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PREPARATION AND STRUCTURE OF (η^5-CYCLOPENTADIENYL) (η^4-TETRAPHENYLCYCLOBUTADIENE)COBALT COORDINATED BY THREE $Cr(CO)_3$ UNITS AT THE PHENYL RINGS

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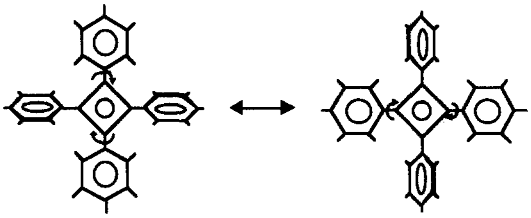
Abstract—The reaction of (η^5-cyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt (**1**) with excess $Cr(CO)_6$ led to five identified heterometallic compounds. They are compounds **2**, **3** (**3′** and **3″**), **4** and **5** with one, two, three and four phenyl ring(s) being complexed with $Cr(CO)_3$ fragment(s), respectively. The X-ray crystal structure of **4** has been determined and can be regarded as an intermediate in the structural change from **3′** to **5**. It shows that one $Cr(CO)_3$ fragment is on the same side of the CpCo fragment, whereas the other two $Cr(CO)_3$ fragments are opposite to the CpCo fragment.

We have previously reported that the reaction of **1** with $Cr(CO)_6$ led to products with $Cr(CO)_3$ fragments attached to phenyl rings (Scheme 1). Compounds **2**, **3′**, **3″**, **4** and **5** were characterized spectrally. The crystal structures of **3′** and **5** were determined as well.[1]

The crystal structure of **3′** shows that the two (arene)$Cr(CO)_3$ fragments point in different directions to the CpCo fragment and are approximately parallel with the cyclobutadiene ring.† The two non-complexed phenyl rings are at rather large angles to the cyclobutadiene ring.‡ The crystal structure of **5** (some repeating units are omitted for clarity) shows that the four (arene)$Cr(CO)_3$ fragments are on the same side of the CpCo fragment, in contrast to most related cases in which the metal fragments point to the opposite direction of the CpCo fragment, so that strong steric interaction can be avoided (Scheme 2).[1b]

Several investigations have demonstrated that a 360° rotation of four phenyl rings in **1** is possible.[2] It might be achieved by rotating two opposite phenyl rings while keeping the other two phenyl rings vertical, and vice versa.



The structural change from **3′** to **5** indicates that a 360° rotation of phenyl rings in **1** is possible. In the cases of **3′** and **5**, the (arene)$Cr(CO)_3$ fragments are much bigger than phenyl rings of **1**; however, the conversion of (arene)$Cr(CO)_3$ fragments are clearly observed from crystal structures, even though they seem too large to allow free rotation at first glance.[1b] Because of these interesting observations, we are interested in how the structure changes

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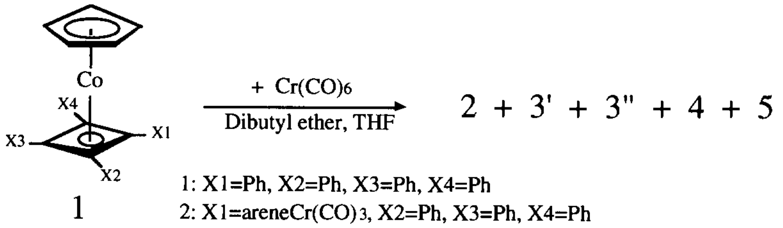
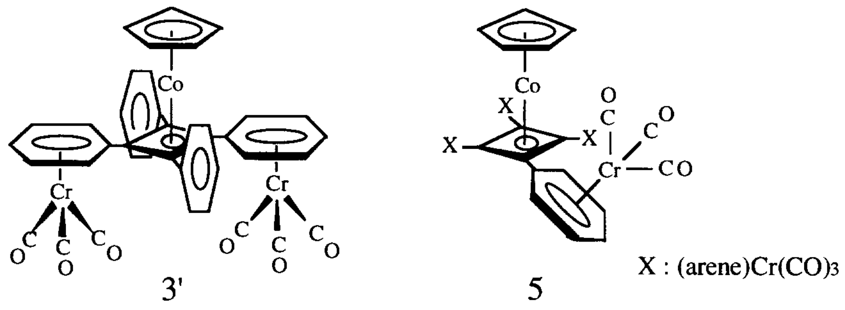
† The dihedral angles between $Cr(CO)_3$ complexed phenyl rings and cyclobutadiene are 12.2 and 8.2°, respectively.

‡ The dihedral angles between non-complexed phenyl rings and cyclobutadiene are 52.9 and 76.0°, respectively.



1: X1=Ph, X2=Ph, X3=Ph, X4=Ph
2: X1=areneCr(CO)3, X2=Ph, X3=Ph, X4=Ph
3': X1=areneCr(CO)3, X2=Ph, X3=areneCr(CO)3, X4=Ph
3'': X1=areneCr(CO)3, X2=areneCr(CO)3, X3=Ph, X4=Ph
4: X1=areneCr(CO)3, X2=areneCr(CO)3, X3=areneCr(CO)3, X4=Ph
5: X1=areneCr(CO)3, X2=areneCr(CO)3, X3=areneCr(CO)3, X4=areneCr(CO)3

Scheme 1.



Scheme 2.

from **3′** to **5** through **4**. The crystal structure of **4** may provide some information on this.

Table 1. Dihedral angle between planes A and B

A	B	Angle (°)
1	2	108.8
1	3	17.4
1	4	52.4
1	5	13.2
2	3	108.7
2	4	58.3
2	5	101.9
3	4	50.5
3	5	29.7
4	5	50.4

Plane 1 : C(1)–C(4)
Plane 2 : C(11)–C(16)
Plane 3 : C(21)–C(26)
Plane 4 : C(31)–C(36)
Plane 5 : C(41)–C(46)

RESULTS AND DISCUSSION

The yield of compound **4** was low under previously reported reaction conditions.[1a] However, it can be enhanced appreciably by the reaction of $Cr(CO)_6$ with purified **3** (**3′** plus **3″**). The product was characterized by mass, IR, ^1H and ^{13}C NMR spectroscopy. Dark red crystals of **4** were recrystallized by diffusing dichloromethane into a toluene solution. The crystal structure of **4** was determined. There are two independent, but chemically similar, molecules in the asymmetric unit. Two dichloromethane and one water molecules were found in the asymmetric unit. Compound **4** shows that there are two (arene)$Cr(CO)_3$ fragments on the opposite side and one (arene)$Cr(CO)_3$ fragment on the same side as the CpCo fragment. The only non-complexed phenyl ring is at a rather large angle to the cyclobutadiene ring to avoid the strong steric interactions with other fragments (Fig. 1, Table 1). The phenyl rings of the three (arene)$Cr(CO)_3$ fragments are all bent outwards away from the CpCo fragment and are all below the cyclobutadiene ring. This arrangement of the molecule is reasonable in terms of avoiding strong steric interaction between different fragments. The structure also demonstrates that a molecule consisting of crowded parts can be stabilized by proper arrangement of each fragment. A top view of **4** is shown in Fig. 2. The structure of **4** can be regarded as a transit from **3′** to **5**. The gradual structural change from **3′** to **4** and then to **5** indicates that the non-complexed phenyl ring(s) or (arene)$Cr(CO)_3$

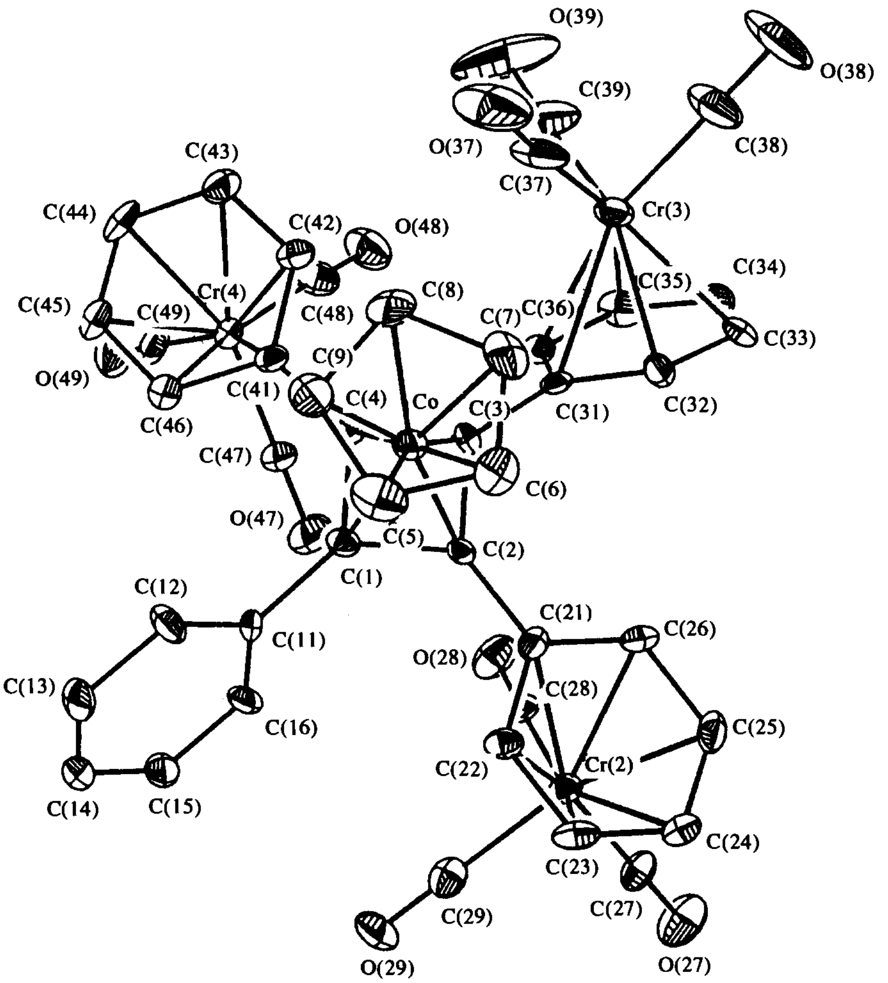


Fig. 1. ORTEP drawing with the numbering scheme of **4**. Hydrogen atoms are omitted for clarity.

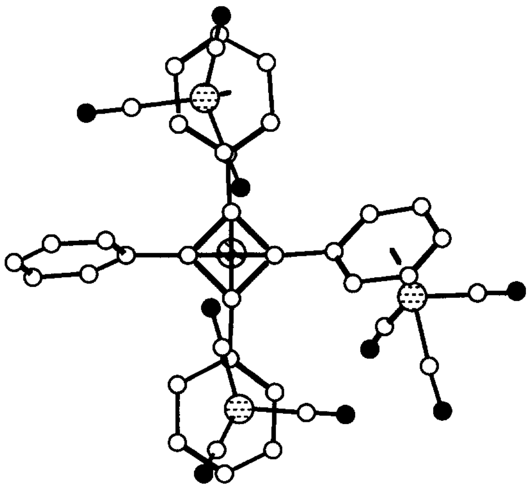


Fig. 2. Top view of **4**. The cyclopentadienyl ring is omitted for clarity.

fragments are able to rotate 360° along the phenyl–cyclobutadiene axis in solution.

The dihedral angles between the cyclobutadiene ring and phenyl rings of (arene)Cr(CO)$_3$ fragments in **4** are relatively small. The result is consistent with the observations from this series of compounds, such as **3′** and **5** (Table 1). This is a significant structural change compared with that of **1**.[2b] In this way a better overlap between the cyclobutadiene ring and the phenyl rings through π interaction takes place. By that process, the Cr(CO)$_3$ complexed phenyl rings may donate more electron density to the cyclobutadiene ring and then to the Cp ring, which causes a sequential downfield shift from **2** to **5** with more Cr(CO)$_3$ complexed to **1** (**2**: 4.76; **3′**: 4.89; **3″**: 4.93; **4**: 5.05; **5**: 5.21). ^{1}H NMR also shows an obvious upfield shift for phenyl rings of (arene)Cr(CO)$_3$ and an almost unaffected phenyl group in the same molecule, which is consistent with well-known observations and is in accord with observations from this series of compounds.[1,3]

Hunter *et al.* pointed out that the planarity of the arene ring can be distorted by a substituent.[4] An inward distortion, $\delta d < 0$, will take place when the substituent is an electron-withdrawing group.

Table 2. Selected bond distances (Å) and angles (°)

Co—C(1)	1.969(11)	Co—C(2)	1.970(11)
Co—C(3)	1.955(12)	Co—C(4)	1.976(12)
Co—C(5)	2.020(17)	Co—C(6)	1.996(17)
Co—C(7)	2.041(15)	Co—C(8)	2.043(15)
Co—C(9)	2.048(16)	Cr(2)—C(21)	2.246(12)
Cr(2)—C(22)	2.185(12)	Cr(2)—C(23)	2.238(13)
Cr(2)—C(24)	2.227(14)	Cr(2)—C(25)	2.170(14)
Cr(2)—C(26)	2.206(12)	Cr(2)—C(27)	1.834(14)
Cr(2)—C(28)	1.805(15)	Cr(2)—C(29)	1.874(16)
Cr(3)—C(31)	2.282(11)	Cr(3)—C(32)	2.228(13)
Cr(3)—C(33)	2.206(14)	Cr(3)—C(34)	2.196(15)
Cr(3)—C(35)	2.207(15)	Cr(3)—C(36)	2.245(12)
Cr(3)—C(37)	1.806(18)	Cr(3)—C(38)	1.836(20)
Cr(3)—C(39)	1.802(21)	Cr(4)—C(41)	2.270(13)
Cr(4)—C(42)	2.202(12)	Cr(4)—C(43)	2.213(14)
Cr(4)—C(44)	2.203(16)	Cr(4)—C(45)	2.195(15)
Cr(4)—C(46)	2.223(14)	Cr(4)—C(47)	1.802(14)
Cr(4)—C(48)	1.808(18)	Cr(4)—C(49)	1.770(17)
C(1)—C(2)	1.455(17)	C(1)—C(4)	1.454(17)
C(1)—C(11)	1.508(17)	C(2)—C(3)	1.469(17)
C(2)—C(21)	1.431(18)	C(3)—C(4)	1.457(17)
C(3)—C(31)	1.483(18)	C(4)—C(41)	1.455(18)
C(5)—C(6)	1.367(28)	C(5)—C(9)	1.418(25)
C(6)—C(7)	1.363(26)	C(7)—C(8)	1.419(25)
C(8)—C(9)	1.383(24)	C(27)—O(27)	1.150(18)
C(28)—O(28)	1.159(19)	C(29)—O(29)	1.134(19)
C(1)—Co—C(2)	43.4(5)	C(1)—Co—C(3)	63.2(5)
C(2)—Co—C(3)	44.0(5)	C(1)—Co—C(4)	43.3(5)
C(2)—Co—C(4)	63.3(5)	C(3)—Co—C(4)	43.5(5)
C(2)—C(1)—C(4)	90.7(9)	C(1)—C(2)—C(3)	89.3(9)
C(2)—C(3)—C(4)	90.1(9)	C(1)—C(4)—C(3)	89.9(10)
C(6)—C(5)—C(9)	109.3(16)	C(5)—C(6)—C(7)	108.7(17)
C(6)—C(7)—C(8)	107.6(15)	C(7)—C(8)—C(9)	108.6(15)
C(5)—C(9)—C(8)	105.7(15)	C(22)—C(21)—C(26)	116.0(12)
C(21)—C(22)—C(23)	124.5(13)	C(22)—C(23)—C(24)	119.8(13)
C(23)—C(24)—C(25)	118.5(13)	C(24)—C(25)—C(26)	121.5(13)
C(21)—C(26)—C(25)	119.6(12)	Cr(2)—C(27)—O(27)	179.7(14)
Cr(2)—C(28)—O(28)	177.6(11)	Cr(2)—C(29)—O(29)	178.2(12)

On the other hand, an outward distortion, $\delta d > 0$, is expected for an electron-donating substituent.* The above rule is obeyed unless a very bulky substituent is present. In our case, $\delta d > 0$ is observed for all three (arene)Cr(CO)$_3$ fragments in **4** (Table 2).† As for the conformation of Cr(CO)$_3$ in (arene) Cr(CO)$_3$, an *anti*-eclipsed form is expected for (arene)Cr(CO)$_3$ with an electron-withdrawing substituent. A *syn*-eclipsed form is expected for (arene) Cr(CO)$_3$ with an electron-donating substituent, provided that no serious steric effect is involved.[5] A pseudo-*anti*-eclipsed form is observed for the (arene)Cr(CO)$_3$ fragment in **4** (Fig. 3). This result supports the deduction that (arene)Cr(CO)$_3$ is attached to an electron-withdrawing group. There-

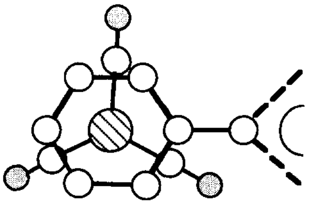


Fig. 3. Top view of (arene)Cr(CO)$_3$ of **4**.

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*The parameter δd is defined as the difference between the Cr—C$_{\text{ipso}}$ bond length and the average of the other Cr—C(H) bond lengths. $\delta d = d(\text{Cr—C}_{\text{ipso}}) - d[\text{Cr—C(H)}_{\text{av}}]$.

†These are 0.041, 0.066 and 0.063 Å.

fore, we believe that the steric effect is an important factor here because of the strong steric interaction between $Cr(CO)_3$ and the rest of the molecular fragment.

EXPERIMENTAL

All operations were performed in a nitrogen-flushed glove box or in a vacuum system. Freshly distilled solvents were used. All processes of separation of products were performed by Centrifugal Thin Layer Chromatography (CTLC; Chromatotron, Harrison model 8924). ^1H and ^{13}C NMR were recorded on a Varian-300 spectrometer at 300 and 75.46 MHz, respectively. Chemical shifts are reported in ppm downfield from internal TMS. IR spectra were recorded in CH_2Cl_2 on a Hitachi 270-30 instrument. Mass spectra were recorded on JEOL JMS-SX/SX 102A GC/MS/MS.

Reaction of $(\eta^5\text{-}C_5H_5)CO(C_4Ph_4)$ *with* $Cr(CO)_6$

The synthesis of the title compound was done according to a procedure in the literature.[1b] Into a 250 cm^3 round-bottomed flask equipped with a condenser and a magnetic stirrer were placed 1.25 g (1.65 mmol) of complex **3** (**3′** and **3″**) and 3.6 g (16.5 mmol) of chromium hexacarbonyl. Anhydrous dibutyl ether (180 cm^3) and 18 cm^3 of anhydrous tetrahydrofuran (THF) were added and the reaction mixture was refluxed under dry N_2 for 36 h. The reactor was cooled to room temperature, filtered through Celite and the solvent removed *in vacuo*.

The residue was dissolved in a small amount of THF–hexane mixed solvent and was then loaded to CTLC for separation. Three bands were collected through the elution of mixed solvents. The ratio of mixed solvent (THF–hexanes) changed from 1 : 8 to 1 : 2 as the separation went on. The first orange band, R_f (0.42) in 1 : 2 THF–hexanes, was identified as a small amount of unreacted **1**. Compound **4**, orange and R_f 0.31, was collected as the second band. Compound **5**, orange and R_f 0.25, was collected as the last band. The separation in CTLC is under N_2. The yields of **4** and **5** were 52.0% (0.65 g) and 20.5% (0.30 g), respectively.

Compound **4** ^1H NMR ($CDCl_3$, δ/ppm): 5.05 (s, 5H, Cp), 5.19 (m, 5H), 5.26 (m, 3H), 5.50 (m, 3H), 5.73 (m, 2H), 5.99 (m, 2H), 7.45 (m, 3H), 7.80 (m, 2H). ^{13}C NMR ($CDCl_3$, δ/ppm): 72.640, 73.500, 80.000 (4C, cyclobutadiene), 83.250 (5C, Cp), 91.292 [2C, C(24), C(44)], 91.625, 91.716 [4C, C(23), C(25), C(43), C(45)], 91.919, 91.979 [6C, C(22), C(26), C(33), C(35), C(42), C(46)], 92.576 [1C, C(34)], 95.520 [2C, C(32), C(36)], 105.786 [2C, C(21), C(41)], 106.110 [1C, C(31)], 128.525 [1C, C(14)], 128.727 [2C, C(13), C(15)], 131.246 [2C, C(12), C(16)], 131.448 [1C, C(11)], 232.355 (3CO), 232.719 (6CO). IR (CH_2Cl_2): ν(CO) 1974, 1894 cm^{-1}. Mass spectrum: m/z 888 (P^+).

Crystal structure determination of **4**

An orange crystal of **4** with size of 0.3 × 0.6 × 0.7 mm was sealed in a capillary and used for X-ray diffraction measurements. The intensities were collected on a Siemens R3m/V diffractometer equipped with graphite-monochromated Mo-K_α radiation, $\lambda = 0.71073$ Å. The positions of heavy atoms in the structure were determined by direct methods, and the remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were considered to ride on carbon atoms with a C—H bond length of 0.96 Å, and the temperature factors were fixed at 0.08 Å. The hydrogen atoms were included for structure factor calculation in the final cycles. All refinements and calculations were carried out with the Siemens SHELXTL PLUS software package on a MicroVAX 3100 computer.

The crystallographic data of complex **4** are summarized in Table 3.

Table 3. Crystal data of **4**

Formula	$C_{42}H_{25}Co_1Cr_3O_9$
Formula weight	888.5
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	23.435(5)
b (Å)	16.586(3)
c (Å)	21.692(4)
β (°)	96.37(3)
V (Å^3)	8379(3)
Z	8
D_c (g cm^{-3})	1.409
λ (Mo-K_α) (Å)	0.71073
μ (mm^{-1})	1.197
Range (°)	3.0–45.0
Scan type	θ–2θ
No. of reflections collected	11190
No. of independent reflections	10883 (R_{int} = 2.03%)
No. of observed reflections	5773 [$F > 2.0\ \sigma(F)$]
No. of refined parameters	1054
R_f[a] for significant reflections	0.0745
R_w[b] for significant reflections	0.0824
GoF[c]	1.15

[a] $R_f = [\Sigma(F_0-F_c)/\Sigma F_0]$.
[b] $R_w = \Sigma w^{1/2}(F_0-F_c)/\Sigma w^{1/2}F_0$.
[c] $\mathrm{GoF} = [\Sigma w(F_0-F_c)^2/(N_{\mathrm{rflns}}-N_{\mathrm{params}})]^{1/2}$.

Supplementary material available

Tables of atomic coordinates and thermal parameters, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates for **4**.

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