Syntheses and crystal structures of 1,2 : 5,6 : 9,10 : 13,14 : 17,18 : 21,22-hexabenzo-3,7,11,15,19,23-hexadehydro[24]annulene (HBC), 1,2 : 5,6 : 9,10 : 13,14-tetrabenzo-3,7,11,15-tetradehydro[16]annulene (QBC) and a tetracobalt complex of QBC. The first example of a transition metal complex of QBC

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Abstract

1,2 : 5,6 : 9,10 : 13,14-Tetrabenzo-3,7,11,15-tetradehydro[16]annulene, or tetrabenzocyclyne (QBC) and 1,2 : 5,6 : 9,10 : 13,14 : 17,18 : 21,22-hexabenzo-3,7,11,15,19,23-hexadehydro[24]annulene (HBC) have been structurally characterized by X-ray crystallography. QBC crystallizes in two different space groups; $P2_1/c$ with $a = 10.652(3)$ Å, $b = 10.624(2)$ Å, $c = 19.549(4)$ Å, $\beta = 93.83(2)°$, $V = 2207.4(8)$ Å^3, and $Z = 4$ and $P4_12_12$ with $a = 9.330(1)$ Å, $c = 25.497(8)$ Å, $V = 2219.6(12)$ Å^3, and $Z = 4$. HBC crystallizes in monoclinic $P2_1/n$ with $a = 14.763(3)$ Å, $b = 10.296(2)$ Å, $c = 22.057(4)$ Å, $\beta = 108.61(3)°$, $V = 3177.4(11)$ Å^3, $T = 133$ K, and $Z = 4$. Reaction of QBC with dicobaltoctacarbonyl has produced a tetracobalt complex which has been characterized by X-ray crystallography. This complex crystallizes in monoclinic $P2_1/c$ with $a = 14.699(3)$ Å, $b = 17.188(3)$ Å, $c = 17.254(3)$ Å, $\beta = 112.63(3)°$, $V = 4023.5(13)$ Å^3, and $Z = 4$. Only two of the four C–C triple bonds of QBC bind to dicobalthexacarbonyl moieties even when excess dicobaltoctacarbonyl is used.

Key words: Cobalt; Annulene; Cyclyne; Hexabenzocyclohexyne; Tetrabenzocyclo tetrayne; Tribenzocyclotriyne; Crystal structure

1. Introduction

The reaction chemistry of tribenzocyclotriyne (TBC), or more appropriately 1,2 : 5,6 : 9,10-tribenzo-3,7,11-tridehydro[12]annulene, with transition metals has shown the versatility of this ligand [1]. The size of the cavity of TBC is such that only first row transition metals fit within it. We have become interested in cyclicpolyalkynes which have larger cavity sizes and have recently reported the synthesis of a trithienocyclotriyne with a slightly larger cavity [2]. TBC is prepared by Stephens–Castro coupling [3] of copper(I) *o*-iodophenylacetylide (eqn. (1)) [4]. In addition to TBC, QBC has been reported to form in low yield [3]. We have recently isolated HBC in very low yield from this reac-

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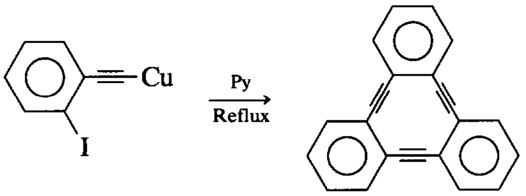
TABLE 1. Summary of crystallographic data for QBC

Solvent	Chloroform	Acetone
Formula	$C_{32}H_{16}$	$C_{32}H_{16}$
Formula weight	400.4	400.4
Space group	$P2_1/c$	$P4_12_12$
Crystal system	Monoclinic	Tetragonal
Cell dimensions		
a (Å)	10.652(3)	9.3300(10)
b (Å)	10.624(2)	
c (Å)	19.549(4)	25.497(8)
β (°)	93.83(2)	
V (Å^3)	2207.4(8)	2219.6(12)
Z	4	4
D (calcd) (g cm^{-3})	1.205	1.198
Absorptions coefficient (mm^{-1})	0.064	0.063
F(000)	832	832
Temperature (K)	295	295
2θ range (°)	8.0–40.0	8.0–40.0
Scan type	$2\theta-\theta$	ω
Scan speed (°/min) in ω	1.50	2.00
Scan range (ω) (°)	0.65	0.65
Reflections collected	8231	4136
Independent reflections	2060	1032
R_{int} (%)	1.31	1.11
Observed reflections	1295 ($F > 6.0\sigma(F)$)	832 ($F > 6.0\sigma(F)$)
$R(F)$ (%)	2.84	2.92
$R_w(F)$ (%)	2.90	3.92
Goodness of fit	1.16	1.02

TABLE 2. Summary of crystallographic data for HBC and $[Co_2(CO)_6]_2QBC$

	HBC	$[Co_2(CO)_6]_2QBC$
Formula	$C_{48}H_{24}$	$C_{44}H_{16}Co_4O_{12}$
Formula weight	600.7	972.3
Space group	$P2_1/n$	$P2_1/c$
Crystal system	Monoclinic	Monoclinic
Cell dimensions		
a (Å)	14.763(3)	14.699(3)
b (Å)	10.296(2)	17.188(3)
c (Å)	22.057(4)	17.254(3)
β (°)	108.61(3)	112.63(3)
V (Å^3)	1388.3(4)	4023.5(13)
Z	4	4
D(calcd) (g cm^{-3})	1.256	1.605
Absorption coefficient (mm^{-1})	0.066	1.680
F(000)	1248	1936
Temperature (K)	133	294
2θ range (°)	3.5–50.0	3.5–45.0
Scan type	ω	$2\theta-\theta$
Scan speed (°/min) in ω	9.77	4.00
Scan range (ω) (°)	1.20	1.00
Reflections collected	7001	5988
Independent reflections	5588	5262
R_{int} (%)	1.29	1.16
Observed reflections	3550 ($F > 4.0\sigma(F)$)	2884 ($F > 4.0\sigma(F)$)
Absolute correction	Not applied	Semi-empirical
Min/max transmission		0.7295/0.7801
$R(F)$ (%)	3.45	3.18
$R_w(F)$ (%)	3.36	2.75
Goodness of fit	1.01	1.33

tion. Formation of HBC has not been previously reported. Here, we report the synthesis, and spectral and crystallographic characterization of hexabenzocyclohexyne (HBC), tetrabenzocyclotetrayne (QBC) and the first transition metal complex of QBC.



(1)

2. Results and discussion

Campbell *et al.* [4] first reported the preparation of QBC, and based on spectral data, they assigned a saddle shaped structure for this ligand. Single crystal X-ray crystallography has confirmed this structure. QBC crystallizes in two different space groups depending on the solvent used for crystallization (chloroform or acetone). Figure 1 shows the thermal ellipsoid plot drawing of the molecular structure of QBC when crystallized from chloroform. Small differences in the QBC structures when crystallized from the two different solvents are observed.

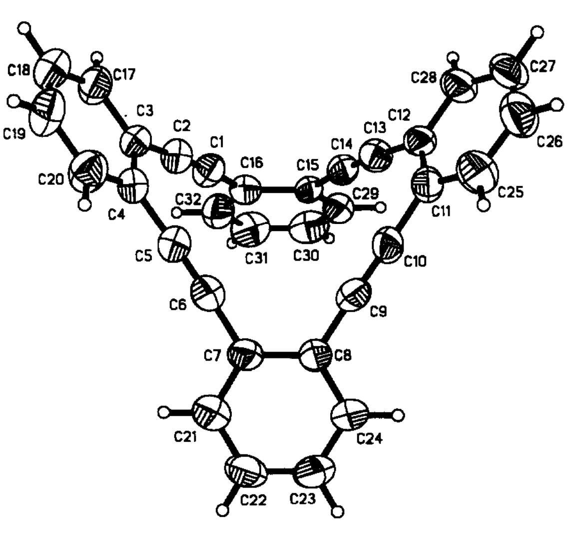


Fig. 1. QBC with thermal ellipsoids drawn at 50% probability.

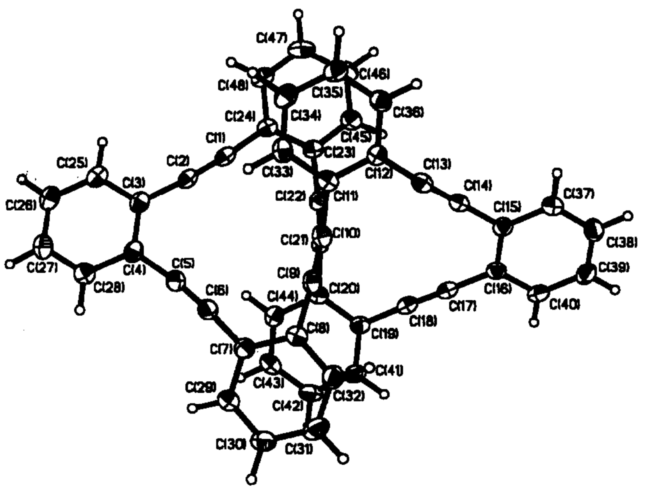


Fig. 2. Thermal ellipsoid plot of HBC with ellipsoids drawn at 50% probability.

The carbon–carbon triple bonds in QBC in the monoclinic $P2_1/c$ space group range from 1.193(4) to 1.200(5) Å with an average value of 1.197(5) Å. These bonds vary from 1.202(4) to 1.208(5) Å with an average value of 1.205(5) Å in the tetragonal $P4_12_12$ space group. The C≡C–C bond angles range from 175.1(3) to 179.2(3)° in the $P2_1/c$ space group and from 173.3(3) to 179.3(3)° in the $P3_12_12$ space group. The distances from the C–C triple bond carbons to the centroid [5*] of the 16-membered ring range from 2.435 to 2.628 Å with an average value of 2.534 Å. This distance is larger by 0.454 Å than the distance between the centroid and the carbons of the C–C triple bonds of the 12-membered ring in TBC [1a] and may be a determining factor as to whether a metal will bind within or outside the cavity of QBC.

HBC crystallizes in the monoclinic space group $P2_1/n$. A thermal ellipsoid plot of HBC is shown in Fig. 2. The C–C triple bonds in HBC range from 1.191(2) to 1.201(3) Å with an average value of 1.196 Å. The C≡C–C bond angles range from 171.9(2) to 177.8(2)°.

One would predict a chair conformation for HBC with D_{3v} symmetry, but a distorted boat conformation is observed in the solid state structure presented here. Two of the diphenylacetylene units in HBC are almost eclipsed which distorts the ligand to approximate D_2 symmetry. The presence of two conformations is consistent with Wittig's and Imgartinger's results on hexaphenylene [6]. The distance between the centers of the two superimposed C–C triple bonds (C9 and C10 with C21 and C22) is 3.345 Å. The large cavity of HBC may allow binding of multiple metal centers within it.

Reaction of QBC with two molar equivalents of dicobaltoctacarbonyl in THF at room temperature results in the formation of the tetracobalt complex $[Co_2(CO)_6]_2(QBC)$. Removal of the solvent and unreacted cobaltcarbonyl *in vacuo*, and subsequent extraction with hexane gave the tetracobalt complex as a black solid in 70% yield. Even when a four-fold excess of dicobaltoctacarbonyl is combined with QBC, only two of the C–C triple bonds of the QBC are complexed. The complex shows CO stretching absorptions at 2086, 2067, 2053, 2029, 2024, 2004, and 1993 cm^{-1}. The uncoordinated C≡C stretch appears at 2105 cm^{-1}, which is lower by 109 cm^{-1} than in free QBC and the coordinated C≡C bond stretch is at 1855 cm^{-1}. The ^{13}C NMR (C_6D_6) shows two different peaks for the C–C triple bond carbons, the uncoordinated C–C triple bond is at 93.7 ppm and the coordinated C–C triple bond is shifted to 97.1 ppm and this compares with the absorbtion of the carbons of QBC's C–C triple bonds at 92.1 ppm. Interestingly, the cobalt complexes of QBC are much more soluble in hexane than uncomplexed QBC.

Recrystallization from diethyl ether provided crystals suitable for X-ray crystallography. X-Ray analysis of $[Co_2(CO)_6]_2(QBC)$ showed that only two C–C triple bonds are bound to dicobalt moieties (Fig. 3). Apparently, the first two equivalents of dicobalthexacarbonyl which bind to QBC sterically hinder the approach of more dicobaltoctacarbonyl, and essentially protect the two unbound C–C triple bonds from reaction with more dicobaltoctacarbonyl.

The two Co–Co bond distances in this complex are 2.456(1) and 2.461(1) Å and the Co–C (C of the C–C

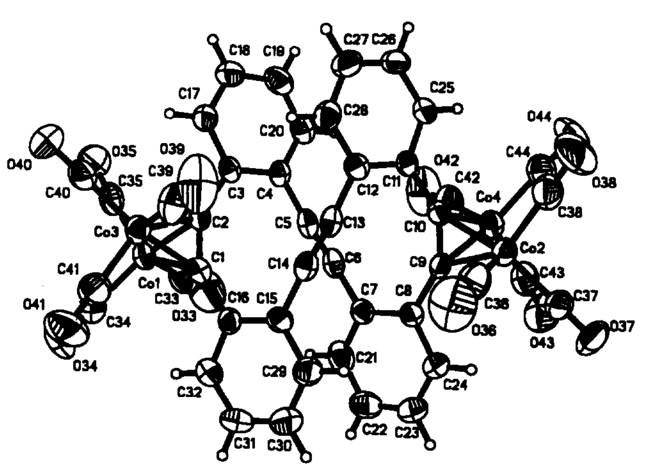


Fig. 3. Diagram of $[Co_2(CO)_6]_2(QBC)$ with 50% thermal probability ellipsoids.

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* Reference number with asterisk indicates a note in the list of references.

triple bond) bond distances range from 1.959(5) to 1.990(3) Å. The Co–Co bond distances in $Co_2(CO)_6(\mu^2\text{-}\eta^2\text{-}PhC{\equiv}CPh)$ [7] and dicobaltoctacarbonyl [8] are 2.47 and 2.524 Å respectively, and the Co–C (C of the C–C triple bond) distances in $Co_2(CO)_6(\mu^2\text{-}\eta^2\text{-}PhC{\equiv}CPh)$ are 1.89–2.02 Å. The C≡C–C bond angles

TABLE 3. Atomic coordinates ($\times 10^5$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^4$) for QBC (CH_3Cl)

	x	y	z	U_{eq} [a]
C(1)	1576(3)	522(2)	878(2)	49(1)
C(2)	2216(3)	507(2)	398(2)	48(1)
C(3)	2761(3)	2710(3)	−398(1)	53(1)
C(4)	2354(3)	3741(3)	−295(1)	53(1)
C(5)	3136(3)	5145(3)	895(2)	53(1)
C(6)	3913(3)	4646(3)	1270(2)	53(1)
C(7)	3348(3)	2472(3)	2076(1)	48(1)
C(8)	2342(3)	1962(3)	2063(1)	49(1)
C(11)	1182(3)	1282(3)	2035(2)	44(1)
C(12)	432(3)	1284(3)	2595(2)	55(1)
C(13)	−649(3)	565(3)	2584(2)	61(1)
C(14)	−1000(3)	−142(3)	2019(2)	68(1)
C(15)	−284(3)	−146(3)	1459(2)	60(1)
C(16)	816(3)	556(3)	1459(2)	45(1)
C(21)	3007(3)	435(3)	−169(1)	42(1)
C(22)	3527(3)	−719(3)	−338(2)	55(1)
C(23)	4306(3)	−804(3)	−866(2)	65(1)
C(24)	4586(3)	246(3)	−1238(2)	68(1)
C(25)	4073(3)	1384(3)	−1076(2)	61(1)
C(26)	3281(3)	1503(3)	−544(1)	46(1)
C(31)	1838(3)	4966(3)	−184(2)	48(1)
C(32)	953(3)	5483(3)	−660(20	59(1)
C(33)	441(3)	6650(3)	−562(2)	63(1)
C(34)	809(3)	7326(3)	15(2)	64(1)
C(35)	1682(3)	6843(3)	489(2)	60(1)
C(36)	2218(3)	5661(3)	402(2)	48(1)
C(41)	4874(3)	4038(3)	1695(1)	44(1)
C(42)	6121(3)	4462(3)	1712(2)	62(1)
C(43)	7048(3)	3860(3)	2107(2)	68(1)
C(44)	6769(3)	2844(3)	2502(2)	65(1)
C(45)	5554(3)	2411(3)	2489(2)	54(1)
C(46)	4590(3)	2992(3)	2092(1)	41(1)

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

TABLE 4. Atomic coordinates ($\times 10^5$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^4$) for QBC (acetone)

	x	y	z	U_{eq} [a]
C(1)	2718(3)	4837(3)	−834(1)	50(1)
C(2)	1709(4)	4768(3)	−542(1)	49(1)
C(3)	1740(4)	5043(3)	598(1)	46(1)
C(4)	2772(3)	5013(3)	883(1)	47(1)
C(11)	4997(3)	4006(3)	−1224(1)	43(1)
C(12)	6102(4)	4188(4)	−1588(1)	56(1)
C(13)	6116(4)	5374(4)	−1916(1)	65(1)
C(14)	5022(4)	6368(4)	−1894(1)	63(1)
C(15)	3901(4)	6179(4)	−1539(1)	56(1)
C(16)	3898(3)	5004(3)	−1201(1)	43(1)
C(21)	425(3)	4763(3)	−237(1)	45(1)
C(22)	−901(4)	4621(4)	−492(1)	56(1)
C(23)	−2160(4)	4751(4)	−217(2)	66(2)
C(24)	−2151(4)	5025(4)	311(2)	65(2)
C(25)	−865(4)	(35133)	570(1)	57(1)
C(26)	433(3)	(34992)	307(1)	42(1)

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

TABLE 5. Atomic coordinates ($\times 10^5$) and equivalent isotropic displacement coefficient ($Å^2 \times 10^4$) for HBC

	x	y	z	U_{eq} [a]
C(1)	67600(13)	−16257(21)	−1428(8)	278(7)
C(2)	64603(13)	−5406(21)	−1656(8)	278(7)
C(3)	60047(13)	7051(20)	−2346(8)	284(7)
C(4)	63760(13)	17389(20)	1877(8)	284(7)
C(5)	72740(14)	16562(19)	6883(9)	297(7)
C(6)	80163(14)	17201(19)	11098(9)	289(7)
C(7)	88623(13)	18721(19)	16502(8)	268(7)
C(8)	96222(13)	9814(18)	17846(8)	259(7)
C(9)	96050(13)	−330(19)	13392(9)	272(7)
C(10)	95828(13)	−8027(19)	9256(9)	274(7)
C(11)	95399(12)	−15621(18)	3764(9)	249(7)
C(12)	100397(12)	−27404(18)	4191(8)	246(7)
C(13)	105229(13)	−33298(19)	10271(9)	272(7)
C(14)	108945(13)	−38925(19)	15183(9)	266(7)
C(15)	113802(13)	−45336(18)	21113(8)	256(7)
C(16)	111736(13)	−42094(18)	26754(8)	254(7)
C(17)	104189(14)	−33172(20)	26583(8)	278(7)
C(18)	97683(14)	−26051(20)	26355(8)	283(7)
C(19)	90273(13)	−16893(19)	26186(8)	256(7)
C(20)	82342(13)	−15224(18)	20631(8)	241(7)
C(21)	80866(12)	−23076(19)	15015(8)	251(7)
C(22)	78885(12)	−29045(19)	10123(8)	250(7)
C(23)	76197(13)	−35834(19)	4121(8)	245(7)
C(24)	70586(13)	−29488(19)	−1504(8)	255(7)
C(25)	51445(14)	8855(22)	−7321(9)	319(8)
C(26)	46641(15)	20553(22)	−8060(10)	357(8)
C(27)	50176(14)	30582(22)	−3820(10)	360(8)
C(28)	58594(14)	28989(21)	1109(9)	327(8)
C(29)	89238(15)	29246(21)	20602(9)	328(8)
C(30)	97044(16)	30847(21)	25967(10)	359(8)
C(31)	104377(16)	21860(22)	27367(10)	386(8)
C(32)	104031(15)	11499(21)	23405(10)	334(8)
C(33)	90164(14)	−10882(21)	−2276(9)	290(7)
C(34)	90026(14)	−17398(21)	−7767(9)	323(8)
C(35)	95264(14)	−28657(21)	−7353(9)	314(8)
C(36)	100387(14)	−33607(20)	−1460(9)	288(7)
C(37)	120762(13)	−54715(20)	21412(9)	295(7)
C(38)	125771(14)	−60470(21)	27129(10)	332(8)
C(39)	124043(14)	−56976(21)	32697(9)	331(8)
C(40)	117052(14)	−47920(20)	32514(9)	302(8)
C(41)	91005(14)	−9169(21)	31498(9)	326(8)
C(42)	84271(15)	230(21)	31326(10)	341(8)
C(43)	76653(15)	2114(21)	25805(10)	327(8)
C(44)	75687(14)	−5519(19)	20535(9)	283(7)
C(45)	78936(14)	−48603(21)	3770(10)	314(8)
C(46)	76088(15)	−55292(23)	−1948(10)	358(8)
C(47)	70430(16)	−49152(23)	−7452(10)	379(9)
C(48)	67823(15)	−36404(21)	−7229(9)	324(8)

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

TABLE 6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for $[Co_2(CO)_6]_2QBC$

	x	y	z	U_{eq} [a]
Co(1)	595(1)	1637(1)	672(1)	42(1)
Co(2)	−4726(1)	2720(1)	1802(1)	43(1)
Co(3)	1127(1)	1757(1)	2201(1)	41(1)
Co(4)	−5346(1)	1893(1)	542(1)	44(1)
C(1)	−74(3)	2183(2)	1299(2)	38(2)
C(2)	−67(3)	1417(2)	1376(2)	34(2)
C(3)	−791(3)	729(2)	1303(2)	33(2)
C(4)	−1816(3)	727(2)	823(2)	33(2)
C(5)	−2320(3)	1432(3)	450(2)	37(2)
C(6)	−2760(3)	2027(3)	215(2)	40(2)
C(7)	−3186(3)	2786(2)	49(2)	37(2)
C(8)	−3794(3)	3050(2)	460(2)	39(2)
C(9)	−4134(3)	2534(2)	975(2)	35(2)
C(10)	−4020(3)	1900(2)	1444(2)	35(2)
C(11)	−3382(3)	1280(2)	1951(2)	34(2)
C(12)	−2362(3)	1387(2)	2397(2)	36(2)
C(13)	−1886(3)	2072(3)	2271(2)	36(2)
C(14)	−1491(3)	2583(2)	2048(2)	37(2)
C(15)	−1121(3)	3171(2)	1656(2)	38(2)
C(16)	−475(3)	2971(2)	1257(2)	38(2)
C(17)	−355(3)	30(2)	1685(2)	44(2)
C(18)	−904(3)	−642(2)	1593(3)	51(2)
C(19)	−1904(3)	−633(3)	1119(3)	53(2)
C(20)	−2351(3)	48(3)	743(3)	45(2)
C(21)	−2954(3)	3287(3)	−483(3)	57(2)
C(22)	−3289(4)	4042(3)	−597(3)	73(3)
C(23)	−3857(3)	4311(3)	−182(3)	75(3)
C(24)	−4111(3)	3820(3)	333(3)	58(2)
C(25)	−3786(3)	557(2)	2014(3)	44(2)
C(26)	−3208(3)	−38(2)	2491(3)	52(2)
C(27)	−2222(4)	77(3)	2931(3)	54(2)
C(28)	−1798(3)	780(3)	2896(2)	48(2)
C(29)	−1458(3)	3934(2)	1613(3)	50(2)
C(30)	−1181(3)	4496(3)	1186(3)	65(2)
C(31)	−550(3)	4305(3)	800(3)	69(3)
C(32)	−193(3)	3554(3)	836(3)	56(2)
C(33)	−360(4)	1728(3)	−348(3)	63(2)
C(34)	1507(3)	2266(3)	541(3)	59(2)
C(35)	1022(3)	650(3)	613(3)	50(2)
C(36)	−3756(4)	3288(3)	2525(3)	68(2)
C(37)	−5650(3)	3470(3)	1394(3)	53(2)
C(38)	−5139(3)	2193(3)	2532(3)	64(2)
C(39)	826(3)	1791(3)	3110(3)	62(2)
C(40)	1995(3)	953(3)	2503(3)	50(2)
C(41)	1951(3)	2580(3)	2384(3)	59(2)
C(42)	−5095(3)	1233(3)	−157(3)	66(2)
C(43)	−6165(3)	2571(3)	−222(3)	57(2)
C(44)	−6128(3)	1300(3)	903(3)	59(2)
O(33)	−977(3)	1808(3)	−983(2)	108(2)
O(34)	2094(3)	2661(2)	478(3)	98(2)
O(35)	1260(2)	22(2)	624(2)	72(2)
O(36)	−3144(3)	3665(3)	2976(3)	115(2)
O(37)	−6237(3)	3936(2)	1117(2)	78(2)
O(38)	−5403(3)	1869(2)	2970(2)	108(2)
O(39)	637(3)	1787(3)	3689(2)	104(2)
O(40)	2557(3)	465(2)	2696(2)	83(2)
O(41)	2465(3)	3097(2)	2486(2)	99(2)
O(42)	−4920(3)	826(3)	−595(3)	111(2)
O(43)	−6683(3)	3007(2)	−697(2)	95(2)
O(44)	−6596(3)	934(2)	1147(2)	92(2)

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

for the uncoordinated C–C triple bonds in $[Co_2(CO)_6]_2(QBC)$ vary from 169.0(5) to 173.1(5)°. These bond angle distortions may be the reason for the appearance of the infrared band at 2105 cm^{-1} of the uncoordinated C–C triple bond. The distances of the Co-coordinated C–C triple bond carbons to the centroid range from 2.964 to 2.976 Å, and the distances of uncoordinated C–C triple bond carbon to the centroid range from 1.631 to 1.684 Å. This shorter distance from uncoordinated C–C triple bond carbons to the centroid may enable a small metal atom, like Ni^0, to bind inside the cavity of $[Co_2(CO)_6]_2(QBC)$.

3. Experimental details

3.1. General procedures

QBC and HBC were prepared by Stephens–Castro coupling [3] of copper(I) *o*-iodophenylacetylide [4] and separated on a silica gel column using hexanes/chloroform (4:1) elutant. QBC: ^1H NMR (300 MHz, C_6D_6): δ 7.34 (m, 8H); 6.69 (m, 8H); ($CDCl_3$) δ 7.53 (m, 8H); 7.26 (m, 8H). ^{13}C NMR (300 MHz, C_6D_6): δ 132.5, 128.2, 126.3, 92.1; ($CDCl_3$) δ 132.3, 128.0, 125.6, 91.1. IR (Nujol) 2214 cm^{-1}. Mass spectrum (EI): m/z 400 (M^+), 374 ($M^+ - C_2H_2$), 200 M^{++}). Anal. Found: C, 95.62; H, 3.90. $C_{32}H_{16}$ calcd.: C, 96.00; H, 4.00%. HBC: ^1H NMR (300 MHz, $CDCl_3$): δ 7.33 (m, 12H); 7.05 (m, 12H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 132.3, 127.5, 125.6, 92.5. Mass spectrum (EI): m/z 600 (M^+), 574 ($M^+ - C_2H_2$), 300 (M^{++}).

3.2. Reaction of QBC with $Co_2(CO)_8$

A solution of QBC (100 mg, 0.250 mmol) and $Co_2(CO)_8$ (171 mg, 0.500 mmol) in 50 ml of THF was allowed to stir for 18 h. The solvent and the unreacted cobaltcarbonyl were removed *in vacuo*. Extraction with hexane gave $[Co_2(CO)_6]_2(QBC)$ as a black solid in 70% yield. ^1H NMR (300 MHz, C_6D_6): δ 7.62 (d, 4H); 7.11 (dd, 4H); 6.64 (d, 4H); 6.40 (dd, 4H). ^{13}C NMR (300 MHz, C_6D_6): δ 199.9, 140.1, 132.3, 131.2, 128.6, 127.6, 122.8, 97.1, 93.7. IR (Nujol): 2105, 2086, 2067, 2029, 2024, 2004, 1993, 1855. Anal. Found C, 53.83; H, 1.59. $C_{44}H_{16}O_{12}Co_4$ calcd.: C, 54.40; H, 1.66%.

3.3. X-Ray analysis

In general a crystal was mounted on a glass fiber or in a capillary (Co compound) and the unit cell determined on a Siemens R3m/V or Syntex P2_1 diffractometer by least-squares refinement of the indices and angles of 15 reflections with $20.0° \leq \theta \leq 30.0°$. Space groups were determined by the systematic absences of the diffraction data. The positions of the cobalt atoms were determined by direct methods. The positions of the carbon atoms were found by successive difference Fourier syntheses, and the models were refined by full-matrix least-square refinement. All the non-hydrogen atoms were refined anisotropically.

4. Conclusion

In contrast to TBC, QBC and HBC have nonplanar structures with QBC conforming to its predicted structure, and HBC giving a structure consistent with one form of hexaphenylene. The X-ray structure of QBC suggests that QBC has the potential to bind second and third row transition metals within its cavity. Only two $Co_2(CO)_6$ units bind to QBC having two uncomplexed C–C triple bonds.

5. Supplementary material available

Tables of data collection and structure solution details, bond distances and angles, atomic coordinates, and thermal parameters, and observed and calculated structure factors have been deposited with the Cambridge Crystallographic Data Centre.

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