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Synthesis and crystal structure of $[\text{Co}_2(\text{CO})_4\{\mu\text{-PhC}\equiv\text{CC}(\text{O})\text{CH}_3\}_3]$. Its role in the cyclotrimerization of 1-phenylbut-1-yn-3-one to 1,3,5-triphenyltris(carboxymethyl)benzene

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Abstract

The reaction of $[\text{Co}_2(\text{CO})_8]$ with 1-phenylbut-1-yn-3-one in refluxing toluene yields $[\text{Co}_2(\text{CO})_6\{\mu\text{-PhC}\equiv\text{CC}(\text{O})\text{CH}_3\}_3]$, the symmetrical trimer $(\text{PhC}_2\text{C}(\text{O})\text{CH}_3)_3$, which were characterized by spectroscopic techniques, and the title complex, the structure of which has been elucidated by X-ray analysis.

The crystals are monoclinic $P2_1/c$ with $a = 10.640(2)$, $b = 17.741(4)$, $c = 17.845(4)$ Å, $\beta = 90.50(3)^\circ$, $Z = 4$. The molecule has a Co–Co bond and the $(\text{PhC}_2\text{C}(\text{O})\text{CH}_3)_3$ chain links the cobalt atoms in a “flyover” arrangement.

To our knowledge, this is the first example of stepwise formation of a symmetrical benzene from an asymmetrical, internal alkyne *via* this type of intermediate.

1. Introduction

The cyclotrimerization of alkynes assisted by transition metals has been long known [1]; nickel, iron and cobalt carbonyls are catalysts in such reactions [2]. When $[\text{Co}_2(\text{CO})_8]$ was used, evidence was obtained for the initial formation of $[\text{Co}_2(\text{CO})_6(\mu\text{-RC}\equiv\text{CR}')]_3$ (Complexes 1) [3]; these are effectively involved in the catalytic cycle and can take up other acetylene molecules to give complexes of general formula $[\text{Co}_2(\text{CO})_4(\text{RC}\equiv\text{CR}')_3]$ (complexes 2) [4]. A structure based on a seven-membered cobaltacycle was originally proposed for the latter [5]; X-ray structure determinations on the complexes with $\text{HC}\equiv\text{CCMe}_3$ (complex 2a) [6] and $\text{HC}\equiv\text{CCF}_3$ (complex 2b) [7] showed that these derivatives contain two $\text{Co}(\text{CO})_2$ units and a six-carbon atom

flyover bridge formed by the head-to-tail-head-to-head trimerization of the alkynes. Oxidation with Br_2 or drastic thermal treatment of complexes 2 gave 1,2,4-substituted benzenes. These trimerizations, characterized by high regioselectivity, represent a useful preparative entry into the chemistry of asymmetrically substituted benzenes. For example, sterically strained 1,2,4-tri-*t*-butylbenzene was obtained for the first time via these reactions [2,5].

We are currently investigating the reactions of metal carbonyls with alkynes, dialkynes, and propargylamines; some of these are useful synthons for substituted aromatic derivatives or undergo co-cyclization reactions with nitriles giving condensed heterocyclic compounds [8]. We aimed for “intermediate models” [9] or trapped reaction intermediates [10] to better understand the alkyne oligomerization and co-oligomerization processes.

Here we describe the reaction of $\text{PhC}\equiv\text{CC}(\text{O})\text{CH}_3$ (1-phenylbut-1-yn-3-one, PBO) with $[\text{Co}_2(\text{CO})_8]$; we

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obtained the expected [Co₂(CO)₆(μ-R₂C≡CR')] (complex **1a**) but we also observed the formation of considerable amounts of a white organic product and a purple complex. These were {PhC≡CC(O)CH₃}₃ (Compound A) and the symmetrically substituted [Co₂(CO)₄{PhC≡CC(O)CH₃}₃] (complex **2c**). These products were characterized by elemental analyses, spectroscopy and mass spectrometry and the crystal structure of **2c** was determined by X-ray diffraction. To our knowledge this is the first example of symmetrically substituted complex of type **2**. X-ray studies on the asymmetrically substituted **2a**, **2b** had been reported before [6,7]. The easy release of the 1,3,5-substituted benzene in the relatively mild reaction is noteworthy.

2. Experimental details

[Co₂(CO)₈] (Strem Chemicals) and PBO (K&K) were commercial products and were used as received; the reactions were performed under dry N₂ in distilled, dried toluene. The reaction solutions were filtered under N₂, reduced to small volume under reduced pressure and purified on TLC preparative plates (Kieselgel P.F., Merck; eluants: mixtures of light petroleum 40–70°C and diethyl ether).

The products were analyzed with a F&M CHN Analyzer and cobalt was determined by F. Pascher Laboratories (Remagen, Germany). IR spectra were measured on a Perkin Elmer 580 B instrument, and ¹H and ¹³C NMR spectra on a Jeol JNM-270 FT instrument. Mass spectra were obtained on a Kratos MS-80 system.

2.1. Reaction of [Co₂(CO)₈] with PBO

[Co₂(CO)₈] (1.0 g, 2.92 mmol) and PBO (1.0 ml, 5.2 mmol) under N₂ in refluxing toluene for 2 min yielded a dark purple solution containing **1a** as the main product (0.77 g, 1.78 mmol, 60%), impure **2c** (0.35 g, 0.59 mmol, 20%) and about 0.36 g (0.55 mmol) of the whitish compound A. Yields of compound A and of **2c** were increased considerably at the expense of **1a** by allowing the reaction to proceed for about 10 min at reflux.

Complex **2c** and compound A appeared on the TLC plates as a broad purple-whitish band; this was collected and crystallization was attempted from heptane–CHCl₃ (70:30) and cooling. A white precipitate mixed with small purple crystals of **2c** was separated by hand. The impure crystals of **2c** were recrystallized, giving compound A, and well-formed purple crystals of **2c**, which were separated by hand, washed with heptane, and air-dried (Yield 0.15 g, ca. 8%). A small sample of pure **2c** (0.20 g, 0.38 mmol) was dissolved in toluene and kept at +70°C for 2 h. After solvent

TABLE 1. Crystal data for Co₂(CO)₄{PhC≡CC(O)CH₃}₃

Empirical formula	C ₃₄ H ₂₁ Co ₂ O ₇
Colour, Habit	purple, prismatic
Crystal size	0.2 × 0.2 × 0.4 mm
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	<i>a</i> = 10.640(2) Å <i>b</i> = 17.741(4) Å <i>c</i> = 17.845(4) Å β = 90.50(3)°
Volume	3368.4(12) Å ³
Z	4
Formula weight	659.4
Density (calc.)	1.300 Mg m ⁻³
Absorption coefficient	1.023 mm ⁻¹
<i>F</i> (000)	1340

evaporation a mixture of **2c** (0.10 g, 0.19 mmol) and A (0.09 g, ca. 0.12 mmol) was obtained. Some metal powder was also observed.

TABLE 2. Data for the collection of intensities, solution and refinement

Diffractometer used	Siemens P4
Radiation	Mo Kα (λ = 0.71073 Å)
Temperature	293 K
Monochromator	Highly oriented graphite crystal
2θ Range	2.0 to 50.0°
Scan type	2θ – θ
Scan speed	Variable; 4.00 to 15.00° min ⁻¹ in ω
Scan range (ω)	2.00° plus Kα-separation
Background measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 35.0% of total scan time
Standard reflections	2 measured every 50 reflections
Index ranges	–12 ≤ <i>h</i> ≤ 12, –21 ≤ <i>k</i> ≤ 21, –12 ≤ <i>l</i> ≤ 21
Reflections collected	7600
Independent reflections	5960 (<i>R</i> _{int} = 10.84%)
Observed reflections	3777 (<i>F</i> > 5.0σ(<i>F</i>))
Absorption correction	semi-empirical
Min./max. transmission	0.067/0.081
System used	Siemens SHELXTL PLUS (PC Version)
Solution	Direct methods
Refinement method	Full-matrix least-squares
Quantity minimized	Σw(<i>F</i> _o – <i>F</i> _c) ²
Hydrogen atoms	Riding model, fixed isotropic <i>U</i>
Weighting scheme	w ⁻¹ = σ ² (<i>F</i>) + 0.0100 <i>F</i> ²
Number of parameters refined	361
Final <i>R</i> indices (obs. data)	<i>R</i> = 6.56, w <i>R</i> = 11.39%
<i>R</i> indices (all data)	<i>R</i> = 9.81, w <i>R</i> = 14.78%
Goodness-of-fit	1.04
Largest and mean Δ/σ	1.676, 0.108
Data-to-parameter ratio	10.5:1
Largest difference peak	1.83 e Å ⁻³
Largest difference hole	–0.40 e Å ⁻³

2.1.1. Complex 1a

Found: C, 44.9; H, 2.1; Co, 27.1. C₁₆H₈Co₂O₇ calcd.: C, 44.7; H, 1.9; Co, 27.4%. IR (C₇H₁₆): 2100 s, 2066 vs, 2038vs(b), 1670 w(vb) cm⁻¹. ¹H NMR (CDCl₃, r.t.): 7.50 m (5H, Ph), 2.45 s (3H, Me) ppm. ¹³C NMR (CDCl₃, r.t.): 31.1 s (CH₃); 92.2 s(b) (C≡C-R); 128.3–129.5 m (Ph); 136.6 s (H–C≡C); 198.2 (b) (6 CO); 201.1 s {–C(O)} ppm.

2.1.2. Complex 2c

Found: C, 61.7; H, 3.8; Co, 17.6. C₃₄H₂₄Co₂O₇ calcd.: C, 61.65; H, 3.65; Co, 17.79%. IR (C₇H₁₆): 2070

s, 2044 vs, 2020 s(vb), 1710–1700 vs, cm⁻¹. ¹H NMR (CDCl₃, r.t.): 7.55–7.35 m (15H, Ph), 2.30 s, 2.06 s, 1.98 s (3,3,3H, CH₃) ppm. ¹³C NMR (CDCl₃, r.t.): 28.5 s, 31.4 s, 31.9 s (CH₃), 126.2–129.4 m (Ph), 128.2 s, 128.9 s, 129.1 s, 136.2 s, 140.0 s, 147.2 s (C₆ ring carbons), ca. 200.0 (b) (fluxional CO's) ppm. Mass spectrum: P⁺ = 662 m/e, loss of five fragments with m/e = 28, followed by competitive fragmentation processes.

2.1.3. Compound A

Found: C, 83.5; H, 5.7. C₃₀H₂₄O₃ calcd.: C, 83.31; H, 5.59%. ¹H NMR (CDCl₃, r.t.): 7.41 m, 7.16 m, 7.00

TABLE 3. Atomic coordinates (×10⁴) and equivalent isotropic displacement coefficients (Å² × 10³)

	x	y	z	U _{eq} ^a
Co(1)	1534(1)	1096(1)	6117(1)	41(1)
Co(2)	1787(1)	2431(1)	5788(1)	36(1)
C(1)	928(6)	1988(4)	6675(4)	39(2)
C(2)	1765(6)	1597(4)	7162(4)	39(2)
C(3)	2979(6)	1510(4)	6821(4)	35(2)
C(4)	3389(6)	2160(4)	6347(4)	32(2)
C(5)	3568(6)	2001(4)	5562(4)	35(2)
C(6)	2561(7)	1551(4)	5301(4)	41(2)
C(7)	-238(4)	2342(3)	6946(3)	42(3)
C(8)	-196	2718	7632	58(3)
C(9)	-1236	3129	7872	73(4)
C(10)	-2317	3163	7427	81(4)
C(11)	-2360	2787	6740	72(4)
C(12)	-1320	2376	6500	57(3)
C(13)	1410(7)	1274(4)	7924(5)	45(3)
C(14)	236(10)	827(7)	8005(7)	71(4)
C(15)	4011(4)	1002(3)	7117(3)	41(2)
C(16)	3745	342	7511	52(3)
C(17)	4723	-94	7804	68(4)
C(18)	5967	129	7702	70(4)
C(19)	6234	788	7308	58(3)
C(20)	5256	1224	7015	46(3)
C(21)	4007(7)	2819(4)	6729(4)	35(2)
C(22)	3793(10)	2933(5)	7549(4)	58(3)
C(23)	4566(4)	2308(3)	5052(3)	36(2)
C(24)	5767	1992	5078	58(3)
C(25)	6692	2247	4591	70(4)
C(26)	6417	2817	4077	69(4)
C(27)	5217	3133	4051	64(4)
C(28)	4292	2879	4538	50(3)
C(29)	2449(8)	1230(5)	4525(4)	52(3)
C(30)	3436(10)	682(6)	4292(6)	77(4)
O(1)	2044(6)	1437(4)	8449(3)	66(2)
O(2)	1557(8)	1369(5)	4126(4)	90(3)
O(3)	4657(5)	3251(3)	6383(3)	51(2)
C(31)	37(9)	850(5)	5718(5)	64(3)
O(31)	-889(7)	684(5)	5453(5)	106(3)
C(32)	2170(9)	166(5)	6057(5)	58(3)
O(32)	2585(7)	-412(4)	5991(4)	89(3)
C(33)	624(7)	2579(5)	5059(5)	54(3)
O(33)	-94(6)	2704(4)	4607(4)	83(3)
C(34)	1694(7)	3381(5)	6090(5)	52(3)
O(34)	1596(7)	3971(4)	6322(5)	92(3)

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

m (5,5,5 H pH), 1.91 s, 1.86 s, 1.80 s (3,3,3H, CH_3) ppm. ^{13}C NMR (CDCl_3 r.t.): 31.6 s, 31.8 s, 32.5 s (CH_3), 127.4–133.9 m (Ph), 136.8 d, 137.2 d, 138.1 s, 140.6 s, 141.7 s, 143.9 s (skeletal C_6), 204.6 s, 205.9 s, 206.2 s ($(\text{CO})\text{CH}_3$) ppm. Mass spectrum: $\text{P}^+ = 432$, loss of three fragments with $m/e = 28$ along with complex and competitive fragmentation processes.

2.1.4. X-ray crystal data collection, structure determination and refinement for the complex 2c

The crystal data and the measurement and refinement parameters are given in Tables 1 and 2, respectively. The fractional atomic coordinates and U_{eq} are listed in Table 3.

Direct methods allowed the location of the Co atoms: subsequently the Fourier difference maps led to the location of all the other atoms. Some of the hydrogen atoms were located on the map: the phenyl and methyl groups were treated as rigid groups with the hydrogen atoms in calculated positions. During the last refinement cycles some peaks appeared round C(14) and C(30) attributable to disordered hydrogen atoms. These hydrogen atom positions were given a 0.5 occupancy factor.

3. Results and discussion

Complex 1a belongs to a well established class [3]. The analytic and spectroscopic data accord with the formulation $[\text{Co}_2(\text{CO})_6\{\mu\text{-PhC}\equiv\text{CC}(\text{O})\text{CH}_3\}]$. Complex 2c has been identified as $[\text{Co}_2(\text{CO})_4\{\text{PBO}\}_3]$ and its structure is discussed below. Compound A has analyses, mass spectrum, and ^1H and ^{13}C NMR spectra consistent with a formulation as a PBO cyclotrimer.

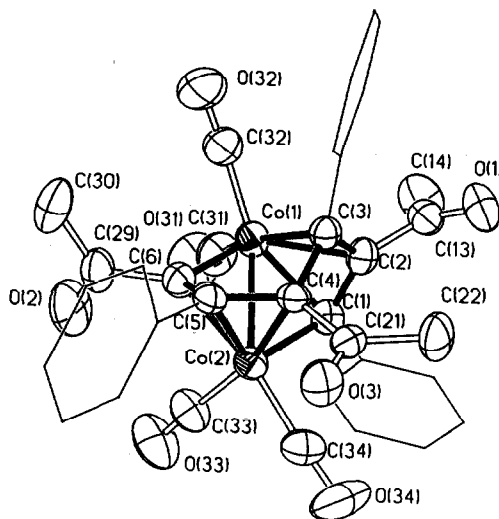


Fig. 1. Molecular structure of $[\text{Co}_2(\text{CO})_4\{\text{PhC}\equiv\text{CC}(\text{O})\text{CH}_3\}_3]$ with the thermal ellipsoids (50% probability) and with the atom labelling scheme.

The presence of more than one signal for the CH_3 in the ^1H and ^{13}C NMR spectra, as well as for the $\text{C}(\text{O})\text{CH}_3$ in the ^{13}C spectrum can be explained if the rotation of the $\text{C}(\text{O})\text{CH}_3$ substituents is restricted, either because of steric reasons or because of the conjugation of the $\text{C}(\text{sp}^2)$ with the coplanar benzene ring. This would create different “conformers” with inequivalent (CO) and CH_3 groups. The 1,3,5- substitution is also supported by the fact that A is the only organic product found in the reaction. A is formed upon heating 2c under mild conditions. The X-ray structure of the precursor 2c also supports this formulation.

TABLE 4. Bond lengths (Å)

Co(1)–Co(2)	2.455(1)	Co(1)–C(31)	1.794(9)
Co(1)–C(32)	1.787(9)	Co(1)–C(1)	1.980(7)
Co(1)–C(2)	2.079(7)	Co(1)–C(3)	2.109(7)
Co(1)–C(6)	1.998(7)	Co(2)–C(33)	1.807(8)
Co(2)–C(34)	1.773(8)	Co(2)–C(1)	1.997(7)
Co(2)–C(4)	2.025(6)	Co(2)–C(5)	2.085(7)
Co(2)–C(6)	1.971(7)	C(1)–C(2)	1.419(10)
C(1)–C(7)	1.476(8)	C(2)–C(3)	1.441(9)
C(2)–C(13)	1.525(11)	C(3)–C(4)	1.497(9)
C(3)–C(15)	1.512(8)	C(4)–C(5)	1.443(9)
C(4)–C(21)	1.503(10)	C(5)–C(6)	1.411(10)
C(5)–C(23)	1.506(8)	C(6)–C(29)	1.501(11)
C(13)–C(14)	1.488(13)	C(13)–O(1)	1.186(10)
C(21)–C(22)	1.496(11)	C(21)–O(3)	1.206(9)
C(29)–C(30)	1.493(14)	C(29)–O(2)	1.208(11)
C(31)–O(31)	1.128(12)	C(32)–O(32)	1.124(11)
C(33)–O(33)	1.128(10)	C(34)–O(34)	1.130(11)

3.1. X-ray structure of complex 2c

The molecular structure of 2c is shown in Fig. 1 and relevant distances and angles are given in Tables 4 and 5.

Complex 2c has a CO₂(CO)₄ skeleton with two axial carbonyls and two equatorial carbonyls with respect to the Co(1)Co(2)C(1)C(6) plane. The equation of the greatly puckered plane is, in fractional coordinates, $8.72x + 0.83y + 10.06z = 7.60$ with deviations of $-0.02(3)$ Å for Co and of $0.09(1)$ Å for C. This

ensemble is bridged by a substituted C₆ chain forming a “flyover” arrangement of two joined allyl groups. Formally C(1) and C(6) form σ -bonds with Co(2) and Co(1), respectively and C(1)C(2)C(3) and C(4)C(5)C(6) have π -interactions with Co(1) and Co(2), respectively. Figures 2a and b show two views of the orientation of the C(1)–C(6) chain with respect to the Co–Co axis.

The Co(1)–C(6) and Co(2)–C(1) bond lengths are 1.998(7) and 1.997(7) Å, respectively, whereas the π -interactions are within the ranges 1.980(7)–2.109(7) Å

TABLE 5. Bond angles (°)

Co(2)–Co(1)–C(31)	103.8(3)	Co(2)–Co(1)–C(32)	146.5(3)
C(31)–Co(1)–C(32)	95.0(4)	Co(2)–Co(1)–C(1)	52.2(2)
C(31)–Co(1)–C(1)	95.9(4)	C(32)–Co(1)–C(1)	153.2(4)
Co(2)–Co(1)–C(2)	77.9(2)	C(31)–Co(1)–C(2)	123.9(4)
C(32)–Co(1)–C(2)	114.0(3)	C(1)–Co(1)–C(2)	40.8(3)
Co(2)–Co(1)–C(3)	74.1(2)	C(31)–Co(1)–C(3)	164.1(4)
C(32)–Co(1)–C(3)	94.7(3)	C(1)–Co(1)–C(3)	70.2(3)
C(2)–Co(1)–C(3)	40.3(3)	Co(2)–Co(1)–C(6)	51.3(2)
C(31)–Co(1)–C(6)	107.4(4)	C(32)–Co(1)–C(6)	96.9(4)
C(1)–Co(1)–C(6)	103.1(3)	C(2)–Co(1)–C(6)	114.9(3)
C(3)–Co(1)–C(6)	83.9(3)	Co(1)–Co(2)–C(33)	103.7(3)
Co(1)–Co(2)–C(34)	146.9(3)	C(33)–Co(2)–C(34)	92.4(4)
Co(1)–Co(2)–C(1)	51.6(2)	C(33)–Co(2)–C(1)	108.2(3)
C(34)–Co(2)–C(1)	96.1(3)	Co(1)–Co(2)–C(4)	75.3(2)
C(33)–Co(2)–C(4)	163.2(3)	C(34)–Co(2)–C(4)	97.2(3)
C(1)–Co(2)–C(4)	84.5(3)	Co(1)–Co(2)–C(5)	78.2(2)
C(33)–Co(2)–C(5)	122.1(3)	C(34)–Co(2)–C(5)	117.4(3)
C(1)–Co(2)–C(5)	115.6(3)	C(4)–Co(2)–C(5)	41.1(3)
Co(1)–Co(2)–C(6)	52.3(2)	C(33)–Co(2)–C(6)	94.8(3)
C(34)–Co(2)–C(6)	155.8(3)	C(1)–Co(2)–C(6)	103.5(3)
C(4)–Co(2)–C(6)	71.1(3)	C(5)–Co(2)–C(6)	40.6(3)
Co(1)–C(1)–Co(2)	76.2(3)	Co(1)–C(1)–C(2)	73.3(4)
Co(2)–C(1)–C(2)	112.9(5)	Co(1)–C(1)–C(7)	141.5(5)
Co(2)–C(1)–C(7)	118.9(5)	C(2)–C(1)–C(7)	122.2(6)
Co(1)–C(2)–C(1)	65.8(4)	Co(1)–C(2)–C(3)	71.0(4)
C(1)–C(2)–C(3)	110.7(6)	Co(1)–C(2)–C(13)	127.6(5)
C(1)–C(2)–C(13)	124.7(6)	C(3)–C(2)–C(13)	124.5(6)
Co(1)–C(3)–C(2)	68.8(4)	Co(1)–C(3)–C(4)	98.4(4)
C(2)–C(3)–C(4)	115.0(6)	Co(1)–C(3)–C(15)	121.6(4)
C(2)–C(3)–C(15)	124.6(6)	C(4)–C(3)–C(15)	116.2(5)
Co(2)–C(4)–C(3)	102.3(4)	Co(2)–C(4)–C(5)	71.7(4)
C(3)–C(4)–C(5)	116.1(6)	Co(2)–C(4)–C(21)	113.7(4)
C(3)–C(4)–C(21)	118.1(6)	C(5)–C(4)–C(21)	122.1(6)
Co(2)–C(5)–C(4)	67.3(4)	Co(2)–C(5)–C(6)	65.4(4)
C(4)–C(5)–C(6)	108.9(6)	Co(2)–C(5)–C(23)	129.2(4)
C(4)–C(5)–C(23)	127.9(5)	C(6)–C(5)–C(23)	122.9(6)
Co(1)–C(6)–Co(2)	76.4(3)	Co(1)–C(6)–C(5)	114.0(5)
Co(2)–C(6)–C(5)	74.0(4)	Co(1)–C(6)–C(29)	118.6(5)
Co(2)–C(6)–C(29)	132.6(5)	C(5)–C(6)–C(29)	124.9(7)
C(1)–C(7)–C(8)	118.0(3)	C(1)–C(7)–C(12)	121.6(3)
C(2)–C(13)–C(14)	120.2(7)	C(2)–C(13)–O(1)	118.0(7)
C(14)–C(13)–O(1)	121.6(8)	C(3)–C(15)–C(16)	121.7(3)
C(3)–C(15)–C(20)	118.2(3)	C(4)–C(21)–C(22)	118.6(6)
C(4)–C(21)–O(3)	120.8(7)	C(22)–C(21)–O(3)	120.6(7)
C(5)–C(23)–C(24)	119.0(3)	C(5)–C(23)–C(28)	120.9(3)
C(6)–C(29)–C(30)	117.0(7)	C(6)–C(29)–O(2)	121.5(8)
C(30)–C(29)–O(2)	121.3(8)	Co(1)–C(31)–O(31)	178.1(8)
Co(1)–C(32)–O(32)	177.2(8)	Co(2)–C(33)–O(33)	176.9(8)
Co(2)–C(34)–O(34)	175.7(8)		

and 1.971(7)–2.085(7) Å for Co(1) and Co(2), respectively. The two planes defined by the two allyl groups form a dihedral angle of 62°, similar to the value found for $[\text{Co}_2(\text{CO})_4(\text{CF}_3\text{C}_2\text{H}_3)]$ [7] and quite different from that for $[\text{Co}_2(\text{CO})_4(\text{C}_2\text{H}^t\text{Bu})_2(\text{C}_2\text{H}_2)]$ (90°) [6]. The bond distances in the C_6 flyover chains are in the range 1.41–1.50 Å.

Complex **2c** is chiral. It is only the third example of such a structure and the first to be symmetrically substituted. The other two, **2a** and **2b**, were formed from alkylacetylenes and contain asymmetrically substituted C_6 chains [6,7].

Complexes **2a** and **2b** are precursors of asymmetrically substituted 1,2,4-benzenes whereas **2c** is the precursor of a symmetrical 1,3,5-benzene.

A comparison of the structures **2a**, **2b** and **2c** is given in Table 6.

3.2. The cyclo-oligomerization of PBO

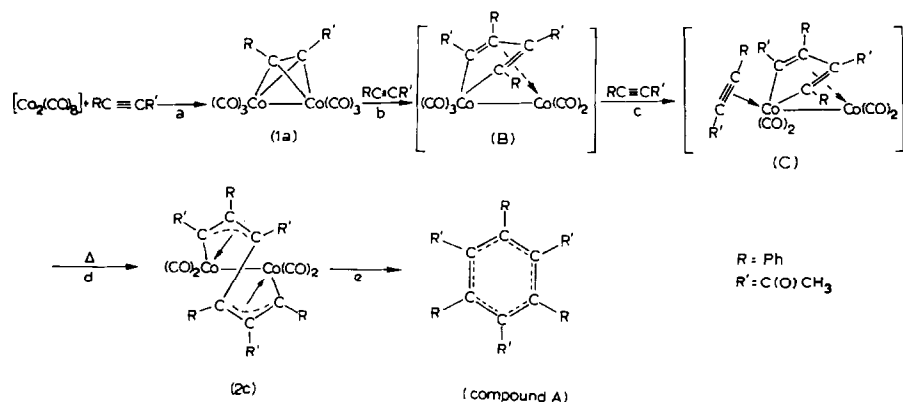
The cyclotrimerization of PBO to compound **A** probably occurs *via* the reaction sequence shown in Scheme 1, as already discussed for $\text{HC}\equiv\text{CR}$ [2a].

Step (a), leading to complexes **1** occurs easily for many alkynes, including PBO. In hypothetical step (b) steric and electronic effects due to the alkyne sub-

TABLE 6. Comparison of bond lengths (Å) of the complexes **2a**, **2b** and **2c**

	2a	2b	2c
Co–Co	–	2.459(6)	2.455(1)
C(1)–C(2)	1.41 av.	1.39(3)	1.419(10)
C(2)–C(3)	1.41 av.	1.39(4)	1.441(9)
C(3)–C(4)	1.50	1.54(4)	1.497(9)
C(4)–C(5)	1.41 av.	1.47(3)	1.443(9)
C(5)–C(6)	1.41 av.	1.42(4)	1.411(10)
Co–C(σ)	2.01 av.	1.96(3)	1.980(7)
		1.98(3)	1.971(7)
Co–C(π)	2.04 av.	1.95(3)	1.980(7)
		2.05(3)	2.079(7)
		2.11(3)	2.109(7)
		1.95(3)	1.971(7)
		2.06(3)	2.025(6)
		2.02(3)	2.085(7)
C(1)⋯C(6)	3.2	3.05(4)	3.12(1)

stituents R, may lead to symmetrically or to asymmetrically substituted metallacycles (B). An alternative hypothesis is competition between alkyne replacement of CO in **1** and alkyne exchange [11]; this explains the different isomers of complexes **2** in the “cross reac-



Scheme 1.

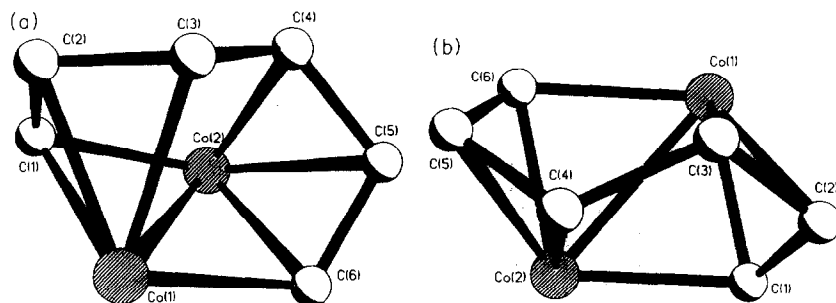


Fig. 2. (a) View of the orientation of the flyover C_6 chain with respect to the Co–Co axis. (b) View of the C_6 chain showing the C_2 axis of the flyover moiety.

tions" between $[Co_2(CO)_6(CF_3C\equiv CCF_3)]/HC\equiv CCF_3$ and $[Co_2(CO)_6(HC\equiv CF_3)]/CF_3C\equiv CCF_3$ [4c].

A few examples of complexes (B) have been fully characterized. We recently obtained $[Co_2(CO)_5\{(HC\equiv CMe_2)_2NMe\}]$ (Complex 3) [10] which is an intermediate in the co-cyclization of a dipropargylamine with RCN or $HC\equiv CPh$; interestingly, this complex is also a catalyst for the cyclotrimerization of $HC\equiv CPh$.

Step (c) has not been directly observed for cobalt. However, $[(CO)_2Fe(\mu-P^tBu_2)(\mu-\eta^4-C_4H_2(Ph)_2)Rh(HC\equiv CPh)]$ has been reported [12]. In this complex a rhodacyclopentadiene system is π -coordinated to $Fe(CO)_2$ and $HC\equiv CPh$ is π -bonded to the rhodium. In Fig. 2a, the core of complex 2c is a metallacyclopentadiene with a third alkyne "side-bound" to one carbon and the two metals. We have recently found that metallacycles $[Fe_2(CO)_6(\mu-\eta^4-C_4R_4)]$ [13] react with alkynes $HC\equiv CR'$ to give $[Fe_2(CO)_5\{(C_2R_2)(CO)-(C_2R_2)(HC\equiv CR')\}]$ with a seven carbon atom flyover ligand [14].

Step (d) is the consequence of the coordination of a third alkyne. The release of 1,2,4-benzenes occurred under rather drastic conditions (oxidation with Br_2 or reflux at 150–170°C for 4 h); with PBO we obtained reasonable amounts of compound A as the only organic product under relatively mild conditions and short reaction times.

Probably cyclotrimerization of alkynes on $Co_2(CO)_8$ occurs with comparable reaction sequences whether $HC\equiv CR$ or $R'C\equiv CR$ are involved. The final products probably depend on the electronic properties and steric requirements of the alkynes.

We are currently investigating the reactivity of PBO with $[Fe_2(CO)_9]$, $[Fe_3(CO)_{12}]$, and $[Ru_3(CO)_{12}]$.

The anisotropic thermal parameters of the Co, C and O atoms and the observed and calculated structure factors are available from the authors (G.G.).

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