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Synthesis and structure of mono- and bis(tricarbonylchromium)complexes of 1,2;5,6-dibenzocycloocta-1,5-diene

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Abstract

The mono- and bis(tricarbonylchromium)complexes of 1,2;5,6-dibenzocycloocta-1,5-diene (**1**) have been synthesized. Crystal structures of mono(tricarbonylchromium) complex of **1** (**2**) ($C_{19}H_{16}CrO_3$, $C2/m$, $a = 11.838$, $b = 11.904$, $c = 12.379$ Å, $\alpha = 90.0$, $\beta = 113.36$, $\gamma = 90.0°$, $Z = 4$) and *cis*-bis(tricarbonylchromium) complex of **1** (**3**) ($C_{22}H_{16}Cr_2O_6$, $P2_1/c$, $a = 12.556$, $b = 11.353$, $c = 14.127$ Å, $\alpha = 90.0$, $\beta = 101.38$, $\gamma = 90.0°$, $Z = 4$) have been determined by X-ray analysis. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Tricarbonylchromium complexes; Conformation analysis; 1,2;5,6-Dibenzocycloocta-1,5-diene; Crystal structure; Stereoisomers

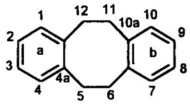
1. Introduction

There are usually three general methods for preparation of arenechromium complexes on practical scale: (1) thermal reaction of $Cr(CO)_6$ with arene, which involves heating $Cr(CO)_6$ with arene in mixture of refluxing di-*n*-butyl ether and tetrahydrofuran (THF) (9:1 v/v), is now established as the best way to prepare $[Cr(CO)_3(\eta^6\text{-arene})]$ complexes routinely [1]; (2) thermal reaction of $[Cr(CO)_3L_3]$ species with arene, in which replacement of three carbonyls of $[Cr(CO)_6]$ by more labile ligands enables subsequent thermal reactions with arenes to be carried out at lower temperatures. Particular attention has been given to those complexes where L = MeCN, py or NH_3 [2]; (3) arene exchange reactions, treating (naphthalene) $Cr(CO)_3$ complex with different arenes leads, in some cases, to arene exchange reactions, a procedure which goes under mild conditions [3,4].

Mono- and bis(tricarbonylchromium) complexes of 1,2;5,6-dibenzocycloocta-1,5-diene are of interest owing to their spectroscopic and structural properties. While **2** has been prepared many years ago with a poor yield of only 1% [5], the complexes **3** and **4** are not yet described. We describe here synthesis of **2**, **3**, **4**[1] with high yield in more convenient condition, and X-ray structures of **2** and **3**.

2. Results and discussion

1,2;5,6-dibenzocycloocta-1,5-diene (**1**) was prepared by the Wurtz reaction between α,α′-dibromo-*o*-xylene and sodium in dioxane [6].



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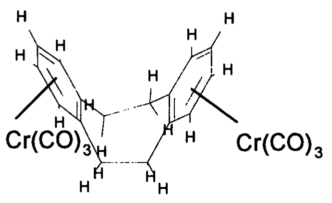

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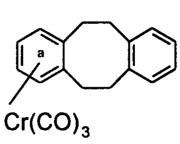

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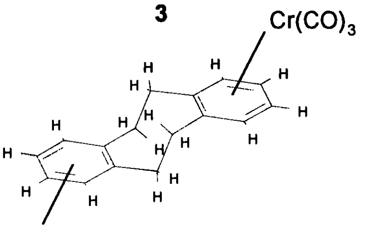

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[1] The chair conformation of *trans* isomer was determined by molecular mechanics calculation using the Hyper Chem package.

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Table 1
^{1}H-NMR data (δ in ppm, T 298 K) of compounds **1**, **2**, **3** and **4**

Compound	Solvent	^{1}H-NMR data
1	$CDCl_3$	CH_2: 2.92 (s); C_6H_4: 6.9 (s)
2	DMSO-d_6	CH_2CH_2: ABCD 2.64–2.74 (m, 2H), 2.78–2.88 (m, 2H), 2.97–3.08 (m, 2H), 3.22-3.31 (m, 2H); C_6H_4 (a): AA′BB′ 5.4–5.45 (m, 2H), 5.47–5.52 (m, 2H); C_6H_4 (b): 7 (s, 4H)
3	DMSO-d_6	CH_2CH_2: 2.63–2.71 (dd, 4H), 3.1–3.23 (dd,4H); C_6H_4: 5.43–5.55 (m, 8H)
4	DMSO-d_6	CH_2CH_2: 2.8–2.91 (br. d, 4H), 2.35–2.5 (br. d, 4H); C_6H_4: AA′BB′ 5.62–5.71 (m, 4H), 5.71–5.79 (m, 4H)

Table 2
^{13}C-NMR data (δ in ppm, T 298 K) of compounds **1**, **2**, **3** and **4**

Compound	Solvent	C_1	C_2	C_{4a}	C_5	C_6	C_{6a}	C_7	C_8	CO
1	$CDCl_3$	129.7	126.1	140.6	35.2					
2	DMSO-d_6	96.6	93.5	113.1	32.6	33.2	139	129.6	126.2	234.3
3	DMSO-d_6	96.9	93.8	111.8	31.3	234.1				
4	DMSO-d_6	96.8	94.0	113.9	34.6	234				

Mono-(tricarbonylchromium) complex **2** and the two stereoisomers of bis-(tricarbonylchromium) complexes [**3** (*cis*-isomer) and **4** (*trans*-isomer)] were synthesized by treating **1** with hexacarbonylchromium. Heating **1** with equimolecular amount of $Cr(CO)_6$ in di-*n*-butylether and tetrahydrofuran (THF) (9:1 v/v) at reflux temperature afforded 72% of complex **2** and 14% the mixture of **3** and **4,** which were separated on a column of alumina. The two isomers **3** and **4** were also separated by HPLC technique. The ^{1}H-NMR spectral parameters of the free ligand **1**, and of the three complexed compounds **2**, **3** and **4** are listed in Table 1 and the ^{13}C-NMR chemical shifts are given in Table 2.

The molecular structures of **2** and **3** are shown in Figs. 1 and 2, and relevant molecular features of all three complexes are discussed below.

2.1. Complex 2

The complexation of **1** at the benzo ring with the $Cr(CO)_3$ group causes a large upfield shift of these aromatic proton resonances (ca. 1.5 ppm) and a smaller upfield shift of the benzylic proton resonances (Table 1). Moreover, in the complexed aromatic ring, hydrogen bearing carbon atoms and junction carbon atoms exhibit an upfield shift of ca. 33 and 27 ppm, respectively (Table 2). These effects are commonly observed when aromatic substrates are complexed with tricarbonylchromium [7].

Fig. 1 shows the structure and the atomic numbering scheme used for the complex **2**. In contrast to the conformation of the free ligand **1**, which is chair in solid-state [6], the conformation of **2**, as determined by X-ray analysis, is almost boat. This complex shows the expected structure for $[Cr(arene)(CO)_3]$ [8] with a tripodal $Cr(CO)_3$ fragment coordinated in a η^6 mode to the arene. However, the $Cr(CO)_3$ is distorted away from the center of the arene ring by the substituents. This presumably arises from slight steric repulsion, which is also deduced by the fact that the substituents lie out of the least squares plane defined by the arene and on the opposite side to the Cr-atom.

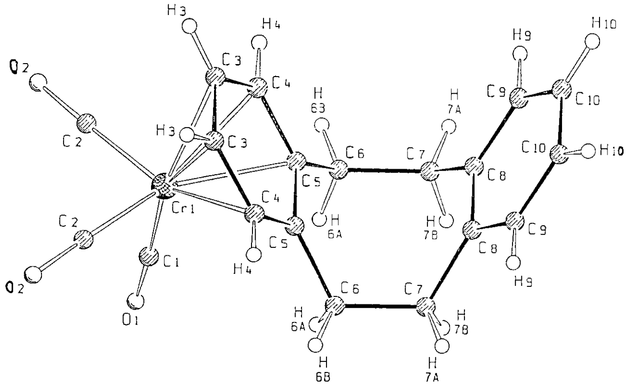

Fig. 1. Molecular structure of mono-tricarbonylchromium complex (**2**).

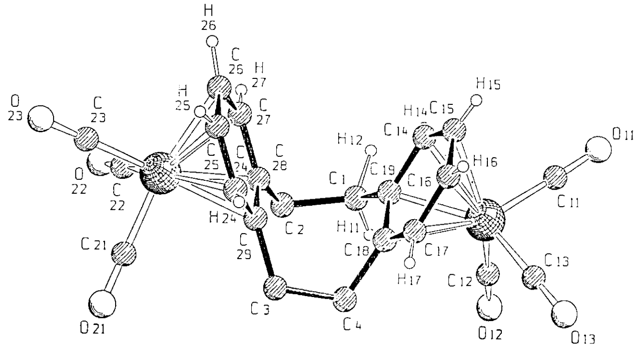

Fig. 2. Molecular structure of *cis*-bis tricarbonylchromium complex (**3**).

Table 3

Crystal data and conditions for crystallographic data collection and structure refinement for $C_{19}H_{16}CrO_3$ and $C_{22}H_{16}Cr_2O_6$

Empirical formula	$C_{19}H_{16}CrO_3$ (**2**)	$C_{22}H_{16}Cr_2O_6$ (**3**)
Formula weight (g mol^{-1})	344.32	480.35
Color	Yellow, transparent	Yellow, transparent
Crystal system	Monoclinic	Monoclinic
Space group	$C2/m$ (No. 12)	$P2_1/c$ (No. 14)
Unit cell dimensions		
a (Å)	11.838(2)	12.559(1)
b (Å)	11.904(2)	11.353(1)
c (Å)	12.379(2)	14.127(1)
α (°)	90.0	90.0
β (°)	113.36(1)	101.38(1)
γ (°)	90.0	90.0
Crystal dimensions (mm)	$0.30 \times 0.27 \times 0.23$	$0.19 \times 0.27 \times 0.30$
V (Å^3)	1601.6(2)	1974.7(3)
Formula units per unit cell, Z	4	4
D_{calc} (g cm^{-3})	1.428	1.616
Linear absorption coefficient (cm^{-1})	7.26	11.38
Diffractometer	Four circle diffractometer AED2 (STOE)	Four circle diffractometer AED2 (STOE)
Radiation	Mo–K$_\alpha$ ($\lambda = 0.71069$ Å)	Mo–K$_\alpha$ ($\lambda = 0.71069$ Å)
Monochromator	Graphite	Graphite
Scan range	$1.79 \leq 2\theta \leq 29.98°$; $-16 \leq h \leq 16$, $-16 \leq k \leq 16$, $-17 \leq l \leq 17$	$1.65 \leq 2\theta \leq 32.00°$; $-18 \leq h \leq 18$, $-16 \leq k \leq 16$, $0 \leq l \leq 21$
Reflections measured	9340	13860
Independent reflections	2444	6850
R_{int}	0.035	0.078
Independent reflections with $F_o > 4\sigma(F_o)$	1954	3395
Applied corrections	Lorentz- and polarization oefficients	Lorentz- and polarization coefficients
Structure determination and refinement	Cr positional parameter from direct methods (program SHELXS-86 [a]-further atoms from ΔF-synthesis (program SHELXL-93 [b], structure refinement by the anisotropic full-matrix least-squares procedure for all non-hydrogen atoms; H atoms refined using a riding model; Atomic scattering factors from [c]	Cr positional parameter from direct methods (program SHELXS-86 [a]-further atoms from ΔF-synthesis (program SHELXL-93 [b], structure refinement by the anisotropic full-matrix least-squares procedure for all non-hydrogen atoms; H atoms refined using a riding model; Atomic scattering factors from [c]
Number of parameters	110	273
$R(F^2)$	0.163	0.178
$R(\|F\|)$	0.0665 for all 2444 reflections	0.157 for all 6850 reflections
$R(\|F\|)$	0.0513 for 1954 reflections with $F_o > 4\sigma(F_o)$	0.0603 for 3395 reflections with $F_o > 4\sigma(F_o)$

[a] See Ref. [10].

[b] See Ref. [11].

[c] See Ref. [12].

Table 4
Bond lengths (Å) for compound $C_{19}H_{16}CrO_3$

Cr(1)–C(1)	1.799(4)	C(3)–C(4)	1.403(4)
Cr(1)–C(2) # 1	1.824(3)	C(4)–C(5)	1.398(3)
Cr(1)–C(2)	1.824(3)	C(5)–C(5) # 1	1.429(4)
Cr(1)–C(3)	2.196(2)	C(5)–C(6)	1.508(3)
Cr(1)–C(3) # 1	2.196(2)	C(6)–C(7)	1.484(4)
Cr(1)–C(4)	2.211(2)	C(7)–C(8)	1.507(4)
Cr(1)–C(4) # 1	2.211(2)	C(8)–C(9) # 2	1.377(4)
Cr(1)–C(5)	2.249(2)	C(8)–C(8) # 1	1.395(6)
Cr(1)–C(5) # 1	2.249(2)	C(9)–C(10) # 3	1.363(5)
C(1)–O(1)	1.139(6)	C(9)–C(8) # 4	1.377(4)
C(2)–O(2)	1.158(4)	C(10)–C(9) # 3	1.362(5)
C(3)–C(3) # 1	1.370(6)	C(10)–C(10) # 1	1.390(7)

This compound shows the *syn* staggered conformation in which one of the CO groups lies in between and below the two substituted C-atoms of the complexed arene ring. The C–C bond distances are slightly different from those in the free ligand, and C–C bond length alternation is observed in the complexed benzo ring. Crystal data and conditions for crystallographic, data collection and structure refinement for complex **2** are given in Table 3. Selected bond distances and angles for this compound are listed in Tables 4 and 5, respectively.

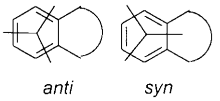

Fig. 3. *anti*- and *syn*-staggered conformation of *ortho*-disubstituted [Cr(arene)$(CO)_3$] complexes.

2.2. Complex 3

The $Cr(CO)_3$ groups have almost the same effects on ^{13}C- and ^1H-NMR chemical shifts of these compounds.

Complex **3** shows the boat conformation in solid-state with the $Cr(CO)_3$ tripods coordinated in a η^6 mode to the arene rings. However, as mentioned for complex **2**, both of the $Cr(CO)_3$ groups are somewhat distorted away from the centers of the arene rings by the repulsion effect of substituents. One of the $Cr(CO)_3$ tripods has the staggered *syn*-conformation [Cr(**2**)$(CO)_3$] while the other has *anti*-conformation [Cr(**1**) $(CO)_3$]. In the *anti*-conformation, the symmetry-unique carbonyl ligand is pointed away from the substituents, but in the *syn*-conformation it is bisecting the disubstituted, fused, C–C bond (Fig. 3).

In this complex the C–C bond distances are slightly different from those in the free ligand, and no C–C bond alternation is observed in the benzo rings. Crystal data and conditions for crystallographic, data collec-

Table 5
Bond angles (°) for compound $C_{19}H_{16}CrO_3$ [a]

C(1)–Cr(1)–C(2) # 1	87.1(2)	C(3) # 1–Cr(1)–C(4) # 1	37.13(11)
C(1)–Cr(1)–C(2)	87.1(2)	C(4)–Cr(1)–C(4) # 1	76.94(13)
C(2) # 1–Cr(1)–C(2)	89.6(2)	C(1)–Cr(1)–C(5) # 1	93.6(2)
C(1)–Cr(1)–C(3)	156.50(13)	C(2) # 1–Cr(1)–C(5) # 1	116.69(11)
C(2) # 1–Cr(1)–C(3)	116.23(14)	C(2)–Cr(1)–C(5) # 1	153.74(11)
C(2)–Cr(1)–C(3)	90.15(13)	C(3)–Cr(1)–C(5) # 1	78.87(9)
C(1)–Cr(1)–C(3) # 1	156.50(13)	C(3) # 1–Cr(1)–C(5) # 1	66.97(9)
C(2) # 1–Cr(1)–C(3) # 1	90.15(13)	C(4)–Cr(1)–C(5) # 1	65.89(8)
C(2)–Cr(1)–C(3) # 1	116.23(14)	C(4) # 1–Cr(1)–C(5) # 1	36.51(9)
C(3)–Cr(1)–C(3) # 1	36.3(2)	C(1)–Cr(1)–C(5)	93.6(2)
C(1)–Cr(1)–C(4)	119.54(13)	C(2) # 1–Cr(1)–C(5)	153.74(11)
C(2) # 1–Cr(1)–C(4)	153.34(14)	C(2)–Cr(1)–C(5)	116.69(11)
C(2)–Cr(1)–C(4)	90.99(11)	C(3)–Cr(1)–C(5)	66.97(9)
C(3)–Cr(1)–C(4)	37.13(11)	C(3) # 1–Cr(1)–C(5)	78.87(9)
C(3) # 1–Cr(1)–C(4)	65.84(11)	C(4)–Cr(1)–C(5)	36.51(9)
C(1)–Cr(1)–C(4) # 1	119.54(13)	C(4) # 1–Cr(1)–C(5)	65.89(8)
C(2) # 1–Cr(1)–C(4) # 1	90.99(11)	C(5) # 1–Cr(1)–C(5)	37.06(11)
C(2)–Cr(1)–C(4) # 1	153.34(14)	O(1)–C(1)–Cr(1)	177.3(5)
C(3)–Cr(1)–C(4) # 1	65.84(11)	O(2)–C(2)–Cr(1)	178.7(3)
C(3) # 1–C(3)–C(4)	119.5(2)	C(4)–C(5)–Cr(1)	70.29(12)
C(3) # 1–C(3)–Cr(1)	71.83(9)	C(5) # 1–C(5)–Cr(1)	71.47(5)
C(4)–C(3)–Cr(1)	72.05(14)	C(6)–C(5)–Cr(1)	130.2(2)
C(5)–C(4)–C(3)	122.2(2)	C(7)–C(6)–C(5)	117.3(2)
C(5)–C(4)–Cr(1)	73.20(13)	C(6)–C(7)–C(8)	119.5(2)
C(3)–C(4)–Cr(1)	70.83(14)	C(9) # 2–C(8)–C(8) # 1	118.2(2)
C(4)–C(5)–C(5) # 1	118.23(14)	C(9) # 2–C(8)–C(7)	119.4(3)
C(4)–C(5)–C(6)	120.3(2)	C(8) # 1–C(8)–C(7)	122.4(2)
C(5) # 1–C(5)–C(6)	121.4(2)	C(10) # 3–C(9)–C(8) # 4	123.2(3)

[a] Symmetry transformations used to generate equivalent atoms: # 1 x, $-y$, z; # 2 $x+1/2$, $y+1/2$, z; # 3 $-x+1/2$, $-y-1/2$, $-z+1$; # 4 $x-1/2$, $y-1/2$, z.

tion and structure refinement for complex **3** are given in Table 3. Selected bond distances and angles for this compound are listed in Tables 6 and 7, respectively.

3. Experimental

All manipulations involving chromium complexes were performed under atmosphere of purified argon and using gas/vacuum double manifold and standard Schlenk technique [9]. THF and Bu_2O were distilled from sodium/benzophenone ketyl immediately prior to use. $Cr(CO)_6$ was purchased from Aldrich and sublimed prior to use. Elemental analyses: Carlo-Erba Modell 1104; IR: Bruker IFS 25. ^1H-and ^{13}C-NMR: Bruker AM-400, Bruker AC-200. MS: Varian MAT 311A, Varian MAT 111; melting points: Büchi SMP-20.

3.1. Synthesis of complexes **2**, **3** and **4**

A mixture of 1,2;5,6-dibenzocycloocta-1,5-diene (**1**) (836 mg, 4 mmol) and freshly sublimed $Cr(CO)_6$ (968 mg, 4.4 mmol) in dibutyl ether (27 ml) and THF (3 ml) was heated under reflux (bath temperature: 160°C) for 60 h. Volatiles were removed in vacuo and the crude yellow solid purified by column chromatography [Al_2O_3 Grade III, 1:1.5 dichloromethane–pentane and then dichloromethane]. Three fractions separated, fraction I was unreacted 1,2;5,6-dibenzocycloocta-1,5-diene (**1**) (14%), fraction II was complex **2** (72%), and fraction III that eluted with dichloromethane, was the mixture of the two stereoisomers **3** and **4** (14%). Crystallization of fraction II from dichloromethane–hexane gave the complex **2** as yellow crystals; m.p. 186°C; IR (THF):

Table 6
Bond lengths (Å) for compound $C_{22}H_{16}Cr_2O_6$

Cr(1)–C(12)	1.835(5)	Cr(2)–C(21)	1.840(4)
Cr(1)–C(13)	1.840(5)	Cr(2)–C(22)	1.852(5)
Cr(1)–C(11)	1.854(5)	Cr(2)–C(27)	2.208(4)
Cr(1)–C(15)	2.192(5)	Cr(2)–C(25)	2.212(4)
Cr(1)–C(17)	2.205(5)	Cr(2)–C(24)	2.217(4)
Cr(1)–C(14)	2.203(4)	Cr(2)–C(26)	2.219(4)
Cr(1)–C(16)	2.225(5)	Cr(2)–C(29)	2.230(4)
Cr(1)–C(18)	2.231(4)	Cr(2)–C(28)	2.240(4)
Cr(1)–C(19)	2.239(4)	C(21)–O(21)	1.132(5)
C(11)–O(11)	1.143(5)	C(22)–O(22)	1.140(5)
C(12)–O(12)	1.141(5)	C(23)–O(23)	1.155(5)
C(13)–O(13)	1.137(5)	C(24)–C(25)	1.392(6)
C(14)–C(19)	1.411(6)	C(24)–C(29)	1.416(6)
C(14)–C(15)	1.431(8)	C(25)–C(26)	1.392(7)
C(15)–C(16)	1.368(8)	C(26)–C(27)	1.390(6)
C(16)–C(17)	1.362(8)	C(27)–C(28)	1.415(5)
C(17)–C(18)	1.379(6)	C(28)–C(29)	1.422(5)
C(18)–C(19)	1.414(5)	C(28)–C(2)	1.492(6)
C(18)–C(4)	1.515(6)	C(29)–C(3)	1.508(6)
C(19)–C(1)	1.503(6)	C(1)–C(2)	1.555(6)
Cr(2)–C(23)	1.835(5)	C(3)–C(4)	1.546(6)

Table 7
Bond angles (°) for compound $C_{22}H_{16}Cr_2O_6$

C(4)–C(18)–Cr(1)	132.0(3)	C(25)–Cr(2)–C(26)	36.6(2)
C(18)–C(19)–C(14)	117.6(4)	C(24)–Cr(2)–C(26)	65.9(2)
C(18)–C(19)–C(1)	123.0(4)	C(23)–Cr(2)–C(29)	148.5(2)
C(14)–C(19)–C(1)	119.4(4)	C(21)–Cr(2)–C(29)	88.7(2)
C(18)–C(19)–Cr(1)	71.3(2)	C(22)–Cr(2)–C(29)	122.2(2)
C(14)–C(19)–Cr(1)	70.1(2)	C(27)–Cr(2)–C(29)	66.4(2)
C(1)–C(19)–Cr(1)	131.4(3)	C(25)–Cr(2)–C(29)	66.8(2)
C(23)–Cr(2)–C(21)	88.6(2)	C(24)–Cr(2)–C(29)	37.1(2)
C(23)–Cr(2)–C(22)	89.1(2)	C(26)–Cr(2)–C(29)	78.9(2)
C(21)–Cr(2)–C(22)	88.5(2)	C(23)–Cr(2)–C(28)	160.2(2)
C(23)–Cr(2)–C(27)	123.3(2)	C(21)–Cr(2)–C(28)	111.2(2)
C(21)–Cr(2)–C(27)	147.8(2)	C(22)–Cr(2)–C(28)	92.5(2)
C(22)–Cr(2)–C(27)	88.3(2)	C(27)–Cr(2)–C(28)	37.09(14)
C(23)–Cr(2)–C(25)	89.2(2)	C(25)–Cr(2)–C(28)	78.9(2)
C(21)–Cr(2)–C(25)	124.2(2)	C(24)–Cr(2)–C(28)	66.53(14)
C(22)–Cr(2)–C(25)	147.2(2)	C(26)–Cr(2)–C(28)	66.9(2)
C(27)–Cr(2)–C(25)	65.7(2)	C(29)–Cr(2)–C(28)	37.09(13)
C(23)–Cr(2)–C(24)	112.1(2)	O(21)–C(21)–Cr(2)	178.8(4)
C(21)–Cr(2)–C(24)	95.1(2)	O(22)–C(22)–Cr(2)	178.7(4)
C(22)–Cr(2)–C(24)	158.6(2)	O(23)–C(23)–Cr(2)	179.1(5)
C(27)–Cr(2)–C(24)	77.5(2)	C(25)–C(24)–C(29)	121.2(4)
C(25)–Cr(2)–C(24)	36.6(2)	C(25)–C(24)–Cr(2)	71.5(2)
C(23)–Cr(2)–C(26)	94.1(2)	C(29)–C(24)–Cr(2)	71.9(2)
C(21)–Cr(2)–C(26)	160.4(2)	C(24)–C(25)–C(26)	120.3(4)
C(22)–Cr(2)–C(26)	111.0(2)	C(24)–C(25)–Cr(2)	71.9(2)
C(27)–Cr(2)–C(26)	36.6(2)	C(26)–C(25)–Cr(2)	72.0(3)
C(27)–C(26)–C(25)	119.1(4)	C(11)–Cr(1)–C(16)	111.8(2)
C(27)–C(26)–Cr(2)	71.3(2)	C(15)–Cr(1)–C(16)	36.1(2)
C(25)–C(26)–Cr(2)	71.4(2)	C(17)–Cr(1)–C(16)	35.8(2)
C(26)–C(27)–C(28)	122.5(4)	C(14)–Cr(1)–C(16)	66.5(2)
C(26)–C(27)–Cr(2)	72.1(2)	C(12)–Cr(1)–C(18)	93.7(2)
C(28)–C(27)–Cr(2)	72.7(2)	C(13)–Cr(1)–C(18)	110.9(2)
C(27)–C(28)–C(29)	117.9(4)	C(11)–Cr(1)–C(18)	158.4(2)
C(27)–C(28)–C(2)	120.5(4)	C(15)–Cr(1)–C(18)	77.8(2)
C(29)–C(28)–C(2)	121.5(4)	C(17)–Cr(1)–C(18)	36.2(2)
C(27)–C(28)–Cr(2)	70.2(2)	C(14)–Cr(1)–C(18)	66.0(2)
C(29)–C(28)–Cr(2)	71.1(2)	C(16)–Cr(1)–C(18)	65.2(2)
C(2)–C(28)–Cr(2)	132.9(3)	C(12)–Cr(1)–C(19)	88.4(2)
C(24)–C(29)–C(28)	119.0(4)	C(13)–Cr(1)–C(19)	147.1(2)
C(24)–C(29)–C(3)	119.0(4)	C(11)–Cr(1)–C(19)	122.2(2)
C(28)–C(29)–C(3)	122.0(4)	C(15)–Cr(1)–C(19)	67.4(2)
C(24)–C(29)–Cr(2)	70.9(2)	C(17)–Cr(1)–C(19)	66.0(2)
C(28)–C(29)–Cr(2)	71.8(2)	C(14)–Cr(1)–C(19)	37.0(2)
C(3)–C(29)–Cr(2)	131.3(3)	C(16)–Cr(1)–C(19)	78.4(2)
C(19)–C(1)–C(2)	114.4(3)	C(18)–Cr(1)–C(19)	36.87(14)
C(28)–C(2)–C(1)	113.0(4)	O(11)–C(11)–Cr(1)	177.8(4)
C(29)–C(3)–C(4)	115.4(3)	O(12)–C(12)–Cr(1)	178.9(4)
C(18)–C(4)–C(3)	111.3(4)	O(13)–C(13)–Cr(1)	178.3(4)
C(12)–Cr(1)–C(13)	88.1(2)	C(19)–C(14)–C(15)	119.8(5)
C(12)–Cr(1)–C(11)	90.1(2)	C(19)–C(14)–Cr(1)	72.9(2)
C(13)–Cr(1)–C(11)	90.4(2)	C(15)–C(14)–Cr(1)	70.6(3)
C(12)–Cr(1)–C(15)	149.9(2)	C(16)–C(15)–C(14)	120.3(5)
C(13)–Cr(1)–C(15)	121.9(2)	C(16)–C(15)–Cr(1)	73.3(3)
C(11)–Cr(1)–C(15)	88.3(2)	C(14)–C(15)–Cr(1)	71.4(3)
C(12)–Cr(1)–C(17)	122.5(2)	C(17)–C(16)–C(15)	119.6(5)
C(13)–Cr(1)–C(17)	88.7(2)	C(17)–C(16)–Cr(1)	71.3(3)
C(11)–Cr(1)–C(17)	147.3(2)	C(15)–C(16)–Cr(1)	70.6(3)
C(15)–Cr(1)–C(17)	64.9(2)	C(16)–C(17)–C(18)	122.4(5)
C(12)–Cr(1)–C(14)	112.2(2)	C(16)–C(17)–Cr(1)	72.9(3)
C(13)–Cr(1)–C(14)	159.4(2)	C(18)–C(17)–Cr(1)	72.9(2)
C(11)–Cr(1)–C(14)	92.9(2)	C(17)–C(18)–C(19)	120.3(4)
C(15)–Cr(1)–C(14)	38.0(2)	C(17)–C(18)–C(4)	120.3(4)
C(17)–Cr(1)–C(14)	77.6(2)	C(19)–C(18)–C(4)	119.4(4)
C(12)–Cr(1)–C(16)	158.0(2)	C(17)–C(18)–Cr(1)	70.9(2)
C(13)–Cr(1)–C(16)	93.4(2)	C(19)–C(18)–Cr(1)	71.9(2)

$\nu_{\text{max.}}$ 1960 and 1885 cm^{-1} (CO). ^{1}H-NMR (400 MHz, DMSO-d_6): $\delta = 2.64$–2.74 (m, 2H), 2.78–2.83 (m, 2H), 2.97–3.08 (m, 2H), 3.22–3.31 (m, 2H), 5.4–5.45 (AA′BB′, 2H, ArH^a), 5.47–5.52 (AA′BB′, 2H, ArH^a), 7 (s, 4H, ArH^b) ppm. ^{13}C-NMR (50 MHz, DMSO-d_6): $\delta = 32.6$ (CH_2), 33.2 (CH_2), 93.5 (CH), 96.6 (CH), 113.1 (C), 126.2 (CH), 129.6 (CH), 139 (C), 234.3 (CO) ppm. MS (70 eV): m/z (%) = 344 (10) [M^+], 260 (100) [$M^+ - 3CO$], 208 (17.5) [$M^+ - Cr(CO)_3$], and 52 (81) [Cr^+]. CHN: Anal. Calc. for $C_{19}H_{16}CrO_3$: C, 66.28; H, 4.83. Found: C, 66.47; H, 4.53%.

Use of the general procedure with 450 mg (2.16 mmol) **1** and 1200 mg (5.4 mmol) of $Cr(CO)_6$ in 18 ml dibutyl ether and 2 ml THF for 60 h followed by chromatography as above yielded, as fraction I ($R_f = 0.6$), 250 mg (34%) of **2**, and as fraction II ($R_f = 0.13$), 685 mg (66%) the mixture of **3** and **4**. Crystallization of the mixture from dichloromethane–hexane gave the crystalline mixture of **3** (68%) and **4** (32%). Ratio of isomers are determined from ^{1}H-NMR spectrum. MS (70 eV): m/z (%) = 480 (5) [M^+], 396 (6) [$M^+ - 3CO$], 368 (1) [$M^+ - 4CO$], 344 (4) [$M^+ - Cr(CO)_3$], 260 (100) [$M^+ - 3CO$–Cr $(CO)_3$], 208 (40) [$M^+ - 2Cr(CO)_3$], 52 (78) [Cr^+]; CHN: Anal. Calc. for $C_{22}H_{16}Cr_2O_6$: C, 55.009; H, 3.35. Found: C, 55.00; H, 3.01%.

The mixture analyzed by HPLC [250 mm, 8 mm, Diol-phase 7 μm column; eluent: 1:4 dichloromethane–hexane]. The retention times for compounds observed at 250 nm were as follows: *trans*-isomer **4** 7.4 min, *cis*-isomer **3** 9.7 min.

*3.1.1. Trans-bis-(tricarbonylchromium) 1,2;5,6-dibenzo-cycloocta-1,5-diene (**4**)*

IR (THF): $\nu_{\text{max.}}$ 1959, 1888 cm^{-1} (CO). ^{1}H-NMR (400 MHz, DMSO-d_6): $\delta = 2.8$–2.91 (br. d, 4H), 2.35–2.5 (br.d, 4H), 5.62–5.71 (AA′BB′, 4H, ArH), 5.71–5.79 (AA′BB′, 4H, ArH) ppm. ^{13}C-NMR (100 MHz, DMSO-d_6): $\delta = 34.6$ (CH_2), 94.0 (CH), 96.8 (CH), 113.9 (C), 234 (CO) ppm.

*3.1.2. Cis-bis (tricarbonylchromium) 1,2;5,6-dibenzo-cycloocta-1,5-diene (**3**)*

IR (THF): $\nu_{\text{max.}}$ 1959, 1888 cm^{-1} (CO). ^{1}H-NMR (400 MHz, DMSO-d_6): $\delta = 2.63$–2.71 (dd, 4H), 3.1–3.23 (dd, 4H), 5.43–5.55 (m, 8H) ppm. ^{13}C-NMR (100 MHz, DMSO-d_6): $\delta = 31.3$ (CH_2), 93.8 (CH), 96.9 (CH), 111.8 (C), 234 (CO) ppm.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Center, CCDC no. 136536 for compound **2** and no. 136537 for compound **3**. Copies of this information may be obtained free of charge from the Director, CCDC, 12, Union Road, Cambridge CB2 1EZ (Fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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