Synthesis and Characterization of Trithienocyclotriyne (TTC) and Its Tetracobalt Complex. The First Example of a Dehydroannulene Containing Thiophene Rings

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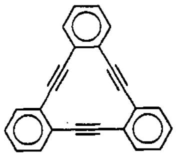
The planar trithienocyclotriyne (TTC) has been synthesized and structurally characterized by X-ray crystallography. TTC crystallizes in the monoclinic space group $C2/c$ with a = 18.481(4) Å, b = 10.836(2) Å, c = 7.490(1) Å, β = 112.25(3)°, V = 1388.3(4) Å^3, and Z = 4. TTC has a larger cavity size than tribenzocyclotriyne (TBC). This significantly alters the way TTC binds to transition metals in comparison to TBC. Reaction of TTC with $Co_2(CO)_8$ has produced a tetracobalt complex in which only two of the three alkynes of TTC bind to hexacarbonyl dicobalt moieties. This complex crystallizes in the triclinic space group $P\bar{1}$ with a = 10.421(2) Å, b = 12.322(2) Å, c = 16.110(3) Å, α = 89.42(3)°, β = 71.24(3)°, γ = 66.07(3)°, V = 1773.1(6) Å^3, and Z = 2.

Introduction

The macrocycle tribenzocyclyne (TBC) has shown interesting reactivity patterns as a ligand to metals both in solution and gas phase.[1] One of the most important factors governing the reaction chemistry of TBC is the distance of the alkyne carbons to the centroid of the 12-membered ring, which is 2.08 Å.[1a] Small, late first-row transition metals like cobalt,[1e] nickel,[1a,g] and copper[1b] reside in the cavity of TBC, whereas larger second-row transition metals like silver[1d] form sandwich complexes. On the basis of these results, we have been investigating the synthesis of cyclotriyne ligands that have different cavity sizes. Here we report the synthesis and characterization of such a cyclotriyne that contains three thieno groups instead of benzene rings (TTC) and its first transition metal complex. A preliminary report on the synthesis of this ligand has appeared previously.[2]



TBC

Experimental Section

General Data. All manipulations were performed using anaerobic techniques[3] unless specified otherwise. Potassium *tert*-butoxide (Aldrich) was sublimed at 150 °C and 10^{-6} Torr. *n*-Butyllithium (2.5 M in hexanes, Aldrich) was titrated against diphenylacetic acid before use.[4] Iodine, cupric sulfate pentahydrate (Fisher Reagents), copper(I) iodide, hydroxylamine hydrochloride, and magnesium bromide etherate (Aldrich reagents) were used as received. 3-Iodothiophene[5] and dichlorobis(benzonitrile)palladium(II)[6] were prepared according to established procedures. Octacarbonyldicobalt (Strem) was used as received. Tetrahydrofuran (THF, Fisher Reagent) and diethyl ether (Fisher Reagent) were distilled under argon from sodium benzophenone ketyl. Pyridine (Fisher Reagent) was distilled under argon from BaO. Diisopropylamine (Aldrich) was distilled under argon from KOH. Flash chromatography[7] was carried out using 40-μm silica gel (Baker).

3-[(Trimethylsilyl)ethynyl]thiophene (1). To a mixture of 3-iodothiophene (13.44 g, 0.064 mol), dichlorobis(benzonitrile)palladium(II) (0.49 g, 0.0013 mol), triphenylphosphine (0.68 g 0.0026 mol), copper(I) iodide (0.26 g, 0.0013 mol), and diisopropylamine (250 mL) was added (trimethylsilyl)acetylene (10.00 mL, 0.071 mol, 2.2 equiv) via syringe. The solution was stirred for 18 h at room temperature and filtered. The solvent was removed at reduced pressure and the residue chromatographed on silica with hexanes. Yield: 11.31 g (98%). ^{1}H NMR ($CDCl_3$): δ 7.48 (m, 1H), 7.23 (m, 1H), 7.13 (m, 1H), 0.25 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 130.1, 129.6, 125.2, 122.4, 99.9, 93.9, 0.0. IR (neat): ν(C≡C) 2155 cm^{-1}. Anal. Calcd for $C_9H_{12}SSi$: C, 59.95; H, 6.69. Found: C, 59.69; H, 6.58. This compound can also be made using 3-bromothiophene at reflux for 18 h. The yield of this reaction is also 98%.

3-Ethynylthiophene (2). To a solution of 1 (11.50 g, 0.064 mol) in methanol (100 mL) was added potassium fluoride (3.71 g, 0.064 mol) and water (5 mL). After the mixture was stirred for 4 h, it was diluted with water and extracted with methylene chloride (3 × 50 mL). The combined organic fractions were dried over $MgSO_4$, and the solvent was removed at reduced pressure. The residue was distilled (trap-to-trap under vacuum) to yield 3-ethynylthiophene as a colorless liquid. Yield: 6.77 g (98%). ^{1}H NMR ($CDCl_3$): δ 7.52 (m, 1H), 7.26 (m, 1H), 7.15 (m, 1H), 3.05 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 129.5, 124.9, 120.7, 78.4, 76.6. IR (neat): ν(≡C—H) 3296, ν(C≡C) 2112 cm^{-1}.

2-Iodo-3-ethynylthiophene (3) and 2-Iodo-4-ethynylthiophene (4). A four-neck, 2-L flask equipped with a mechanical stirrer was charged with KO^{t}Bu (15.43 g, 0.138 mol) and ^{n}BuLi (110 mL, 2.5 M in hexanes, 0.275 mol). A separate powder addition tube was charged with $MgBr_2 \cdot OEt_2$ (80.70 g, 0.313 mol)

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and attached to the reaction flask. The flask was fitted with a valve and a septum and removed from the drybox, and a mineral oil bubbler was attached. The flask was cooled to −78 °C, as was 450 mL of THF in a separate flask. Throughout the remainder of the procedure, the reaction mixture was stirred and maintained at −78 °C. THF was slowly transferred to the reaction mixture via cannula. The mixture was then allowed to stir until a homogeneous red-brown solution resulted (~1 h). 3-Ethynylthiophene (13.5 g, 0.125 mol) was added via syringe. After 3 h, $MgBr_2{\cdot}OEt_2$ was added slowly to the reaction mixture. The reaction was allowed to stir for another 45 min. In a separate flask, iodine (31.73 g, 0.125 mol) was dissolved in 250 mL of THF, cooled to −40 °C, and transferred via cannula to the reaction mixture. At this point, the reaction mixture was allowed to warm to room temperature over 16 h with stirring. The reaction mixture was then acidified to pH 5 with 1 M HCl and extracted with diethyl ether (250 mL × 3). The organic layer was washed twice with both saturated aqueous $Na_2S_2O_3$ (300 mL) and saturated aqueous NaCl (300 mL). The extract was dried over $MgSO_4$ and concentrated in vacuo. Unreacted 3-ethynylthiophene was removed from the crude product by trap-to-trap fractionation at 21 °C and 10^{-6} Torr over 12 h. Chromatography on silica with hexanes separated the two isomers. 2-Iodo-3-ethynylthiophene (**3**): Yield 15.00 g (52%); ^{1}H NMR ($CDCl_3$) δ 7.73 (d, J = 5.5 Hz, 1H), 6.94 (d, J = 5.5 Hz, 1H), 3.29 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 130.9, 130.5, 129.5, 82.4, 80.4, 79.3; IR (neat) ν(C≡H) 3287, ν(C≡C); 2104 cm^{-1}. Anal. Calcd for C_6H_3IS: C, 30.76; H, 1.28. Found: C, 30.64; H, 1.24. 2-Iodo-4-ethynylthiophene (**4**): yield 3.80 g (13%); ^{1}H NMR ($CDCl_3$) δ 7.47 (s, 1H), 7.23 (s, 1H), 3.02 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 139.0, 135.7, 123.0, 77.9, 77.1, 73.1; IR (neat) ν(≡C—H) 3290, ν(C≡C) 2106 cm^{-1}. Anal. Calcd for C_6H_3IS: C, 30.76; H, 1.28. Found: C, 30.70; H, 1.27.

Copper(I) Salt of 2-Iodo-3-ethynylthiophene (5). $CuSO_4{\cdot}5H_2O$ (16.00 g, 0.064 mol) and ammonium hydroxide (28%, 150 mL) were placed in a 2-L Erlenmeyer flask. The mixture was stirred for 15 min before adding 400 mL of water and NH_2OHHCl (8.89 g, 0.13 mol). Addition of 2-iodo-3-ethynylthiophene (15.00 g, 0.064 mol in 500 mL of ethanol) resulted in the formation of a yellow precipitate. The slurry was stirred for 0.5 h and filtered. The yellow copper salt was washed three times each with 200 mL of water, ethanol, and ether and allowed to air dry for 24 h. Yield: 14.03 g (74%).

TTC. A 1-L flask was charged with the copper(I) salt of 2-iodo-3-ethynylthiophene (14.00 g, 0.047 mol) and placed under an active vacuum to remove remaining volatiles (~18 h at 10^{-4} Torr). Pyridine (500 mL) was added to give an approximate 0.1 M suspension of the copper acetylide. The mixture was refluxed for 6.5 h and the pyridine was removed in vacuo. The crude product was extracted with acetone or diethyl ether (~1 L); the residue was discarded. TTC was sublimed at 160 °C and 10^{-6} Torr for 48 h. The sublimed TTC was further purified by recrystallization from hot toluene to afford TTC as a red crystalline compound. Yield: 1.06 g (21%). ^{1}H NMR ($CDCl_3$) δ 6.89 (d, J = 5.2, 3H), 6.54 (d, J = 5.2, 3H); (C_6D_6) δ 6.11 (d, J = 5.2, 3H), 6.01 (d, J = 5.2, 3H). ^{13}C NMR (C_6D_6): δ 129.5, 127.3, 126.9, 126.5, 94.8, 88.8. IR (Nujol): ν(C≡C) 2203 cm^{-1}. Anal. Calcd for $C_{18}H_6S_3$: C, 67.92; H, 1.88. Found: C, 67.15; H, 1.88. UV/Vis (dichloromethane): λ_{max} (nm) 296 sh (ϵ 73 250), 308 (99 800), 328 (32 050), 337 (32 300), 352 (30 500).

$[Co_2(CO)_6]_2(TTC)$. A solution of TTC (0.10 g, 0.31 mmol) and $Co_2(CO)_8$ (0.22 g, 0.63 mmol) in diethyl ether (50 mL) was stirred for 18 h at 25 °C. The solvent and any unreacted carbonylcobalt were removed at reduced pressure, the residue was extracted with hexane, the hexane was removed in vacuo, and the black solid was recrystallized from ether. Yield: 0.28 g (85%). ^{1}H NMR (C_6D_6): δ 6.86 (d, J = 5.4 Hz, 1H), 6.60 (d, J = 5.5 Hz, 1H), 6.51 (d, J = 5.2 Hz, 1H), 6.47 (d, J = 5.4, 1H), 6.45 (d, J = 5.2 Hz, 1H), 6.25 (d, J = 5.5, 1H). ^{13}C NMR (C_6D_6): δ 200.0, 199.4, 147.3, 140.4, 137.2, 134.6, 132.2, 130.7, 1296.9, 126.7, 126.5, 126.2, 124.6, 121.1, 97.1, 91.5, 91.3, 87.0, 86.3, 84.7. IR (Nujol): ν(free C≡C) 2096, ν(C≡O) 2089, 2052, 2029, 2005, 1994, 1988, 1896, ν(complexed C≡C) 1856 cm^{-1}. Anal. Calcd for $C_{30}H_6Co_4O_{12}S_3$: C, 40.45; H, 0.67. Found: C, 40. 39; H, 0.65.

Table 1. Summary of Crystallographic Data for TTC and $[Co_2(CO)_6]_2TTC{\cdot}{}^1/_2Et_2O$

	TTC	$[Co_2(CO)_6]_2(TTC)$
formula	$C_{18}H_6S_3$	$C_{30}H_6Co_4O_{12}S_3{\cdot}{}^1/_2Et_2O$
fw	318.4	922.3
space group	$C2/c$	$P\bar{1}$
cryst syst	monoclinic	triclinic
cell dimens		
a, Å	18.481(4)	10.421(2)
b, Å	10.836(2)	12.322(2)
c, Å	7.4900(10)	16.110(3)
α, deg		89.42(3)
β, deg	112.25(3)	71.24(3)
γ, deg		66.07(3)
V, Å^3	1388.3(4)	1773.1(6)
Z	4	2
D(calcd), g/cm^3	1.524	1.727
abs coeff, mm^{-1}	0.656	2.066
F(000)	648	908
temp, K	294	294
2θ range, deg	3.5–50.0	3.5–45.0
scan type	ω	ω
scan speed, deg/min in ω	4.19	3.08
scan range (ω), deg	1.60	2.00
no. of reflns collcd	1488	5530
no. of ind reflns	1223	4619
R_{int}, %	1.01	1.01
no. of obsd reflns	788 ($F > 6.0\sigma(F)$)	2884 ($F > 4.0s(F)$)
abs correctn	not applied	semiempirical
min/max transm		0.4994/0.6173
$R(F)$, %	5.54	2.83
$R_w(F)$, %	7.41	3.11
goodness of fit	1.35	1.06

X-ray Analysis of TTC. A red crystal grown from chloroform was mounted on a glass fiber, and data were collected on a Syntex $P2_1$ diffractometer. Important crystallographic data are summarized in Table 1. The systematic absences of the diffraction data indicated the space group was either $C2/c$ or Cc. The structure was successfully solved and refined in $C2/c$ using Siemens SHELXTL PLUS programs. A disorder model for sulfur atoms was used. The positions of the sulfur and carbon atoms were found by successive difference Fourier syntheses, and the model was refined by full-matrix least-squares refinement. All the non-hydrogen atoms were refined anisotropically. The final R values for the 862 data with $F > 4.0\sigma(F)$ are $R(F)$ = 0.049 and $R_w(F)$ = 0.066.

X-ray Analysis of $[Co_2(CO)_6]_2(TTC){\cdot}{}^1/_2Et_2O$. A black crystal grown from diethyl ether was mounted on a glass fiber, and data were collected on a Syntex $P2_1$ diffractometer. Important crystallographic data are summarized in Table 1. The diffraction data indicated the space group was $P\bar{1}$. The positions of the cobalt atoms were determined by direct methods. The positions of the sulfur and carbon atoms were found by successive difference Fourier syntheses, and the model was refined by full-matrix least-squares refinement. All the non-hydrogen atoms were refined anisotropically. A semiempirical absorption correction was applied to the data. The final R values for the 2884 data with $F > 4.0\sigma(F)$ are $R(F)$ = 0.028 and $R_w(F)$ = 0.031.

Results and Discussion

Synthesis of TTC. 3-Ethynylthiophene is prepared by the well documented palladium catalyzed coupling reaction[8] of 3-iodothiophene and (trimethylsilyl)acetylene followed by the removal of the trimethylsilyl protecting group. This compound had been previously prepared in two steps using 3-thiophenecarboxaldehyde in a total yield of 52%.[9] The yield of this compound has increased by 44% using the palladium catalyzed coupling reaction. Iodination of **2** using the general procedure developed by

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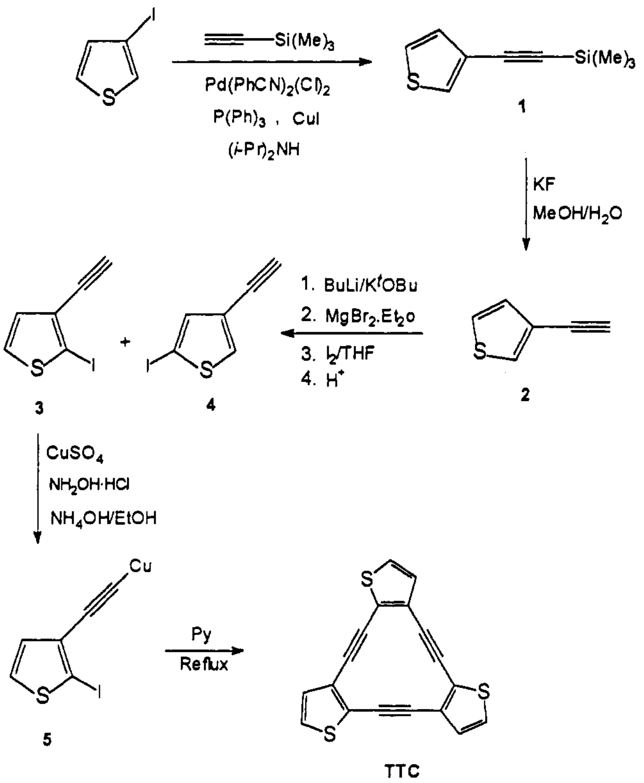
Scheme 1



Brandsma[10] resulted in the formation of 3 and 4 in a 3:1 ratio. The C≡C—Li and the sulfur atom each direct the reaction to the adjacent carbon, resulting in the observed ratio. The two isomers are chromatographically separated with difficulty on silica with hexanes. Using the Stephens–Castro coupling reaction,[11] TTC is obtained from the refluxing of the copper salt 5 in pyridine in 21% yield. The yield of TTC is lower than TBC (48%)[12] since the alkyne units in TTC are forced to bend, and as a result formation of polymeric materials are more favorable. TTC was characterized by ^1H and ^{13}C NMR, IR, elemental analysis, and an X-ray structural study. The ^{13}C NMR shows two different peaks at 94.8 and 88.8 ppm for the alkyne carbons. Only one C≡C stretch is observed in the infrared spectrum of TTC, which appears at 2203 cm^{-1}. This peak is lower by 14 cm^{-1} than that of TBC. The UV/vis spectrum of TTC shows three more peaks beyond 300 nm which are not observed in the UV/vis spectrum of TBC. These two observations may indicate the 12-membered ring in TTC is more conjugated than in TBC.

Synthesis of $[Co_2(CO)_6]_2(TTC)$. Reaction of TTC with 2 molar equiv of octacarbonyldicobalt produced $[Co_2(CO)_6]_2(TTC)$ in 85% yield. The solubility of this complex in hexane is rather surprising because free TTC does not dissolve in hexane.

Formation of $[Co_2(CO)_6]_2(TTC)$ in which two of the three alkynes interact with $Co_2(CO)_6$ moieties was unexpected. The reaction of TBC and octacarbonyldicobalt produced the complex $Co_4(CO)_9(TBC)$ in which one cobalt atom resides in the cavity of TBC and one cobalt atom is above each alkyne (Figure 1).[1e] These differences may arise from different cavity sizes in TBC and TTC. We believe the reaction of TBC with octacarbonyldicobalt also proceeds through the same intermediate; however, the third alkyne in TBC is closer for binding to cobalt centers than the alkyne in TTC.[13] $[Co_2(CO)_6]_2(TTC)$ fails to decarbonylate and rearrange to complex the remaining alkyne of TTC to form the TBC-like complex within the reaction time of 2 weeks. The third alkyne of TTC also fails to react when TTC is treated with 3 equiv of octacarbonyldicobalt. The $[Co_2(CO)_6]_2(TTC)$ complex shows CO stretching absorptions at 2089, 2052, 2029, 2005, 1994, 1988, and 1896 cm^{-1}. The coordinated C≡C bond stretch is at 1856 cm^{-1}. The uncoordinated C≡C stretch appears at 2096 cm^{-1}, which is lower by 93 cm^{-1} than that in free TTC. A similar lowering of the uncoordinated C≡C stretch is also observed in the tetracobalt complex of tetrabenzocyclotetrayne, where only two of the alkyne units are bound to cobalt centers and the other two alkynes are uncomplexed.[14] The ^{13}C NMR (C_6D_6) shows six different peaks for the alkyne carbons at 97.1, 91.5, 91.3, 87.0, 86.3, and 84.7 ppm and two peaks at 200.0 and 199.4 ppm for the carbonyl carbons.

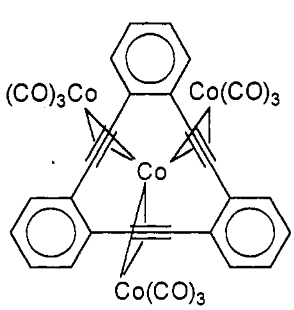


Figure 1. $Co_4(CO)_9(TBC)$.

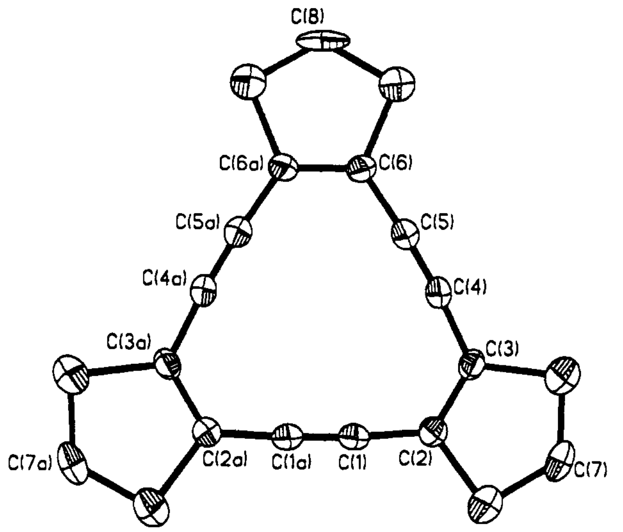


Figure 2. Thermal ellipsoid labeling of TTC. The thermal ellipsoids are drawn at the 50% probability level.

Description of the Structure of TTC. Figure 2 shows the thermal ellipsoid labeling diagram of TTC where a disorder model for the sulfur atoms was used. The unlabeled atoms in Figure 2 were modeled as a 50:50 site occupancy disorder of sulfur and carbon. Selected bond distances and bond angles are listed in Table 3. The least-squares plane defined by 18 carbons and three sulfurs in TTC (root-mean-sequence deviation = 0.024 Å) indicates

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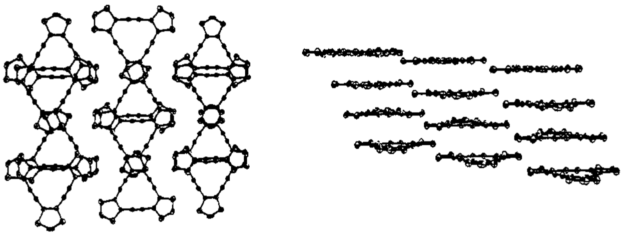

Figure 3. Packing diagram of TTC from the top (left) and the side (right).

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for TTC

atom	*x*	*y*	*z*	*U*(eq)^a
S(1)	1643(1)	−1588(2)	327(3)	50(1)
S(2)	2413(1)	562(2)	1662(3)	49(1)
S(3)	720(1)	5350(2)	−1188(3)	49(1)
C(1)	326(2)	−443(4)	−1928(6)	32(2)
C(2)	1111(2)	−361(4)	−566(6)	30(2)
C(3)	1491(2)	744(4)	99(6)	29(2)
C(4)	1145(2)	1919(4)	−460(6)	33(2)
C(5)	812(2)	2868(4)	−1029(6)	34(2)
C(6)	380(2)	3946(4)	−1810(6)	29(2)
C(7)	2391(3)	−861(5)	1629(7)	43(2)
C(8)	0	6044(6)	−2500	53(4)

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

Table 3. Selected Bond Lengths (Å) and Angles (deg) for TTC

Distances			
C(1)–C(2)	1.426(5)	C(4)–C(5)	1.191(6)
C(1)–C(1A)	1.184(7)	C(5)–C(6)	1.411(6)
C(2)–C(3)	1.382(6)	C(6)–C(6A)	1.393(7)
C(3)–C(4)	1.416(6)		
Angles			
C(2)–C(1)–C(1A)	176.4(3)	C(3)–C(4)–C(5)	175.5(4)
C(1)–C(2)–C(3)	123.5(4)	C(4)–C(5)–C(6)	176.0(4)
C(2)–C(3)–C(4)	124.1(3)	C(5)–C(6)–C(6A)	124.1(2)

the molecule is planar with C_3 symmetry. The C≡C bond distances in TTC are 1.191(6) and 1.184(7) Å, which compare to 1.192(2) Å in TBC.[15] The C≡C—C bond angles in TTC range from 175.5(4) to 176.4(3)° with an average value of 176.0(4)°, which is smaller by 2.8° than that in TBC (178.8(10)°).[14] These larger C≡C—C bendings result in the formation of a larger cavity in TTC than in TBC. The distances from the center of the cavity of TTC to C1, C4, and C5 are 2.130, 2.150, and 2.142 Å, respectively. The comparable distance is 2.08 Å in TBC.[1a]

Another important aspect of the crystal structure of TTC is the packing in the unit cell. TTC packs in a slipped column pattern with an interplanar distance of 3.801 Å, and the molecules have a staggered configuration with respect to each other. Figure 3 shows the packing diagrams of TTC from the top and side views. In contrast, TBC packs in a slip-stacked herringbone pattern with an interplanar distance of 3.2 Å.[14]

The difference in the packing of TTC and TBC may arise from the fact that the number of H atoms in TTC is half that in TBC. The reduction in the number of H atoms in TTC reduces H···H and H···thiophene ring interactions, which results in more efficient packing. The longer interplanar distance in TTC (3.801 Å) may result from the repulsion of the lone pairs of electrons on the S atoms in the thiophene rings. However, we cannot verify this point because of the disorder in the structure.

Description of the Structure of $[Co_2(CO)_6]_2(TTC)\cdot{}^1/_2Et_2O$. Figure 4 shows the thermal ellipsoid labeling diagram of $[Co_2(CO)_6]_2(TTC)$. The unit cell of this complex contains a disordered diethyl ether solvent molecule situated on an inversion center. Selected bond distances and angles are listed in Tables 5 and 6, respectively. X-ray analysis of this complex showed that only two of the alkynes are bound to the dicobalt moieties where the Co—$C_{C≡C}$ bond distance ranges from 1.956(6) to 2.034(6) Å. The Co—Co bond distances are 2.446(1) and 2.450(1) Å. The Co—$C_{C≡C}$ bond distances in this complex are comparable to those in $Co_4(CO)_9(TBC)$; however Co—Co bond distances in $[Co_2(CO)_6]_2(TTC)$ are shorter by an average value of 0.21 Å than those in $Co_4(CO)_9(TBC)$. The Co—Co bond distances in $Co_2(CO)_6(\mu^2\text{-}\eta^2\text{-PhC≡CPh})$[16] and octacarbonyldicobalt[17] are 2.47 and 2.524 Å, respectively, and the Co—C(alkyne) distances in $Co_2(CO)_6(\mu^2\text{-}\eta^2\text{-PhC≡CPh})$ are 1.89–2.02 Å. The C≡C-(Co-coordinated) bond distances of 1.340(8) and 1.326(8) Å in $[Co_2(CO)_6]_2(TTC)$ are slightly longer than that of $Co_4(TBC)(CO)_9$ (1.306(7) Å). The uncoordinated C≡C bond distance is 1.203(7) Å.

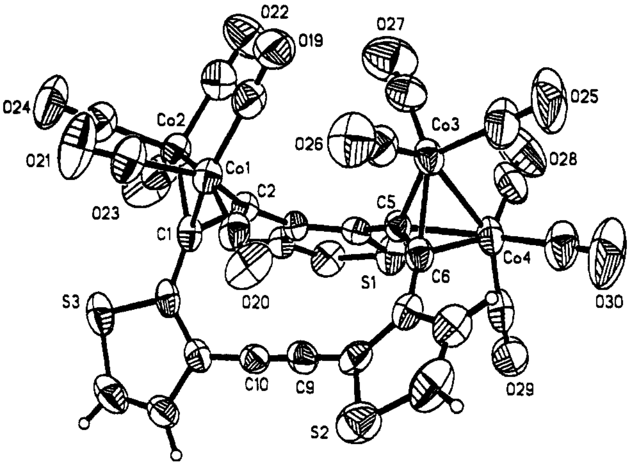

Figure 4. Thermal ellipsoid labeling of $[Co_2(CO)_6]_2(TTC)$. The thermal ellipsoids are drawn at the 50% probability level.

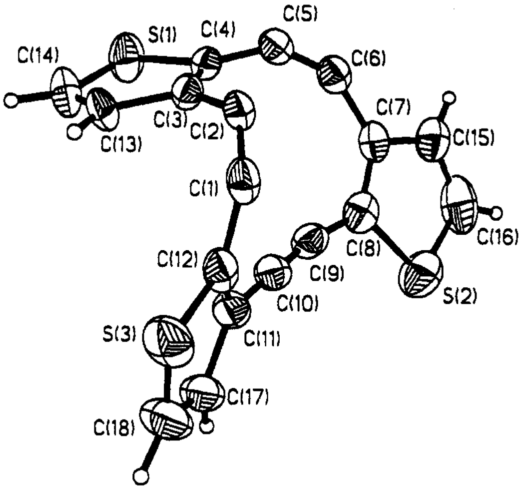

Figure 5. TTC ligand in the $[Co_2(CO)_6]_2(TTC)$ complex.

The TTC ligand in the $[Co_2(CO)_6]_2(TTC)$ complex is considerably distorted from planarity. Figure 5 shows the TTC ligand in the $[Co_2(CO)_6]_2(TTC)$ complex. The Co-coordinated alkynes are distorted from linearity to a *cis* alkene-like geometry. The C(2)—C(1)—C(12) and C(1)—C(2)—C(3) bond angles are 132.2(6) and 131.7(6)°, respectively. The corresponding angles are 146.4(6) and

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Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $[Co_2(CO)_6]_2(TTC)$

atom	*x*	*y*	*z*	*U*(eq)[a]
Co(1)	−2272(1)	−4465(1)	6970(1)	43(1)
Co(2)	−4465(1)	−3938(1)	8316(1)	49(1)
Co(3)	1321(1)	−8259(1)	6902(1)	49(1)
Co(4)	2720(1)	−8617(1)	7919(1)	52(1)
S(1)	−88(2)	−6696(1)	9692(1)	57(1)
S(2)	3986(2)	−5029(2)	6249(1)	71(1)
S(3)	−3932(2)	−1117(1)	8810(1)	64(1)
O(19)	−2234(5)	−6684(4)	6302(3)	91(3)
O(20)	626(5)	−4597(4)	5799(3)	73(3)
O(21)	−3911(6)	−2806(5)	5967(3)	108(3)
O(22)	−4779(6)	−6197(5)	8242(3)	94(3)
O(23)	−6270(6)	−2804(5)	10144(3)	111(4)
O(24)	−6783(6)	−2330(5)	7658(3)	101(3)
O(25)	3398(7)	−10595(4)	5841(4)	149(4)
O(26)	1117(6)	−7199(4)	5300(3)	86(3)
O(27)	−1465(7)	−8494(5)	7845(4)	114(4)
O(28)	1321(8)	−10008(5)	9040(4)	126(5)
O(29)	3927(5)	−7900(4)	9107(3)	78(3)
O(30)	5704(6)	−10305(5)	6712(4)	130(4)
C(1)	−2824(6)	−3500(5)	8102(3)	40(3)
C(2)	−2261(6)	−4670(5)	8178(3)	36(3)
C(3)	−1596(6)	−5326(4)	8806(3)	34(3)
C(4)	−312(6)	−6352(5)	8680(3)	36(3)
C(5)	948(7)	−7135(5)	7916(3)	39(3)
C(6)	2178(7)	−7262(5)	7258(4)	43(3)
C(7)	3033(6)	−6623(5)	6794(3)	42(3)
C(8)	2638(6)	−5414(6)	6960(3)	45(3)
C(9)	1316(7)	−4484(5)	7542(4)	44(3)
C(10)	200(7)	−3604(5)	7936(3)	41(3)
C(11)	−1172(7)	−2576(5)	8332(3)	42(3)
C(12)	−2533(7)	−2528(5)	8363(3)	42(3)
C(13)	−2369(6)	−4821(5)	9724(3)	42(3)
C(14)	−1669(6)	−5467(5)	10255(4)	56(3)
C(15)	4429(7)	−7238(6)	6071(4)	58(4)
C(16)	5015(7)	−6476(7)	5748(4)	77(4)
C(17)	−1281(7)	−1442(5)	8658(4)	51(3)
C(18)	−2706(8)	−611(6)	8942(4)	69(4)
C(19)	−2218(7)	−5839(6)	6552(4)	58(4)
C(20)	−461(8)	−4559(5)	6285(4)	50(3)
C(21)	−3253(7)	−3436(6)	6351(4)	66(4)
C(22)	−4681(8)	−5320(7)	8283(4)	64(4)
C(23)	−5529(7)	−3284(7)	9447(5)	70(4)
C(24)	−5868(8)	−2942(6)	7900(4)	64(4)
C(25)	2604(9)	−9695(7)	6265(5)	92(5)
C(26)	1121(7)	−7577(6)	5947(4)	60(4)
C(27)	−378(9)	−8454(7)	7464(5)	69(4)
C(28)	1894(9)	−9486(6)	8607(5)	75(5)
C(29)	3420(7)	−8145(5)	8650(4)	58(4)
C(30)	4559(9)	−9680(7)	7179(5)	76(4)
O(1S)	−313(19)	−29(20)	4832(12)	192(7)
C(1S)	373(29)	−785(19)	5438(14)	177(11)
C(2S)	−685(26)	−1030(23)	6240(14)	153(9)
C(3S)	894(19)	254(16)	4223(11)	128(7)
C(4S)	−262(26)	1348(18)	4011(17)	151(9)

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

143.5(5)° for C(4)—C(5)—C(6) and C(5)—C(6)—C(7), respectively. These alkyne distortions are comparable to those of $Co_2(CO)_6(\mu^2\text{-}\eta^2\text{-}PhC{\equiv}CPh)$ which has C≡C—Ph bond angles of 137 and 139°. The uncoordinated alkyne is also distorted from linearity. The C(8)—C(9)—C(10) and C(9)—C(10)—C(11) bond angles are 170.7(7) and 174.3(8)°. This sizable and inequivalent distortion may be the reason for the appearance of a very strong peak at 2096 cm^{-1} in the infrared spectrum for the C≡C stretch. This peak is not observed in the infrared spectrum of $Co_4(CO)_9(TBC)$. The C≡O bond distances for the carbonyl groups range from 1.129(11) to 1.138(9) Å. It was mentioned earlier that TTC did not react with a third equivalent of $Co_2(CO)_8$. Presumably, this is due to the protection of the alkyne by the two carbonyls containing O(20) and O(26).

Table 5. Selected Bond Distances (Å) for $[Co_2(CO)_6]_2(TTC)$

Co(1)–Co(2)	2.446(1)	S(2)–C(16)	1.704(7)
Co(1)–C(1)	1.971(5)	S(3)–C(12)	1.721(5)
Co(1)–C(2)	1.963(5)	S(3)–C(18)	1.700(10)
Co(1)–C(19)	1.800(8)	C(1)–C(2)	1.340(8)
Co(1)–C(20)	1.811(7)	C(1)–C(12)	1.446(10)
Co(1)–C(21)	1.796(7)	C(2)–C(3)	1.462(8)
Co(2)–C(1)	1.923(7)	C(3)–C(4)	1.374(7)
Co(2)–C(2)	2.034(6)	C(3)–C(13)	1.439(6)
Co(2)–C(22)	1.810(9)	C(4)–C(5)	1.459(6)
Co(2)–C(23)	1.790(6)	C(5)–C(6)	1.326(8)
Co(2)–C(24)	1.802(7)	C(6)–C(7)	1.450(10)
Co(3)–Co(4)	2.450(1)	C(7)–C(8)	1.379(10)
Co(3)–C(5)	1.983(6)	C(7)–C(15)	1.442(7)
Co(3)–C(6)	1.966(8)	C(8)–C(9)	1.414(7)
Co(3)–C(25)	1.792(7)	C(9)–C(10)	1.203(7)
Co(3)–C(26)	1.777(7)	C(10)–C(11)	1.420(7)
Co(3)–C(27)	1.822(9)	C(11)–C(12)	1.380(11)
Co(4)–C(5)	2.003(5)	C(11)–C(17)	1.444(10)
Co(4)–C(6)	1.956(6)	C(13)–C(14)	1.346(8)
S(1)–C(4)	1.744(6)	C(15)–C(16)	1.334(12)
S(1)–C(14)	1.695(5)	C(17)–C(18)	1.342(8)
S(2)–C(8)	1.734(7)		

Table 6. Selected Bond Angles (deg) for $[Co_2(CO)_6]_2(TTC)$

Co(2)–Co(1)–C(1)	50.2(2)	Co(3)–C(5)–Co(4)	75.9(2)
Co(2)–Co(1)–C(2)	53.6(2)	Co(3)–C(5)–C(4)	138.2(6)
C(1)–Co(1)–C(2)	39.8(2)	Co(4)–C(5)–C(4)	127.5(4)
Co(1)–Co(2)–C(1)	52.0(1)	Co(3)–C(5)–C(6)	69.7(4)
Co(1)–Co(2)–C(2)	51.0(1)	Co(4)–C(5)–C(6)	68.5(3)
C(1)–Co(2)–C(2)	39.5(2)	C(4)–C(5)–C(6)	146.4(6)
Co(4)–Co(3)–C(5)	52.4(2)	Co(3)–C(6)–Co(4)	77.3(2)
Co(4)–Co(3)–C(6)	51.2(2)	Co(3)–C(6)–C(5)	71.1(5)
C(5)–Co(3)–C(6)	39.2(2)	Co(4)–C(6)–C(5)	72.4(3)
Co(3)–Co(4)–C(5)	51.7(2)	Co(3)–C(6)–C(7)	134.8(5)
Co(3)–Co(4)–C(6)	51.5(2)	Co(4)–C(6)–C(7)	130.4(5)
C(5)–Co(4)–C(6)	39.1(2)	C(5)–C(6)–C(7)	143.5(5)
C(4)–S(1)–C(14)	92.0(3)	C(6)–C(7)–C(8)	126.2(4)
C(8)–S(2)–C(16)	90.6(3)	C(6)–C(7)–C(15)	120.9(6)
C(12)–S(3)–C(18)	92.2(3)	C(8)–C(7)–C(15)	112.9(6)
Co(1)–C(1)–Co(2)	77.8(3)	S(2)–C(8)–C(7)	110.8(4)
Co(1)–C(1)–C(2)	69.8(3)	S(2)–C(8)–C(9)	118.1(6)
Co(2)–C(1)–C(2)	74.7(4)	C(7)–C(8)–C(9)	130.9(6)
Co(1)–C(1)–C(12)	134.9(4)	C(8)–C(9)–C(10)	170.7(7)
Co(2)–C(1)–C(12)	139.5(3)	C(9)–C(10)–C(11)	174.3(8)
C(2)–C(1)–C(12)	132.2(6)	C(10)–C(11)–C(12)	122.7(6)
Co(1)–C(2)–Co(2)	75.4(2)	C(10)–C(11)–C(17)	124.1(7)
Co(1)–C(2)–C(1)	70.4(3)	C(12)–C(11)–C(17)	113.0(5)
Co(2)–C(2)–C(1)	65.8(4)	S(3)–C(12)–C(1)	122.5(5)
Co(1)–C(2)–C(3)	151.6(3)	S(3)–C(12)–C(11)	110.2(5)
Co(2)–C(2)–C(3)	126.8(4)	C(1)–C(12)–C(11)	127.3(4)
C(1)–C(2)–C(3)	131.7(6)	C(3)–C(13)–C(14)	112.6(4)
C(2)–C(3)–C(4)	131.5(4)	S(1)–C(14)–C(13)	112.9(4)
C(2)–C(3)–C(13)	116.4(4)	C(7)–C(15)–C(16)	110.4(6)
C(4)–C(3)–C(13)	112.1(5)	S(2)–C(16)–C(15)	115.2(4)
S(1)–C(4)–C(3)	110.4(3)	C(11)–C(17)–C(18)	111.0(7)
S(1)–C(4)–C(5)	113.7(4)	S(3)–C(18)–C(17)	113.6(6)
C(3)–C(4)–C(5)	135.6(5)		

Preparation of other dehydroannulenes containing substituted thiophenes and desulfurization of these ligands using transition and main group metals are currently under investigation.

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Supplementary Material Available: Tables of crystal data, data collection details, atomic coordinates, thermal parameters for non-hydrogen atoms, bond distances and angles, and hydrogen atom coordinates for both structures (15 pages). Ordering information is given on any current masthead page.

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