Journal of Organometallic Chemistry, 480 (1994) 75–79

Preparation and structure of (η^5-cyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt coordinated by four $Cr(CO)_3$ units at the phenyl rings

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(Received November 4, 1993; in final form December 19, 1993)

Abstract

The reaction of (η^5-cyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt (1) with excess $Cr(CO)_6$ yielded several heterometallic compounds: 2, 3 (3′ and 3″), 4 and 5 with, respectively, one, two, three and four phenyl rings complexed with $Cr(CO)_3$ fragment(s). These compounds were characterized by mass, infrared, ^{1}H and ^{13}C NMR spectra. The crystal structure of 5 was determined. In 5 the four $Cr(CO)_3$ fragments are on the same side of the CpCo fragment; whereas, the two $Cr(CO)_3$ fragments of 3′, the precursor of 5, are pointed in a different direction from the CpCo fragment. The cyclopentadienyl ring shows a static disorder around the axis that passes through the cobalt and the centre of the ring.

Key words: Cobalt; Chromium

1. Introduction

The potential of heteronuclear metal complexes in catalysis has been the subject of a very large number of studies [1]. The cooperative effect of the different metal centres is crucial to the catalytic properties of these complexes. This effect will be enhanced by a jointed π-ring when held in close proximity. We were therefore interested in preparing this type of compounds and examining their properties.

The (η^5-cyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt (1) is a sandwich-like compound with four phenyl rings attached to four carbons of the cyclobutadiene ring. 1 has four active sites — four phenyl groups — for $Cr(CO)_3$ π-complexation. The chemistry of (arene)$Cr(CO)_3$ has been intensively investigated because of, firstly, interest in fundamental structural and electronic features of metal–arene interactions and, secondly, various applications in organic synthesis [2]. Diverse conformations of (arene)$Cr(CO)_3$ have attracted much attention due to its significant influence on the regioselectivity of nucleophilic/electrophilic attack on arene[3]. Both theoretical and experimental studies on crystal structures of related compounds have been reported [4]. The conformation of (arene)$Cr(CO)_3$ in either *syn*-eclipsed, *anti*-eclipsed or staggered form is affected by the electron-withdrawing or -donating ability of the substituent unless a bulky substituent is present [5].

The crystal structure of 1 was determined [6] (Fig. 1). The dihedral angles between the phenyl and cyclobutadiene rings vary from 31.6° to 41.7°. It seems that the space between phenyl rings is too small to accommodate any $Cr(CO)_3$ fragment without significant structural change. It was, therefore, of interest to

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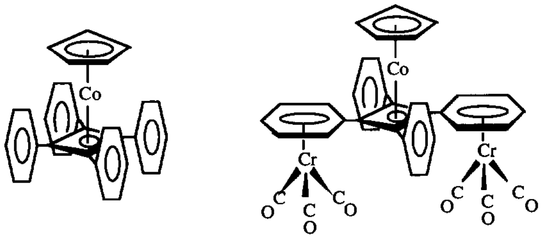


Fig. 1. Structures of **1** and **3′**.

study the possibility of incorporating as many $Cr(CO)_3$ fragments as possible into the phenyl rings and to monitor the structural change and effects thus caused.

Our previous work showed that the reaction of **1** with $Cr(CO)_6$ in dibutyl ether in the presence of trace tetrahydrofuran resulted in attachment of $Cr(CO)_3$ fragments to the phenyl groups (Scheme 1). **2**, **3′**, **3″** and **4** were characterized spectroscopically [7]. These compounds can be regarded as metal fragments that are linked by a conjugated π-π ring system.

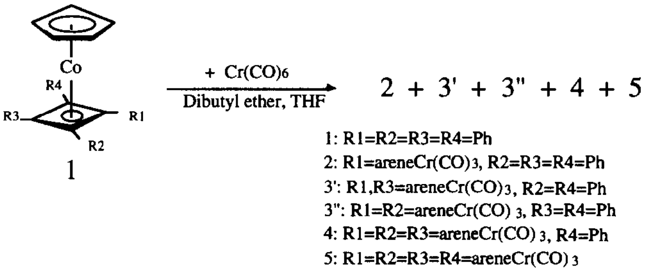
The crystal structure of **3′** was determined (Fig. 1). **3′** shows that the angles between the $Cr(CO)_3$ complexed phenyl and cyclobutadiene rings are 12.2° and 8.1°, whereas the angles between cyclobutadiene and the non-complexed phenyl rings are 76.0° and 52.9°. **3′** also shows that the two $Cr(CO)_3$ fragments are pointed in a different direction from the CpCo fragment. There is a rather significant structural change from **1** to **3′** after the $Cr(CO)_3$ complexation.

We now report the preparation and the crystal structure determination of **5** which contains mixed metals through the directly jointed π-rings.

2. Results and discussion

The presence of **5** was previously overlooked because of its low yield under the reported reaction conditions [8 *]. The yield did not increase noticeably even under excess of $Cr(CO)_6$ and with a long reaction time. However, it can be enhanced appreciably by the reaction of $Cr(CO)_6$ with purified **3** (**3′** plus **3″**). **5** was characterized by mass, infrared, ^1H and ^{13}C NMR spectroscopy. It was crystallized by diffusing CH_2Cl_2 from a solution to toluene, and dark orange crystallites were obtained. In the structure of **5**, apart from the five carbon atoms of the cyclopentadienyl ring, the rest of the molecule could be fitted into a tetragonal $P4/n$ space symmetry group.

A disorder of the cyclopentadienyl ring was observed but the reason for this disorder is uncertain. Two possible reasons suggest themselves; (1) one might think that the four (arene)$Cr(CO)_3$ fragments in **5** form a "pocket" large enough to accommodate the cyclopentadienyl ring and to free it from contact with other molecules. In this way, the ring might still retain a certain degree of free rotation in solid state at room temperature thus causing difficulty in locating the positions of the five carbon atoms of the cyclopentadienyl ring; (2) as reported in a related case another proposed static disordered model where the molecules possess various orientations of cyclopentadienyl ring is also more likely here [9].



Scheme 1.

Hunter pointed out that the planarity of the arene ring can be distorted by a substituent [4b,4c]. An inward distortion, $\delta d < 0$, will take place when the substituent is an electron-withdrawing group. However, an outward distortion, $\delta d > 0$, is expected for an electron-donating substituent [10 *]. The above rule is obeyed unless a very bulky substituent is present. In

TABLE 1. Selected bond distances (Å) and angles (°)

Bond distances (Å)			
Co(1)–C(10)	1.985(2)	Co(1)–C(11)	2.075(6)
Co(1)–C(12)	2.064(5)	Co(1)–C(13)	2.071(6)
Cr(1)–C(1)	1.827(2)	Cr(1)–C(2)	1.852(2)
Cr(1)–C(3)	1.838(2)	Cr(1)–C(4)	2.220(2)
Cr(1)–C(5)	2.203(2)	Cr(1)–C(6)	2.203(2)
Cr(1)–C(7)	2.206(2)	Cr(1)–C(8)	2.227(2)
Cr(1)–C(9)	2.259(2)	O(1)–C(1)	1.145(4)
O(2)–C(2)	1.145(3)	O(3)–C(3)	1.140(3)
C(4)–C(5)	1.413(3)	C(4)–C(9)	1.412(2)
C(5)–C(6)	1.385(3)	C(6)–C(7)	1.410(3)
C(7)–C(8)	1.402(3)	C(8)–C(9)	1.419(2)
C(9)–C(10)	1.463(2)	C(10)–C(10B)	1.463(2)
C(11)–C(12)	1.269(15)	C(11)–C(13)	1.265(14)
Bond angles (°)			
C(10)–Co(1)–C(10A)	62.8(1)	C(10)–Co(1)–C(10B)	43.2(1)
C(1)–Cr(1)–C(2)	88.2(1)	C(1)–Cr(1)–C(3)	86.8(1)
C(2)–Cr(1)–C(3)	85.3(1)	C(4)–Cr(1)–C(5)	37.3(1)
C(4)–Cr(1)–C(6)	66.4(1)	C(4)–Cr(1)–C(7)	78.7(1)
Cr(1)–C(1)–O(1)	177.4(2)	Cr(1)–C(2)–O(2)	175.9(2)
Cr(1)–C(3)–O(3)	177.0(2)	C(5)–C(4)–C(9)	120.4(2)
Cr(1)–C(5)–C(4)	72.0(1)	Cr(1)–C(5)–C(6)	71.7(1)
Cr(1)–C(9)–C(10)	138.7(1)	Co(1)–C(10)–C(9)	139.4(1)
C(9)–C(10)–C(10B)	129.5(2)	C(9)–C(10)–C(10C)	135.0(2)

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

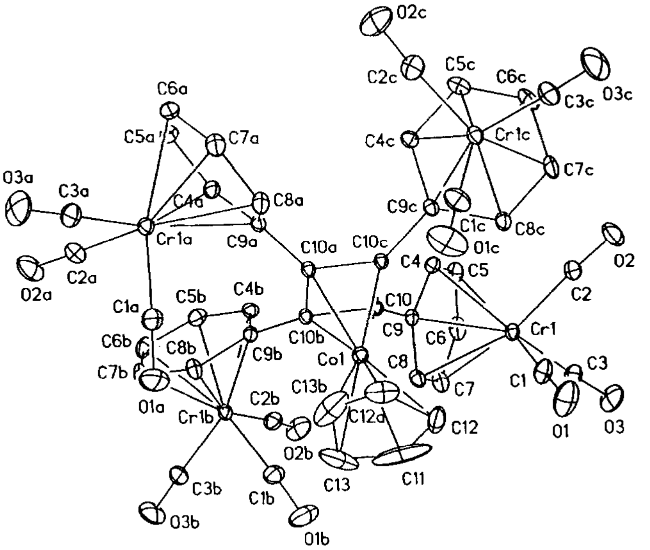

Fig. 2. ORTEP drawing with the numbering scheme of **5**. Hydrogen atoms were omitted for clarity.

our case, $\delta d > 0$ is observed in **5** (Table 1) [11 *]. We believe that the steric effect is also an important factor here because of the strong steric interaction between $Cr(CO)_3$ and the rest of the molecular fragment.

Another unexpected observation is that the four (arene)$Cr(CO)_3$ fragments are on the same side of the CpCo fragment (Fig. 2). This is different from closely related cases in which the metal fragments are almost always in different directions, thus avoiding strong steric interaction [7,12]. For example, in the case of **3'**, the precursor of **5**, the two $Cr(CO)_3$ fragments are in the opposite direction from CpCo fragment. The reason for this unusual observation is uncertain. However, the packing effect might play an important role in the solid state. A more compact arrangement like **5** might be favoured during the course of crystallization. Of course, the solid state structure does not necessarily reflect the situation of the molecule in solution. The angle between phenyl and cyclobutadiene rings is about 59° in **5** which is larger than that of **1**. This arrangement of the molecule is reasonable in terms of avoiding strong steric interaction between CpCo and $Cr(CO)_3$ fragments (Fig. 3).

The orientation of $Cr(CO)_3$ in (arene)$Cr(CO)_3$ has been the subject of extensive studies. An *anti*-eclipsed form is observed for (arene)$Cr(CO)_3$ with an electron withdrawing substituent. However, a *syn*-eclipsed form is observed for (arene)$Cr(CO)_3$ with an electron donating substituent [3b,4a]. However, it may be distorted to a nearly staggered structure when the substituent is bulky. A pseudo-staggered form was observed in **5** for the (arene)$Cr(CO)_3$ fragments (Fig. 4). This result supports the observation that in **5** the (arene)$Cr(CO)_3$ is attached by a bulky group.

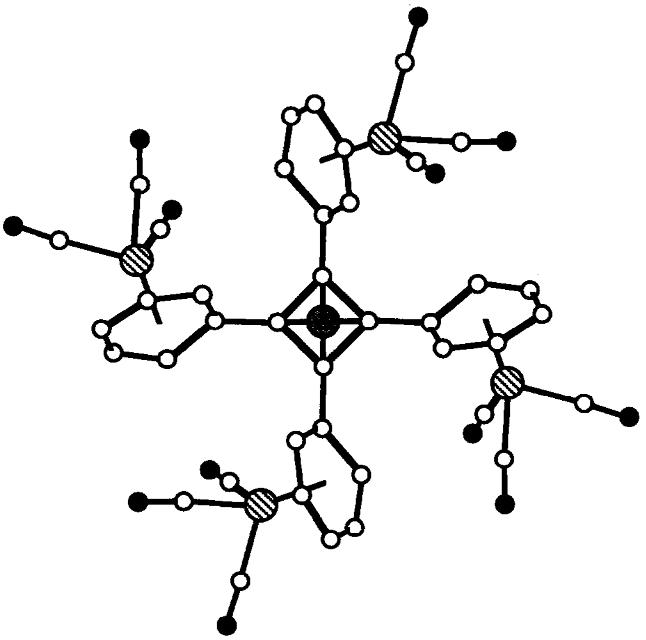

Fig. 3. Top view of **5**. The cyclopentadienyl ring has been omitted for clarity.

^1H NMR shows an obvious upfield shift for all four $Cr(CO)_3$ complexed phenyl rings which is consistent with well known observations [13]. Also, the down-field shift of the Cp in ^1H NMR from **1** (4.63) to **5** (5.21) can be attributed to the structural change [7].

It is rather interesting to find that four $Cr(CO)_3$ fragments can be inserted into the already crowded area of **1** in forming **5**. In a related case, only two $Cr(CO)_3$ fragments were able to be put into tetracarbon carborane $(PhCH_2)_4C_4B_8H_8$, even though four phenyl groups and more room are available in that compound [14]. The successful preparation of **5** shows that a molecule consisting of crowded parts can be stabilized by proper arrangement of each fragment.

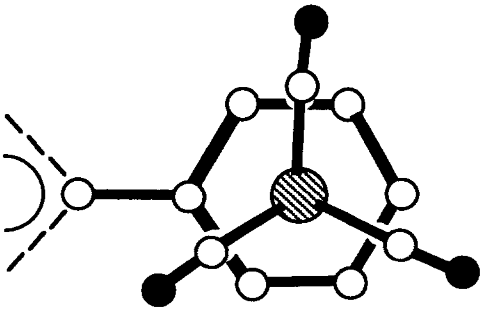

Fig. 4. Top view of (arene)$Cr(CO)_3$ of **5**.

3. Experimental section

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. ^{1}H 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. Mass spectra were recorded on Jeol JMS-SX/SX 102A GC/MS/MS.

3.1. Preparation of (η^5-C_5H_5)(PPh_3)Co(C_4Ph_4)

The synthesis of the title compound was based on the procedure in the literature [15].

3.2. Preparation of 1, (η^5-C_5H_5)Co(C_4Ph_4)

Reflux of (η^5-C_5H_5)(PPh_3)Co(C_4Ph_4) in toluene for 12 h leads to a quantitative yield of the title compound.

3.3. Reaction of (η^5-C_5H_5)Co(C_4Ph_4) with $Cr(CO)_6$

Into a 250 ml round-bottom flask equipped with a condenser and a magnetic stirrer were placed 0.65 g (0.88 mmol) of complex **3** (**3′** and **3″**) and 1.94 g (8.8 mmol) of chromium hexacarbonyl. Anhydrous dibutyl ether (100 ml) and 10 ml of anhydrous tetrahydrofuran (THF) were added and the reaction mixture was refluxed under dry N_2 for 24 h. The reactor was cooled to room temperature and filtered through Celite and the solvent removed *in vacuo*.

The residue was dissolved in a small amount of THF/hexane mixture solvent and then was loaded to CTLC for separation. Three bands were collected through the elution of mixture solvents. The ratio of mixture solvent (THF/hexanes) changed from 1:8 to 1:2 as the separation went. The first orange band, R_f (0.42) in 1:2 of THF/hexanes, was identified as a small amount of unreacted **1**. **4**, orange and R_f (0.31), was collected as the second band. **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** are 48.63% (0.38 g) and 26.63% (0.24 g), respectively.

5. ^{1}H NMR ($CDCl_3$): δ 5.21 (s, 5H, Cp), 5.42 (m, 12H, m,*p*-arene), 5.80 (m, 8H, *o*-arene). ^{13}C NMR ($CDCl_3$): δ 75.266 (4C, cyclobutadiene), 84.475 (5C, Cp), 93.240 (8C, *m*-(arene)$Cr(CO)_3$), 93.928(4C, *p*-(arene)$Cr(CO)_3$), 96.143 (8C, *o*-(arene)$Cr(CO)_3$), 105.630 (4C, *ipso*-(arene)$Cr(CO)_3$), 233.557 (12C, CO). IR (CH_2Cl_2): $\nu_{(CO)}$ 1972, 1896 cm^{-1}. Mass spectrum: m/z 1024 (P^+).

TABLE 2. Crystal data of **5**

Formula	$C_{45}H_{20}Co_1Cr_4O_{12}$
Formula weight	1019.5
Crystal system	tetragonal
Space group	$P4/n$
a(Å)	15.019(2) Å
c(Å)	8.492(2) Å
V(Å^3)	1915.5(7) Å^3
Z	2
D_c(g cm^{-3})	1.768
λ(Mo Kα), Å	0.71073
μ(mm^{-1})	1.592
Range, deg	3.0 to 60.0°
Scan type	$\theta/2\theta$
No. reflections collctd	5996
No. independent reflctns	2810 (R_{int} = 0.90%)
No. obsd reflections	2241 ($I > 3.0\ \sigma(I)$)
No. refined parameters	143
R_f [a] for significant reflectns	0.0362
R_w [b] for sigft reflctns	0.0357
GoF [c]	1.14

[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] GoF $= [\Sigma w(F_o - F_c)^2/(N_{rflns} - N_{params})]^{1/2}$.

3.4. Crystal structure determination of 5

An orange crystal of **5** of size $0.2 \times 0.3 \times 0.3$ mm^3 was used for X-ray diffraction measurements. The intensities were collected on a Siemens R3m/V diffractometer equipped with graphite-monochromated Mo Kα 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 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 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 Micro VAX 3100 computer.

The crystallographic data of complex **5** are summarized in Table 2.

Supplementary material available

Tables of atomic coordinates (Table 3) and thermal parameters, bond lengths and angles, anisotropic thermal parameters, and H atom coordinates for **5**.

Acknowledgment

We thank the National Research Council of Taiwan (Grant NSC-83-0208-M-005-031) for support.

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

	x	y	z	U_{eq}
Co(1)	2500	2500	322(1)	24(1)
Cr(1)	1730(1)	−386(1)	2532(1)	25(1)
O(1)	1057(2)	80(2)	−653(3)	79(1)
O(2)	−171(1)	−521(2)	3568(3)	65(1)
O(3)	1432(2)	−2273(1)	1595(3)	70(1)
C(1)	1325(2)	−80(2)	577(3)	43(1)
C(2)	556(1)	−438(2)	3194(3)	40(1)
C(3)	1568(2)	−1551(1)	1934(3)	40(1)
C(4)	2078(1)	661(1)	4272(2)	28(1)
C(5)	2206(1)	−186(1)	4960(2)	35(1)
C(6)	2755(1)	−803(1)	4236(3)	39(1)
C(7)	3176(1)	−599(1)	2796(3)	39(1)
C(8)	3053(1)	238(1)	2100(3)	31(1)
C(9)	2512(1)	886(1)	2852(2)	23(1)
C(10)	2484(1)	1811(1)	2317(2)	21(1)
C(11)	2710(9)	1668(4)	−1594(6)	23(1)
C(12)	1929(6)	1987(5)	−1694(4)	36(1)
C(13)	3274(5)	2292(8)	−1663(5)	50(1)

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

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8 The yield of **5** was less than 1%.

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

11 $\delta d = 0.047$ Å.

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