{CO})_6$ [7] (which can be prepared from the corresponding cobalt carbonyl acetylene complexes $\text{Co}_2(\text{HC}_2\text{R})(\text{CO})_6$ under CO pressure) react in hexane solu-

[☆] Dedicated to Professor Henri Brunner in recognition of his fundamental achievements in organometallic chemistry, on the occasion of his 60th birthday.

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Table 1

Preparative yields and analytical data of $\text{Co}_2(\text{H}, \text{R}, \text{C}_4\text{O}_2\chi\mu_2\text{-CO})(\text{CO})_4(\text{L-L})$ [(L-L) = diamine] complexes

Complex	R	(L-L)	N, % found (calc.)	Co, % found (calc.)
1	H	tmeda	5.9 (6.14)	25.5 (25.84)
3	H	<i>trans</i> -dach	6.0 (6.17)	25.4 (25.95)
8b	ⁿ Bu	phen	4.9 (4.86)	20.8 (20.45)
9	ⁿ Bu	dipy	5.1 (5.07)	20.8 (21.34)

tion easily and under mild conditions undergoing CO substitution with several kinds of N-bases such as aliphatic mono- and di-amines, and heterocyclic compounds.

The reactions were performed at room temperature and could be followed most conveniently by IR spectroscopy. The IR spectra of the reaction mixtures obtained with monodentate N-bases showed similarities to those of butenolide cobalt carbonyl complexes substituted by a tertiary phosphine or trialkyl phosphite ligand [8]. These products were, however, not very stable and up to now we could not isolate pure products containing such ligands.

We were more successful, however, with the bidentate N-bases *N,N,N',N'*-tetramethylethylenediamine (tmeda), *cis*- and *trans*-1,2-diamino cyclohexane (dach), *o*-phenylene diamine (opda), 1,10-phenanthroline (phen) and 2,2'-dipyridyl (dipy). Using these ligands in 20%–100% molar excess and working in hexane as solvent

Table 3

Yields of the diamine-substituted complexes $\text{Co}_2(\text{H}, \text{R}, \text{C}_4\text{O}_2\chi\mu_2\text{-CO})(\text{CO})_4(\text{L-L})$ in benzene solution obtained with equimolar amounts of reagents as estimated from the IR spectra of the reaction mixtures

Product complex	R	L-L	Yield (%) under	
			Ar	CO
1	H	tmeda	100	30
2	H	<i>cis</i> -dach	75	55
3	H	<i>trans</i> -dach	90	75
4	H	phen	100	95
5	H	dipy	100	65
6	<i>n</i> -Bu	tmeda	100	45
7	<i>n</i> -Bu	opda	40	0
8b	<i>n</i> -Bu	phen	100	85
9	<i>n</i> -Bu	dipy	90	15

the substituted butenolide complexes precipitated as dark powders from the reaction mixture. We have compiled in Table 1 the analytical data of those complexes which were recrystallised and thus isolated in a pure state in solid form. Some of the complexes were only identified by their IR spectra in nujol which — as can be seen from the data in Table 2 — were rather similar and could be therefore regarded as sufficient evidence for the analogous composition and structure of these compounds.

It follows from the structure of the butenolide complexes that three different substitutional isomers are possible with such bidentate ligands. The crude solid products which separated from the reaction mixtures when *N,N,N',N'*-tetramethyl ethylene diamine, the two 1,2-diaminocyclohexanes, or 2,2'-bipyridyl were used as ligands contained only one isomer. In these complexes

Table 2

IR spectra of the $\text{Co}_2(\text{H}, \text{R}, \text{C}_4\text{O}_2\chi\mu_2\text{-CO})(\text{CO})_4(\text{L-L})$ [(L-L) = diamine] complexes in nujol mull in the ν_{CO} range (cm^{-1})

Complex (R, L-L)	ν_1	ν_2	ν_3	ν_4	ν_5 (bridge)	ν_{CO} (average)	ν_6 (organic)
1 H, tmeda	2052s	1997s	1983vs	1970vs	1789m	1958	1724m, br
2 H, <i>c</i> -dach	2049s	2001m	1986vs	1978s, sh	1795m	1962	1683vs
3 H, <i>tr</i> -dach	2047s	2005w	1981s, sh	1971vs	1814m	1964	1689s
4 H, phen	2059s	2018s	2004s	1972vs	1789s	1968	1734s
5 H, dipy	2061vs	2017s	2006s	1970vs	1793s	1969	1725s
6 Bu, tmeda	2047s	1996vs	1974s, sh	1968vs	1782s	1953	1722s
7 Bu, opda	2055m	1991s, sh	1982s	1975vs	1775s	1955	1702s, br
8a Bu, phen	2051s	2016s	1985vs	1971vs	1773m	1965	1713m, br
8b Bu, phen	2056s	2016s	1985vs	1971vs	1795m	1965	1713m, br
9 Bu, dipy	2061s	2019s	1997vs	1963vs	1794m	1967	1726m, br
9 Bu, dipy	2055s	2008s	1992vs	1981vs	1774m	1962	1717m, br

(as proven by the X-ray structure determinations of **1** and **9**, see later) the diamine ligands occupy the two equatorial positions *trans* to the bridging CO and “lactone” ligands.

More than one isomer was obtained, however, when 1,10-phenanthroline reacted with $\text{Co}_2(\text{H}^n\text{Bu}, \text{C}_4\text{O}_2)(\mu_2\text{-CO})(\text{CO})_6$. The black solid product that precipitated from the reaction mixture consisted of isomer **8a**. On recrystallising this crude, microcrystalline product from CH_2Cl_2 /hexane, well-shaped crystals of isomer **8b** were obtained. Isomer **8a** is apparently the kinetically favoured substitution product which precipitates from hexane because of its low solubility but is stable only in the solid state. It isomerises in dichloromethane solution to the thermodynamically favoured stable isomer **8b** which contains the diamine ligand in the same eq–eq position that was found in complexes **1** and **9**. In isomer **8a**, therefore, one nitrogen atom has to occupy the axial position on one of the cobalt atoms and the other nitrogen one of the equatorial positions on the same cobalt atom. The crude isomer **8a** which precipitated from the reaction mixture was always contaminated by some 1,10-phenanthroline (because of the low solubility of the latter in hexane) and could not be prepared in a pure state since in solution it immediately transformed into isomer **8b**.

The $\text{Co}_2(\text{H}^n\text{Bu}, \text{C}_4\text{O}_2)(\mu_2\text{-CO})(\text{CO})_4(\text{opda})$ complex (**7**) apparently also precipitated as a mixture of isomers from the hexane solution. This is shown by the splitting or broadening of all ν_{CO} bands of the IR spectrum of this precipitate taken in nujol (Table 2). These complexes, however, were found to be stable only in the solid state and therefore could not be recrystallised and isolated in a pure state. Dissolving the crude precipitate in benzene or carbon tetrachloride

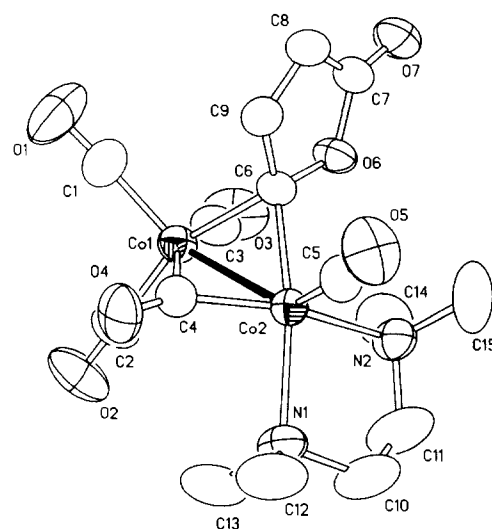


Fig. 2. ORTEP view (50% probability) and atom labelling scheme for complex **1**.

under Ar the complexes partially decomposed to the unsubstituted butenolide complex. If such a solution was prepared under CO only the starting butenolide complex could be observed which proves that the formation of the substituted derivative from the butenolide complex and the diamine is easily reversible.

This observation prompted us to investigate the reversibility of the reaction on a few other representative examples. Equimolar amounts of the selected butenolide complex and the diamine were reacted both under Ar and under CO in benzene in which the diamine-substituted products are well soluble. Based on the relative intensities of the characteristic C–O stretching vibrations of the starting complexes and the substituted derivatives the approximate compositions of the ob-

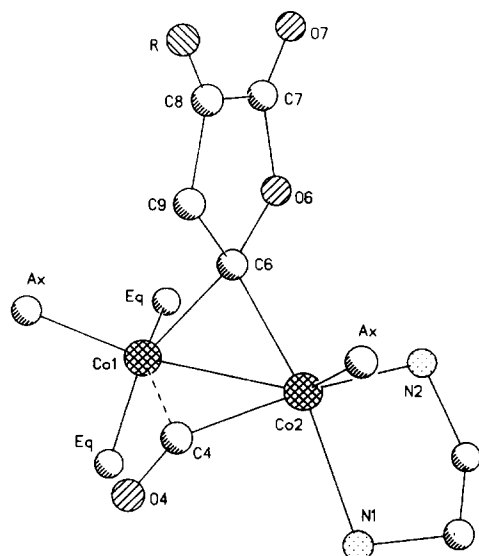


Fig. 1. Scheme of the common framework of complexes **1**, **8b** and **9**.

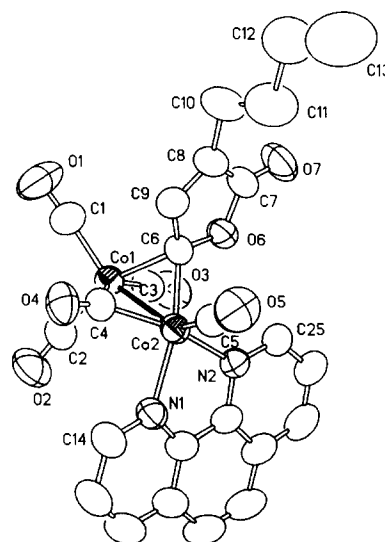
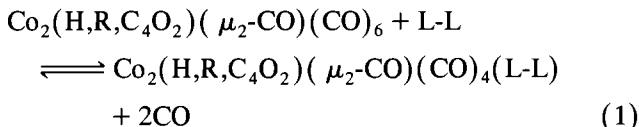


Fig. 3. ORTEP view (50% probability) and atom labelling scheme for complex **8b**.

tained solutions could be calculated. The results are compiled in Table 3.

As can be seen from the data, if the reactions were performed under CO, only partial conversions could be achieved. Accordingly, all reactions leading to the substituted complexes can be at least partially reversed under 1 bar of CO (eqn. (1)):



In many cases the conversion was not complete even if the reaction was started under an atmosphere of Ar because the small amount of carbon monoxide liberated during the reaction and confined in the reaction vessel was enough to establish an observable equilibrium composition. The numerical data obviously cannot be used to calculate equilibrium constants and may serve only as indicators for the relative stabilities of the amine com-

Table 4
Bond lengths (Å) and bond angles (°) for complex 1

Co(1)–Co(2)	2.487(1)	Co(1)–C(1)	1.753(3)
Co(1)–C(2)	1.787(4)	Co(1)–C(3)	1.720(5)
Co(1)–C(4)	1.936(4)	Co(1)–C(6)	2.004(3)
Co(2)–C(4)	1.772(3)	Co(2)–C(5)	1.727(3)
Co(2)–C(6)	1.947(3)	Co(2)–N(1)	2.137(3)
Co(2)–N(2)	2.056(3)	C(1)–O(1)	1.093(5)
C(2)–O(2)	1.125(5)	C(3)–O(3)	1.076(6)
C(4)–O(4)	1.124(5)	C(5)–O(5)	1.093(4)
C(6)–O(6)	1.378(4)	C(6)–C(9)	1.404(4)
O(6)–C(7)	1.363(4)	C(7)–O(7)	1.186(6)
C(7)–C(8)	1.341(5)	C(8)–C(9)	1.345(6)
C(10)–C(11)	1.308(10)	C(10)–N(1)	1.433(6)
C(11)–N(2)	1.467(7)	C(12)–N(1)	1.400(6)
C(13)–N(1)	1.461(6)	C(14)–N(2)	1.421(6)
C(15)–N(2)	1.468(6)		
Co(2)–Co(1)–C(1)	130.1(1)	Co(2)–Co(1)–C(2)	107.8(1)
C(1)–Co(1)–C(2)	102.7(2)	Co(2)–Co(1)–C(3)	111.3(1)
C(1)–Co(1)–C(3)	104.6(2)	C(2)–Co(1)–C(3)	94.2(2)
C(1)–Co(1)–C(4)	98.5(2)	C(2)–Co(1)–C(4)	88.7(2)
C(3)–Co(1)–C(4)	155.4(1)	C(1)–Co(1)–C(6)	97.4(1)
C(2)–Co(1)–C(6)	157.2(1)	C(3)–Co(1)–C(6)	90.9(2)
Co(1)–Co(2)–C(5)	135.0(1)	C(4)–Co(2)–C(5)	103.8(1)
C(5)–Co(2)–C(6)	94.0(1)	Co(1)–Co(2)–N(1)	116.4(1)
C(4)–Co(2)–N(1)	90.0(1)	C(5)–Co(2)–N(1)	97.1(1)
C(6)–Co(2)–N(1)	168.2(1)	Co(1)–Co(2)–N(2)	114.0(1)
C(4)–Co(2)–N(2)	157.7(1)	C(5)–Co(2)–N(2)	98.1(1)
C(6)–Co(2)–N(2)	99.1(1)	N(1)–Co(2)–N(2)	83.5(1)
Co(1)–C(1)–O(1)	177.9(5)	Co(1)–C(2)–O(2)	176.8(5)
Co(1)–C(3)–O(3)	177.5(4)	Co(1)–C(4)–Co(2)	84.1(2)
Co(1)–C(4)–O(4)	132.9(3)	Co(2)–C(4)–O(4)	142.8(3)
Co(2)–C(5)–O(5)	172.6(3)	Co(1)–C(6)–Co(2)	78.0(1)
Co(1)–C(6)–O(6)	120.1(2)	Co(2)–C(6)–O(6)	121.1(2)
Co(1)–C(6)–C(9)	117.0(2)	Co(2)–C(6)–C(9)	122.4(3)
O(6)–C(6)–C(9)	99.2(3)	C(6)–O(6)–C(7)	113.9(2)
O(6)–C(7)–O(7)	123.4(3)	O(6)–C(7)–C(8)	106.3(3)
O(7)–C(7)–C(8)	130.3(3)	C(7)–C(8)–C(9)	107.1(3)
C(6)–C(9)–C(8)	113.4(3)	C(11)–C(10)–N(1)	113.4(4)
C(10)–C(11)–N(2)	120.9(4)	Co(2)–N(1)–C(10)	104.8(3)
Co(2)–N(2)–C(11)	104.4(3)		

Table 5
Bond lengths (Å) and bond angles (°) for complex 8b

Co(1)–Co(2)	2.419(1)	Co(1)–C(1)	1.783(4)
Co(1)–C(2)	1.792(4)	Co(1)–C(3)	1.822(4)
Co(1)–C(4)	1.998(4)	Co(1)–C(6)	2.018(3)
Co(2)–C(4)	1.842(3)	Co(2)–C(5)	1.776(4)
Co(2)–C(6)	1.947(3)	Co(2)–N(1)	2.011(3)
Co(2)–N(2)	2.069(2)	C(1)–O(1)	1.131(5)
C(2)–O(2)	1.130(5)	C(3)–O(3)	1.132(5)
C(4)–O(4)	1.154(4)	C(5)–O(5)	1.124(5)
C(6)–O(6)	1.415(4)	C(6)–C(9)	1.446(5)
O(6)–C(7)	1.383(4)	C(7)–O(7)	1.204(5)
C(7)–C(8)	1.441(6)	C(8)–C(9)	1.342(5)
C(8)–C(10)	1.504(6)	C(10)–C(11)	1.507(11)
C(11)–C(12)	1.513(6)	C(12)–C(13)	1.370(1)
C(14)–C(15)	1.388(6)	C(14)–N(1)	1.333(4)
C(15)–C(16)	1.366(6)	C(16)–C(17)	1.392(6)
C(17)–C(18)	1.403(5)	C(17)–C(19)	1.427(6)
C(18)–C(22)	1.409(4)	C(18)–N(1)	1.355(4)
C(19)–C(20)	1.339(6)	C(20)–C(21)	1.433(6)
C(21)–C(22)	1.404(4)	C(21)–C(23)	1.404(5)
C(22)–N(2)	1.359(4)	C(23)–C(24)	1.360(6)
C(24)–C(25)	1.388(5)	C(25)–N(2)	1.332(4)
Co(2)–Co(1)–C(1)	137.0(2)	Co(2)–Co(1)–C(2)	103.1(1)
C(1)–Co(1)–C(2)	103.3(2)	Co(2)–Co(1)–C(3)	100.4(1)
C(1)–Co(1)–C(3)	110.1(2)	C(2)–Co(1)–C(3)	95.7(2)
C(1)–Co(1)–C(4)	100.3(2)	C(2)–Co(1)–C(4)	87.1(2)
C(3)–Co(1)–C(4)	147.8(2)	C(1)–Co(1)–C(6)	98.2(2)
C(2)–Co(1)–C(6)	154.1(2)	C(3)–Co(1)–C(6)	90.1(1)
C(4)–Co(1)–C(6)	75.0(1)	Co(1)–Co(2)–C(5)	140.7(1)
C(4)–Co(2)–C(5)	101.0(2)	C(4)–Co(2)–C(6)	80.3(1)
C(5)–Co(2)–C(6)	96.4(2)	Co(1)–Co(2)–N(1)	107.2(1)
C(4)–Co(2)–N(1)	91.5(1)	C(5)–Co(2)–N(1)	102.6(1)
C(6)–Co(2)–N(1)	160.5(1)	Co(1)–Co(2)–N(2)	105.4(1)
C(4)–Co(2)–N(2)	154.4(1)	C(5)–Co(2)–N(2)	104.4(1)
C(6)–Co(2)–N(2)	99.6(1)	N(1)–Co(2)–N(2)	80.2(1)
Co(1)–C(1)–O(1)	177.5(4)	Co(1)–C(2)–O(2)	176.8(4)
Co(1)–C(3)–O(3)	177.9(4)	Co(1)–C(4)–Co(2)	78.0(1)
Co(1)–C(4)–O(4)	136.2(3)	Co(2)–C(4)–O(4)	145.7(3)
Co(2)–C(5)–O(5)	174.5(3)	Co(1)–C(6)–Co(2)	75.2(1)
Co(1)C(6)O(6)	117.3(2)	Co(2)–C(6)–O(6)	119.9(2)
Co(1)–C(6)–C(9)	119.0(2)	Co(2)C(6)C(9)	120.0(3)
O(6)–C(6)–C(9)	104.4(2)	C(6)O(6)C(9)	109.4(3)
O(6)–C(7)–O(7)	120.0(3)	O(6)–C(7)–C(8)	108.1(3)
O(7)–C(7)C(8)	131.9(4)	C(7)–C(8)–C(9)	106.8(3)
C(7)–C(8)–C(10)	122.6(4)	C(9)–C(8)–C(10)	130.5(4)
C(6)–C(9)–C(8)	111.2(3)	C(8)–C(10)–C(11)	114.1(5)
C(10)–C(11)C(12)	115.6(5)	C(11)–C(12)–C(13)	115.0(3)

plexes. The stabilities of the *trans*-1,2-diamino cyclohexane and 2,2'-dipyridyl complexes (**3** and **9**, respectively) were still high enough for recrystallisation under Ar but *o*-phenylene diamine proved to be too weak a ligand to form a stable complex in solution. The formation of the $\text{Co}_2(\text{H}, \text{}^n\text{Bu}, \text{C}_4\text{O}_2)(\mu_2\text{-CO})(\text{CO})_4(\text{opda})$ complexes (**7**, two isomers?) under the preparative conditions was made possible only by their insolubility in hexane which also drove the equilibrium reaction (1) to completion in this case. The corresponding $\text{Co}_2(\text{H}, \text{H}, \text{C}_4\text{O}_2)(\mu_2\text{-CO})(\text{CO})_4(\text{opda})$ derivative was so labile, however, that it could not be isolated as a solid even under such conditions.

It is worth mentioning the significant difference between the reactivities of the three dinuclear cobalt carbonyls $\text{Co}_2(\text{CO})_8$, $\text{Co}_2(\text{HC}_2\text{R})(\text{CO})_6$, and $\text{Co}_2(\text{H,R,C}_4\text{O}_2)(\text{CO})_7$ against amines. As described already in 1953, $\text{Co}_2(\text{CO})_8$ reacts rapidly with amines by valence disproportionation and forms ionic derivatives of the type $[\text{CoL}_6][\text{Co}(\text{CO})_4]_2$ [9]. The acetylene complexes $\text{Co}_2(\text{HC}_2\text{R})(\text{CO})_6$, however, are, according to our experience, inert against amines under the mild conditions used in this study. The characteristic tendency of the butenolide complexes to give simple substitution reactions with ligands not commonly used in cobalt carbonyl chemistry should merit further studies.

2.2. X-Ray structures

The three complexes **1**, **8b** and **9** have the common framework shown in Fig. 1, where R = H (complex **1**) or R = $n\text{-C}_4\text{H}_9$ (complexes **8b** and **9**), and the chelating N1-N2 ligand is ethylenediamine (complex **1**), 1,10-phenanthroline (complex **8b**), or 2,2'-dipyridil (complex **9**) and the axial and equatorial ligands are carbonyl groups.

Fig. 2 shows the view and the atom labels of complex **1** and in Table 4 the corresponding bond distances and angles are listed. Fig. 3 and Table 5 cover complex **8b** and Fig. 4 and Table 6 deal with complex **9**.

Some features of the three structures are common to both complexes and others are quite different. The common features are represented by a similar disposal of the ligands. Viewing the structures along the Co–Co bond, the carbonyls and the nitrogen atoms appear in an eclipsed configuration. The lactone ring is perpendicular to the Co–Co bond and the two bridges are more

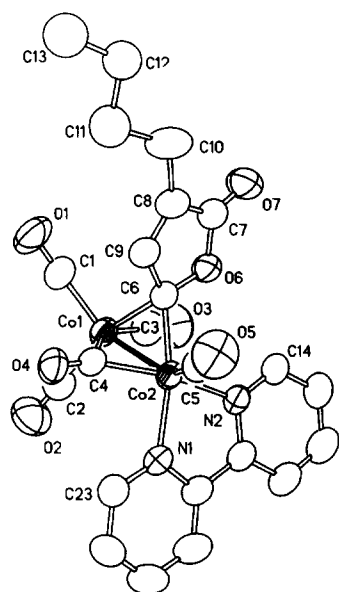


Fig. 4. ORTEP view (50% probability) and atom labelling scheme for complex **9**.

Table 6
Bond lengths (Å) and bond angles (°) for complex **9**

Co(1)–Co(2)	2.426(2)	Co(1)–C(1)	1.789(4)
Co(1)–C(2)	1.811(4)	Co(1)–C(3)	1.827(4)
Co(1)–C(4)	1.980(3)	Co(1)–C(6)	2.018(3)
Co(2)–C(4)	1.848(3)	Co(2)–C(5)	1.775(4)
Co(2)–C(6)	1.956(3)	Co(2)–N(1)	2.007(3)
Co(2)–N(2)	2.066(3)	C(1)–O(1)	1.125(5)
C(2)–O(2)	1.130(5)	C(3)–O(3)	1.121(6)
C(4)–O(4)	1.166(4)	C(5)–O(5)	1.124(5)
C(6)–O(6)	1.421(4)	C(6)–C(9)	1.462(5)
O(6)–C(7)	1.383(4)	C(7)–O(7)	1.205(5)
C(7)–C(8)	1.454(6)	C(8)–C(9)	1.333(5)
C(8)–C(10)	1.513(6)	C(10)–C(11)	1.524(17)
C(11)–C(12)	1.524(19)	C(12)–C(13)	1.524(26)
C(14)–C(15)	1.394(6)	C(14)–N(2)	1.335(5)
C(15)–C(16)	1.369(6)	C(16)–C(17)	1.360(6)
C(17)–C(18)	1.405(5)	C(18)–C(19)	1.459(5)
C(18)–N(2)	1.359(4)	C(19)–C(20)	1.389(5)
C(19)–N(1)	1.369(4)	C(20)–C(21)	1.376(6)
C(21)–C(22)	1.348(6)	C(22)–C(23)	1.394(5)
C(23)–N(1)	1.347(5)		
Co(2)–Co(1)–C(1)	136.0(1)	Co(2)–Co(1)–C(2)	107.1(1)
C(1)–Co(1)–C(2)	102.2(2)	Co(2)–Co(1)–C(3)	99.8(1)
C(1)–Co(1)–C(3)	107.6(2)	C(2)–Co(1)–C(3)	98.4(2)
C(1)–Co(1)–C(4)	102.2(2)	C(2)–Co(1)–C(4)	87.6(2)
C(3)–Co(1)–C(4)	147.5(1)	C(1)–Co(1)–C(6)	94.4(2)
C(2)–Co(1)–C(6)	158.0(1)	C(3)–Co(1)–C(6)	90.0(2)
Co(1)–Co(2)–C(5)	138.8(1)	C(4)–Co(2)–C(5)	100.0(2)
C(5)–Co(2)–C(6)	94.9(1)	Co(1)–Co(2)–N(1)	109.8(1)
C(4)–Co(2)–N(1)	91.9(1)	C(5)–Co(2)–N(1)	100.7(1)
C(6)–Co(2)–N(1)	163.2(1)	Co(1)–Co(2)–N(2)	106.9(1)
C(4)–Co(2)–N(2)	154.4(1)	C(5)–Co(2)–N(2)	105.3(1)
C(6)–Co(2)–N(2)	102.1(1)	N(1)–Co(2)–N(2)	79.8(1)
Co(1)–C(1)–O(1)	178.5(4)	Co(1)–C(2)–O(2)	179.1(4)
Co(1)–C(3)–O(3)	178.4(4)	Co(1)–C(4)–Co(2)	78.6(1)
Co(1)–C(4)–O(4)	137.0(2)	Co(2)–C(4)–O(4)	144.4(3)
Co(2)–C(5)–O(5)	174.5(3)	Co(1)–C(6)–Co(2)	75.2(1)
Co(1)–C(6)–O(6)	118.2(2)	Co(2)–C(6)–O(6)	122.6(2)
Co(1)–C(6)–C(9)	115.6(2)	Co(2)–C(6)–C(9)	120.3(2)
O(6)–C(6)–C(9)	103.6(3)	C6–O6–C7	109.8(3)
O(6)–C(7)–O(7)	121.2(4)	O(6)–C(7)–C(8)	108.1(3)
O(7)–C(7)–C(8)	130.7(4)	C(7)–C(8)–C(9)	106.7(3)
O(7)–O(8)–O(10)	120.9(4)	O(9)–C(8)–C(10)	132.4(4)
O(6)–C(9)–C(8)	111.8(3)	O(8)–O(10)–O(11)	116.6(6)
O(10)–O(11)–C(12)	101.3(9)	O(11)–O(12)–O(13)	108.5(12)

($\mu\text{-C4}$) or less ($\mu\text{-C6}$) asymmetric; the Co1–C6 bond is nearly 21–23 σ longer than Co2–C6, and Co1–C4 is 44–55 σ longer than Co2–C4. The Co1–Co2–C6 plane forms angles of 117°, 107° and 105° with the Co1–Co2–C4–O4 plane in complexes **1**, **8b** and **9**, respectively.

In the parent complex $\text{Co}_2(\text{H,H,C}_4\text{O}_2)(\mu\text{-CO})(\text{CO})_6$ [10] the C4 bridge is symmetric within the e.s.d. values; the great asymmetry of the C4 bridge in our complexes could be correlated to the substitution of two CO groups with stronger σ -donor ligands that strengthen the π -back-bonding of Co2 towards C4. This hypothesis is confirmed by comparing the values of the ethylenediamine complex (shorter Co2–C4 bond, better σ -donor ligand) with those of the phen and dipy complexes (longer Co2–C4 bonds, weaker σ -donor and better π -

Table 7

IR spectra of the $\text{Co}_2(\text{H,R,C}_4\text{O}_2)(\mu_2\text{-CO})(\text{CO})_4(\text{L-L})$ [(L-L) = diamine) complexes in benzene solution in the ν_{CO} range (cm^{-1})

Complex	ν_1	ν_2	ν_3	ν_4	ν_5 (bridge)	ν_{CO} (average)	ν_6 (organic)
1	2059vs	2003vs	1994s,sh	1967vs	1781m	1961	1735s
2	2050s	2002m	1985vs,br	1970vs,sh	1795s	1960	1733w 1682s
3	2052s	1980vs,br		1970vs	1798m,br	—	1733m 1682m,br
4	2061s	2007s	1995vs	1982vs	1789m	1967	1735s
5	2061s	2008vs	1995vs	1983vs	1790m	1967	1736s
6	2057s	2000s	1992m,sh	1963vs	1779m	1958	1732s
7	2053s	2015m	1992vs,sh 1984vs,br	1974vs	1783m 1776m	1961	1732m 1707m
8b	2058vs	2004vs	1994vs	1980vs	1788m	1965	1735s
9	2058vs	2005vs	1992vs	1978vs	1785m	1964	1732s

acceptor ligands); in fact the mean Co2-N distance is also longer for complex **1** (2.096 Å) and shorter for complexes **8b** and **9** (2.040 Å and 2.036 Å on average, respectively). As the previous values show, the most significant differences occur between complex **1** and the two other complexes (**8b** and **9**). Also, the Co–Co distances are in keeping with this trend (2.487(1) Å for **1**, 2.419(1) Å for **8b**, 2.426(2) Å for **9**).

An asymmetry also appears in the Co2–N bonds with Co2–N2 < Co2–N1 for complex **1** and Co2–N2 > Co2–N1 for complexes **8b** and **9**. The dipy and phen ligands are planar. The ethylenediamine ligand shows an abnormally short C(10)–C(11) bond, probably owing to a very high thermal motion that reflects a disorder between the δ and λ conformations of the ring. Attempts to separate the two conformations during refinement failed.

The planar γ -lactone ring also shows some differences in the three complexes. Complex **1** exhibits no difference between the C7–C8 and C8–C9 bonds and all the distances in the ring are smaller than in the complexes **8b** and **9**, in both of which a double bond character can be assigned to C8–C9. Also, the C9–C6–O6 and Co1–C6–Co2 angles are smaller (99°) and wider (78°) in complex **1** than in complexes **8b** and **9** (104° av., 75° av.). The parent compound does not allow a useful comparison owing to the high e.s.d.'s of the structural analysis [10]; a rough analysis of the bond and angle data show a larger ring than that present in complex **1**.

The crystal packing of complexes **8b** and **9** shows short intermolecular contacts between O7 and a hydrogen atom of dipyridyl (O7···H20, 2.36 Å) or of

phenanthroline (O7···H23, 2.34 Å). Complex **1** exhibits closer packing; short intermolecular contacts occur between O7 and one of the hydrogen atoms of C15 methyl (2.43 Å) and between O7 and the hydrogen atom of C8 (2.51 Å). One hydrogen atom of C14 methyl also contacts the O5 (2.54 Å) of another molecule. The Co2–C5–O5 group shows a significant deviation from linearity (173°), probably due to this packing influence.

Finally, it should be mentioned that the structures presented here furnish a further proof for the high stereo- and regio-selectivity of carbonylation of the cobalt carbonyl acetylene complexes $\text{Co}_2(\text{HC}_2\text{R})(\text{CO})_6$. This manifests itself in two respects. First, in the orientation of the lactone ring which is directed in complexes **8b** and **9** with its C–C “double” bond towards the bridging CO ligand like that observed in the case of the parent complex $\text{Co}_2(\text{H,H,C}_4\text{O}_2)(\mu\text{-CO})(\text{CO})_6$ [10]. Second, in the position of the ⁿBu group in these two complexes on C6: these structures represent the first crystallographic evidence for the rule formulated on the basis of spectroscopic evidence, *i.e.* that the carbonylation of the cobalt carbonyl complexes of terminal acetylenes yields exclusively butene-2-olide complexes in which the H atom is in the 2-, and the bulky group in the 3-position of the lactone ring [11–14].

2.3. IR spectra

In order to obtain information about the overall σ -donor and π -acceptor properties of the amine ligands in these compounds it was informative to compare the IR spectra of the new complexes with those of the

Table 8

IR spectra of the starting $\text{Co}_2(\text{H,R,C}_4\text{O}_2)(\mu_2\text{-CO})(\text{CO})_6$ complexes in benzene solution in the ν_{CO} range (cm^{-1})

R	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7 (bridge)	ν_{CO} (average)	ν_6 (organic)
H	2113m	2078vs	2062vs	2049w,sh	2043s	2035w,sh	1839m	2031	1773s
ⁿ Bu	2112m	2076vs	2060s	2045w,sh	2040s	2032w,sh	1837m	2029	1758m

Table 9
Crystal data for complexes **1**, **8b** and **9**

Complex	1	8b	9
Empirical Formula	C ₁₅ H ₁₈ Co ₂ N ₂ O ₇	C ₂₅ H ₁₈ Co ₂ N ₂ O ₇	C ₂₃ H ₁₈ Co ₂ N ₂ O ₇
Color; habit	brown, lamellar	dark brown-red, prismatic	dark brown, prismatic
Crystal size (mm)	0.10 × 0.42 × 0.52	0.42 × 0.58 × 0.80	0.60 × 0.88 × 1.00
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions	<i>a</i> = 7.442(2) Å <i>b</i> = 9.159(2) Å <i>c</i> = 14.182(3) Å α = 79.34(3)° β = 82.34(3)° γ = 70.07(3)°	<i>a</i> = 10.953(2) Å <i>b</i> = 16.464(4) Å <i>c</i> = 14.537(3) Å β = 110.47(2)°	<i>a</i> = 9.698(6) Å <i>b</i> = 15.508(6) Å <i>c</i> = 15.966(8) Å β = 79.30(4)°
Volume	950.6(7) Å ³	2455.8(10) Å ³	2359(2) Å ³
<i>Z</i>	2	4	4
Formula weight	456.2	576.3	552.3
Density (calc.)	1.594 Mg m ⁻³	1.559 Mg m ⁻³	1.555 Mg m ⁻³
Absorption coefficient	1.782 mm ⁻¹	1.398 mm ⁻¹	1.452 mm ⁻¹
<i>F</i> (000)	464	1168	1120

starting butenolide complexes. This could not be done for the spectra obtained in nujol because the spectra of the nonsubstituted butenolide complexes were found to

be very poorly resolved. Therefore, the IR absorption bands of the complexes **1–9** and of the starting butenolide complexes in the C–O stretching region were

Table 10
X-ray data collection and refinement

Complex	1	8b	9
Diffractometer		Siemens P4	
Radiation		Mo K α (λ = 0.71073 Å)	
Temperature (K)		293	
Monochromator		Highly oriented graphite crystal	
2 θ range	2.0°–55.0°	2.0 to 55.0°	2.0° to 60.0°
Scan type	θ –2 θ	θ –2 θ	θ –2 θ
Scan speed		Variable; 4.00 to 20.00°/min.	
Scan range	2.00°	2.20°	2.00°
Background measurement		Stationary crystal and stationary counter at beginning and end of scan, each for 30.0% of total scan time	
Standard reflections		2 measured every 50 reflections	
Index ranges	–10 ≤ <i>h</i> ≤ 10, –11 ≤ <i>k</i> ≤ 11 0 ≤ <i>l</i> ≤ 18	–14 ≤ <i>h</i> ≤ 13, 0 ≤ <i>k</i> ≤ 21 0 ≤ <i>l</i> ≤ 18	–13 ≤ <i>h</i> ≤ 13, –21 ≤ <i>k</i> ≤ 0 0 ≤ <i>l</i> ≤ 22
Reflections collected	4611	5867	7165
Independent reflections	4347 (<i>R</i> _{int} = 1.30%)	5648 (<i>R</i> _{int} = 2.03%)	6817 (<i>R</i> _{int} = 1.48%)
Observed reflections	3370 (<i>F</i> > 4.0 σ (<i>F</i>))	4108 (<i>F</i> > 4.0 σ (<i>F</i>))	4600 (<i>F</i> > 4.0 σ (<i>F</i>))
Absorption correction		Semi-empirical	
Min./max. transmission	0.4266/0.5582	0.0239/0.0732	0.0722/0.1201
System Used		Siemens SHELXTL IRIS	
Solution		Direct Methods	
Refinement method		Full-Matrix Least-Squares	
Quantity minimised		$\sum w(F_o - F_c)^2$	
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0024F^2$	$w^{-1} = \sigma^2(F) + 0.0010F^2$	$w^{-1} = \sigma^2(F) + 0.0018F^2$
Number of parameters refined	235	319	318
Final <i>R</i> indices (obs. data)	<i>R</i> = 3.72%, <i>wR</i> = 5.54%	<i>R</i> = 4.13%, <i>wR</i> = 5.51%	<i>R</i> = 4.66%, <i>wR</i> = 6.52%
<i>R</i> indices (all data)	<i>R</i> = 5.10%, <i>wR</i> = 8.93%	<i>R</i> = 5.82%, <i>wR</i> = 5.96%	<i>R</i> = 6.74%, <i>wR</i> = 7.29%
Goodness-of-fit	0.95	1.29	1.21
Largest and mean Δ/σ	0.156, 0.007	0.177, 0.012	7.944, 0.075
Data-to-Parameter Ratio	14.3 : 1	12.9 : 1	14.5 : 1
Largest difference peak	0.70 eÅ ⁻³	0.58 eÅ ⁻³	0.79 eÅ ⁻³
Largest difference hole	–0.57 eÅ ⁻³	–0.34 eÅ ⁻³	–0.32 eÅ ⁻³

recorded in benzene solution. They are compiled in Tables 7 and 8.

It can be seen that on substituting two CO ligands by the diamines there is a strong shift (average 60–70 cm^{-1}) of all “inorganic” ν_{CO} bands towards lower wavenumbers. Such a shift could obviously be expected.

More important is the fact that the shift of the ν_{CO} vibration belonging to the “organic” lactone group is also significant. The magnitude of this shift is, however, somewhat obscured by the fact that complexes **2**, **3** and **7** show two bands in this region. In the case of complex **7** this may be explained by the presence of two substitutional isomers since the ν_{CO} vibration of the bridging carbonyl group is also split. No such explanation is possible for complexes **2** and **3**, therefore we probably have to account this splitting to a Fermi resonance, which is well known for γ -lactones [15] and has been observed already also in these types of complexes [8,11].

We attribute the unexpectedly large difference between wavenumbers of the “organic” ν_{CO} vibrations of the two starting lactone butenolide complexes in benzene (see Table 8) also to this Fermi effect. Apparently the H,H complex shows no Fermi splitting but the H, ^nBu complex does (compare [11]) and we regard the band observed at 1758 cm^{-1} as the lower frequency component. The higher frequency component which we would expect at around 1770 cm^{-1} is apparently so weak in this solvent, that it cannot be identified with certainty. This interpretation is supported by the IR spectrum of the complex in hexane and in a 4:1 mixture of hexane and benzene where the “organic” ν_{CO} vibration appears at 1778w, 1769w,sh cm^{-1} , and at 1774w, 1767m-w cm^{-1} , respectively (well observable splitting). This intensity shift in favour of the lower frequency band in changing the solvent from hexane to benzene is in accord with the observation that increasing polarity of the solvent strengthens in such cases the lower lying band [15].

Accepting this interpretation and comparing only the higher frequency bands (where necessary) it can be concluded, that the shift of the “organic” ν_{CO} band caused by substituting two CO ligands by diamines is 35–40 cm^{-1} , i.e. although somewhat smaller but still of the same order of magnitude as that of the “inorganic” ν_{CO} vibrations. This proves that the μ_2 carbon atom of the organic group has significant carbenoid character which conducts electronic effects more like an sp^2 -type carbon atom and does not act as an “insulating” sp^3 -type carbon atom as suggested earlier [11,16]. The difference between the shifts of the “inorganic” and “organic” C–O vibrations should be attributed not to such an insulating effect but rather to the fact that the “lactone” ligand has a larger delocalised π -electron system.

The IR spectra of the new complexes in benzene allow one further conclusion. As can be seen, there is a

small but systematic difference between the average “inorganic” C–O stretching vibrations of the complexes containing aliphatic amines (tmeda, dach) on the one side and heterocyclic amines (phen, dipy) on the other side: the average wavenumbers of those of the phen- and dipy-substituted complexes are somewhat higher. This has to be ascribed to the better π -acceptor capacity of these heterocyclic ligands. The small difference at the same time shows that also these ligands are rather poor π -acceptors, a conclusion which is in accordance with earlier observations [17].

3. Experimental

3.1. General procedures

All reactions were carried out under Ar. The IR spectra were recorded on a Specord 75 (Carl Zeiss Jena) spectrometer. The starting butenolide complexes were prepared from $\text{Co}_2(\text{CO})_8$ and the corresponding acetylene at 70–80 $^\circ\text{C}$ and 300 bar CO pressure as described by Sternberg et al. [7a]. The amines used were commercial products.

3.2. Preparation of the complexes

The cobalt carbonyl butenolide complex (0.5 mmol) and the diamine (0.6–1.0 mmol) were stirred in a

Table 11
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for complex **1**

	x	y	z	U_{eq}^a
Co(1)	3422(1)	7851(1)	8562(1)	39(1)
Co(2)	3284(1)	10202(1)	7344(1)	32(1)
C(1)	5316(6)	6084(5)	8808(3)	60(1)
O(1)	6521(5)	5011(4)	8976(3)	102(2)
C(2)	2729(5)	8471(5)	9714(3)	54(1)
O(2)	2234(5)	8830(5)	10447(2)	88(2)
C(3)	1455(6)	7259(5)	8562(3)	57(1)
O(3)	246(5)	6858(4)	8590(3)	93(2)
C(4)	4894(4)	9271(4)	8254(2)	41(1)
O(4)	6126(3)	9369(3)	8589(2)	61(1)
C(5)	4736(4)	10636(4)	6353(2)	44(1)
O(5)	5785(4)	10758(4)	5752(2)	70(1)
C(6)	3788(4)	8058(3)	7123(2)	37(1)
O(6)	2585(3)	7691(3)	6616(2)	44(1)
C(7)	3519(5)	6649(4)	5998(2)	48(1)
O(7)	2720(4)	6148(3)	5531(2)	67(1)
C(8)	5398(5)	6326(4)	6070(2)	51(1)
C(9)	5561(4)	7162(4)	6722(2)	42(1)
C(10)	1070(8)	13448(5)	7313(5)	102(3)
C(11)	–73(8)	12788(6)	7073(6)	121(3)
C(12)	4008(6)	13071(5)	7694(4)	73(2)
C(13)	2035(7)	12288(6)	8917(3)	80(2)
C(14)	–686(5)	10481(6)	7111(4)	79(2)
C(15)	873(6)	11334(7)	5698(3)	83(2)
N(1)	2563(4)	12377(3)	7883(2)	49(1)
N(2)	690(4)	11246(3)	6749(2)	53(1)

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

Schlenk tube in 20 ml hexane at room temperature. Depending on the reactants the reaction was complete within 10–60 min, as shown by the formation of a dark precipitate and the solution becoming practically colourless. The solid product was separated by filtration and its IR spectrum recorded both in nujol mull and benzene solution. To obtain pure samples for X-ray crystallography and elementary analysis the precipitates were dissolved in dichloromethane and crystallised by layering hexane on the top of the solution thus using the method of diffusion controlled crystallisation.

3.3. X-Ray crystal data collection, structure determination and refinement for complexes **1**, **8b** and **9**

Crystal data are collected in Table 9; the parameters of structure determinations and refinements are listed in

Table 12
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for complex **8b**

	x	y	z	U_{eq}^a
Co(1)	9964(1)	1882(1)	491(1)	55(1)
Co(2)	7914(1)	1723(1)	754(1)	49(1)
C(1)	11291(4)	2581(2)	848(3)	75(2)
O(1)	12156(3)	3006(2)	1101(3)	118(2)
C(2)	10740(3)	919(2)	861(3)	68(1)
O(2)	11186(3)	302(2)	1112(3)	98(1)
C(3)	9444(4)	1685(2)	-824(3)	65(1)
O(3)	9095(4)	1544(2)	-1638(2)	96(1)
C(4)	9527(3)	1856(2)	1715(2)	58(1)
O(4)	10101(3)	1886(2)	2548(2)	80(1)
C(5)	6902(3)	2237(2)	1289(2)	61(1)
O(5)	6320(3)	2616(2)	1631(2)	96(1)
C(6)	8499(3)	2689(2)	255(2)	53(1)
O(6)	7843(2)	2944(1)	-724(2)	62(1)
C(7)	7686(3)	3777(2)	-746(3)	71(1)
O(7)	7146(3)	4117(2)	-1515(2)	98(1)
C(8)	8275(4)	4080(2)	240(3)	74(2)
C(9)	8742(3)	3434(2)	819(3)	63(1)
C(10)	8263(6)	4965(3)	493(4)	124(3)
C(11)	7068(6)	5226(3)	704(6)	140(4)
C(12)	6999	6120	926	153(4)
C(13)	5845	6367	1004	216(7)
C(14)	8378(4)	235(2)	2045(3)	72(1)
C(15)	8308(4)	-589(3)	2221(3)	87(2)
C(16)	7627(4)	-1089(3)	1467(4)	89(2)
C(17)	6989(3)	-767(2)	536(3)	69(2)
C(18)	7117(3)	71(2)	417(3)	58(1)
C(19)	6206(4)	-1225(3)	-294(4)	85(2)
C(20)	5562(4)	-873(3)	-1158(3)	83(2)
C(21)	5649(3)	-14(2)	-1285(3)	67(1)
C(22)	6457(3)	447(2)	-493(2)	55(1)
C(23)	4981(4)	392(3)	-2168(3)	80(2)
C(24)	5136(4)	1209(3)	-2213(3)	76(2)
C(25)	5962(3)	1617(2)	-1397(3)	66(1)
N(1)	7817(2)	564(2)	1159(2)	57(1)
N(2)	6632(2)	1260(2)	-548(2)	54(1)

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

Table 13
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for complex **9**

	x	y	z	U_{eq}^a
Co(1)	7747(1)	1645(1)	139(1)	53(1)
Co(2)	5758(1)	1979(1)	1255(1)	46(1)
C(1)	8237(4)	1865(3)	-977(2)	67(1)
O(1)	8548(4)	2021(2)	-1675(2)	103(1)
C(2)	8050(4)	496(3)	184(2)	69(1)
O(2)	8223(4)	-224(2)	209(2)	102(1)
C(3)	9177(4)	2012(3)	651(3)	72(1)
O(3)	10041(4)	2255(3)	969(3)	107(2)
C(4)	5722(3)	1381(2)	258(2)	53(1)
O(4)	4995(3)	1037(2)	-142(2)	69(1)
C(5)	4128(4)	2529(2)	1374(2)	60(1)
O(5)	3118(3)	2887(2)	1382(2)	100(1)
C(6)	6759(3)	2784(2)	412(2)	51(1)
O(6)	7550(3)	3490(2)	637(1)	59(1)
C(7)	7385(4)	4197(2)	136(2)	63(1)
O(7)	7994(3)	4863(2)	202(2)	85(1)
C(8)	6436(4)	3955(2)	-430(2)	64(1)
C(9)	6073(4)	3137(2)	-255(2)	56(1)
C(10)	6030(6)	4597(3)	-1055(3)	94(2)
C(11)	5514(23)	4225(8)	-1825(8)	88(5)
C(12)	5225(17)	5044(8)	-2292(9)	76(3)
C(13)	4588(24)	4790(13)	-3060(11)	97(5)
C(14)	7209(4)	3009(2)	2495(2)	62(1)
C(15)	7593(4)	3173(3)	3278(2)	73(1)
C(16)	7294(4)	2572(3)	3914(2)	73(1)
C(17)	6643(4)	1827(3)	3763(2)	69(1)
C(18)	6279(3)	1690(2)	2962(2)	52(1)
C(19)	5554(3)	915(2)	2757(2)	53(1)
C(20)	5237(4)	210(3)	3294(3)	72(1)
C(21)	4558(5)	-496(3)	3041(3)	78(1)
C(22)	4198(4)	-484(3)	2265(3)	72(1)
C(23)	4516(4)	232(2)	1737(2)	63(1)
N(1)	5194(2)	926(2)	1967(2)	49(1)
N(2)	6557(3)	2287(2)	2330(2)	50(1)

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

Table 10. Absorption correction was applied according to the method developed by North et al. [18]. All atoms were refined anisotropically except the disordered atoms of the C11-C12-C13 chain of complex **9**, which were refined isotropically keeping the C–C distances fixed. Most hydrogen atoms were located on the final Fourier-difference maps and corresponded to the calculated positions; they were refined riding on the corresponding C atoms with fixed U_{iso} .

Atomic fractional coordinates are listed in Tables 11, 12 and 13 for complexes **1**, **8b** and **9**, respectively.

3.4. Supplementary material

Full lists exist of coordinates for complex **9** as do full tables of distances and angles, hydrogen coordinates, anisotropic displacement coefficients, calculated and observed structure factors for complexes **1**, **8b** and **9**.

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