X-ray structural study of the first bicluster π-arene complex $[\eta^6\text{-PhCo}_4(\text{CO})_9]_2\text{CH}_2$ and binuclear complex $[\eta^6\text{-PhCr}(\text{CO})_3]_2\text{CH}_2$

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It has been established by X-ray structural study that the bicluster cobalt π-arene complex of diphenylmethane $[\eta^6\text{-PhCo}_4(\text{CO})_9]_2\text{CH}_2$ and binuclear complex $[\eta^6\text{-PhCr}(\text{CO})_3]_2\text{CH}_2$ have an *s-trans-s-trans* conformation in their crystals.

Key words: arene π-complexes, cobalt clusters, diphenylmethane, X-ray structural study.

Previously, we have synthesized a series of arenenonacarbonyltetracobalt clusters, (arene)$\text{Co}_4(\text{CO})_9$, and investigated their chemical properties[1–3] and the structures of some of these compounds by X-ray structural study.[4,5] Recently, we have obtained a new π-arene bicluster complex, in which two tetrahedral $\text{Co}_4(\text{CO})_9$ groups are bonded to two arene rings of diphenylmethane.[6] A large series of chromium tricarbonyl derivatives of the $[\eta^6\text{-PhCr}(\text{CO})_3]_2\text{X}$ type (X = NH, CHOH, CH_2, CHPh, CO, C=CH_2, *etc.*) was known for mononuclear fragments coordinated to the arene nucleus.[7] The synthesis of bicluster complexes of this type is of interest not only for elucidating the effect of the nature of the bridging X group on the ability of the second arene ring to coordinate to the metal complex group but also owing to the fact that the presence of two of these groups may impose some requirements on the realization of a particular molecular conformation.

In this work, the structure of the first obtained bicluster complex of diphenylmethane, $[\eta^6\text{-PhCo}_4(\text{CO})_9]_2\text{CH}_2$, was investigated by X-ray structural study with the aim of establishing the conformation of the molecule. The structure of binuclear complex $[\eta^6\text{-PhCr}(\text{CO})_3]_2\text{CH}_2$, to which an *anti* conformation of type **A** was previously assigned (see below),[8,9] was also studied by the X-ray structural method.

Results and Discussion

The direct reaction of diphenylmethane with cobalt carbonyl affords only monocluster product **1** even after prolonged refluxing with excess carbonyl:

$$\text{Ph}_2\text{CH}_2 + \text{Co}_2(\text{CO})_8 \longrightarrow [\text{PhCo}_4(\text{CO})_9]\text{CH}_2\text{Ph}$$

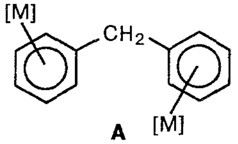
1

Complex **1** can be repeatedly introduced into the reaction with $\text{Co}_2(\text{CO})_8$, which makes it possible to obtain bicluster derivative **2** in 10 % yield[6]:

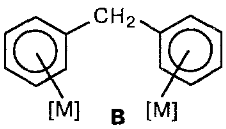
$$1 + \text{Co}_2(\text{CO})_8 \longrightarrow [\text{PhCo}_4(\text{CO})_9]_2\text{CH}_2.$$

2

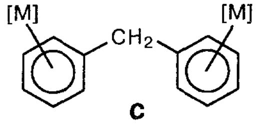
The ^{1}H NMR spectra of complex **2** (see Refs. 6 and 10) are indicative of the additive effect of both cluster groups on the protons of the bridging CH_2 group, whereas no mutual effect of arene protons on the chemical shift is observed. When complex **2** is frozen to −80 °C, the spectrum is unchanged, which, apparently, points either to retention of the free rotation about the CH_2—Ph bonds or retention of the stable initial conformation. When conformational possibilities of complex **2** are considered, at least three conformations (**A**, **B**, and **C**) should be taken into account, one of which (**A**) is an *anti* conformation, while the two others (**B** and **C**) are *syn* conformations:



A



B



C

We have to discard the terms *syn* and *anti* and to use the following nomenclature: *s-cis-s-trans* for the **A** conformer, *s-cis-s-cis* for the **B** conformer, and *s-trans-s-*

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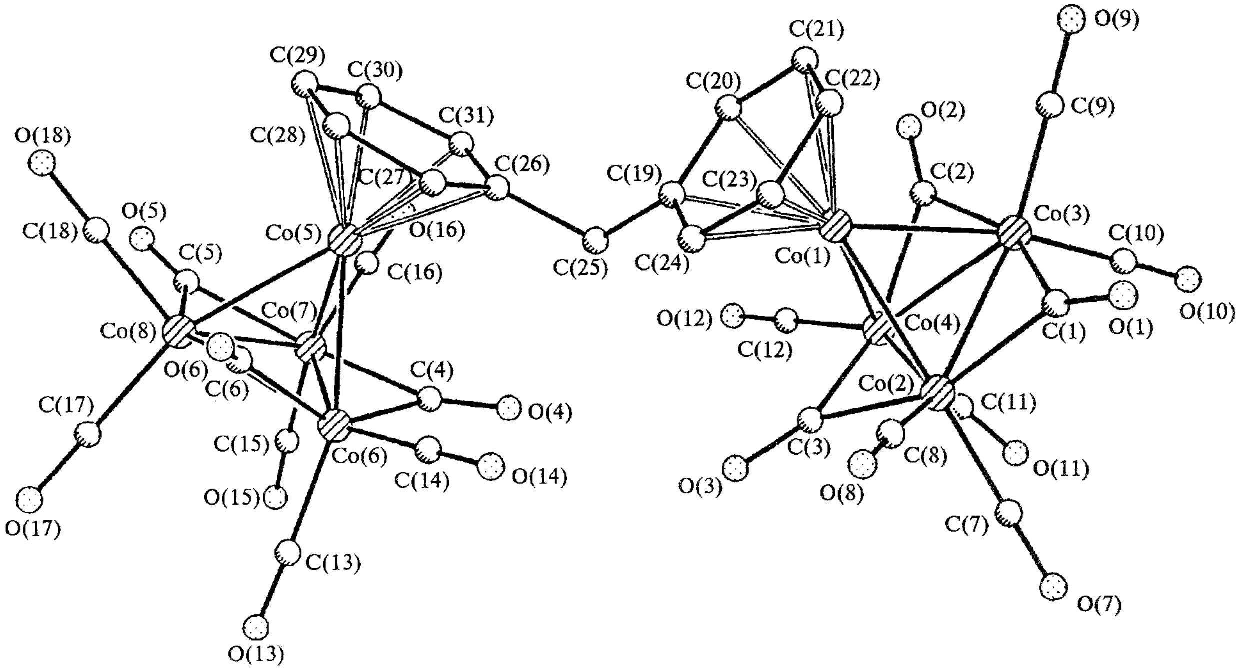

Fig. 1. Structure of molecule **2**.

trans for the **C** conformer (this nomenclature was used previously when NMR spectra of different derivatives of diphenylmethane were discussed[10]). In these cases, *s-cis* and *s-trans* notations mean the orientation of the metal-containing group with respect to the bond between the CH_2 group and the second benzene ring.

Table 1. Bond lengths (*d*) in the structure of **2**

Bond	*d*/Å		Bond	*d*/Å		Bond	*d*/Å	
	2a	**2b**		**2a**	**2b**		**2a**	**2b**
Co(1)—Co(2)	2.498(2)	2.493(2)	Co(5)—C(26)	2.171(8)	2.155(8)	O(7)—C(7)	1.134(10)	1.113(10)
Co(1)—Co(3)	2.483(2)	2.465(2)	Co(5)—C(27)	2.124(8)	2.132(8)	O(8)—C(8)	1.119(11)	1.141(11)
Co(1)—Co(4)	2.475(1)	2.480(1)	Co(5)—C(28)	2.156(8)	2.143(7)	O(9)—C(9)	1.135(11)	1.130(14)
Co(1)—C(19)	2.150(8)	2.149(8)	Co(5)—C(29)	2.146(8)	2.125(8)	O(10)—C(10)	1.139(11)	1.127(11)
Co(1)—C(20)	2.143(8)	2.125(8)	Co(5)—C(30)	2.113(9)	2.122(10)	O(11)—C(11)	1.139(9)	1.141(9)
Co(1)—C(21)	2.145(8)	2.122(9)	Co(5)—C(31)	2.147(9)	2.132(9)	O(12)—C(12)	1.154(12)	1.124(11)
Co(1)—C(22)	2.146(8)	2.149(8)	Co(6)—Co(7)	2.452(2)	2.452(2)	O(13)—C(13)	1.112(13)	1.113(12)
Co(1)—C(23)	2.146(8)	2.142(8)	Co(6)—Co(8)	2.443(2)	2.450(2)	O(14)—C(14)	1.152(14)	1.140(11)
Co(1)—C(24)	2.121(8)	2.128(8)	Co(6)—C(4)	1.932(8)	1.911(8)	O(15)—C(15)	1.143(10)	1.156(11)
Co(2)—Co(3)	2.478(2)	2.457(2)	Co(6)—C(6)	1.928(7)	1.944(7)	O(16)—C(16)	1.135(12)	1.116(11)
Co(2)—Co(4)	2.436(2)	2.453(2)	Co(6)—C(13)	1.816(11)	1.816(9)	O(17)—C(17)	1.146(14)	1.139(14)
Co(2)—C(1)	1.929(10)	1.914(10)	Co(6)—C(14)	1.757(11)	1.782(9)	O(18)—C(18)	1.136(11)	1.141(10)
Co(2)—C(3)	1.946(9)	1.937(9)	Co(7)—Co(8)	2.457(2)	2.463(2)	C(19)—C(20)	1.408(12)	1.407(12)
Co(2)—C(7)	1.807(8)	1.821(8)	Co(7)—C(4)	1.934(9)	1.966(8)	C(19)—C(24)	1.398(11)	1.421(11)
Co(2)—C(8)	1.790(9)	1.785(9)	Co(7)—C(5)	1.935(8)	1.905(8)	C(19)—C(25)	1.518(12)	1.507(14)
Co(3)—Co(4)	2.449(2)	2.449(2)	Co(7)—C(15)	1.796(8)	1.779(8)	C(20)—C(21)	1.412(13)	1.402(13)
Co(3)—C(1)	1.937(9)	1.941(9)	Co(7)—C(16)	1.794(10)	1.792(9)	C(21)—C(22)	1.435(13)	1.395(12)
Co(3)—C(2)	1.923(8)	1.908(9)	Co(8)—C(5)	1.935(8)	1.955(8)	C(22)—C(23)	1.408(15)	1.431(14)
Co(3)—C(9)	1.795(9)	1.784(11)	Co(8)—C(6)	1.908(9)	1.914(8)	C(23)—C(24)	1.410(13)	1.394(14)
Co(3)—C(10)	1.794(9)	1.810(9)	Co(8)—C(17)	1.799(11)	1.809(11)	C(25)—C(26)	1.493(11)	1.506(11)
Co(4)—C(2)	1.928(9)	1.946(10)	Co(8)—C(18)	1.781(8)	1.784(8)	C(26)—C(27)	1.429(10)	1.410(10)
Co(4)—C(3)	1.919(9)	1.935(9)	O(1)—C(1)	1.167(11)	1.168(11)	C(26)—C(31)	1.408(11)	1.400(11)
Co(4)—C(11)	1.802(8)	1.801(8)	O(2)—C(2)	1.172(10)	1.170(11)	C(27)—C(28)	1.418(11)	1.428(12)
Co(4)—C(12)	1.777(9)	1.798(9)	O(3)—C(3)	1.178(12)	1.162(12)	C(28)—C(29)	1.410(12)	1.410(13)
Co(5)—Co(6)	2.445(2)	2.473(2)	O(4)—C(4)	1.155(11)	1.150(10)	C(29)—C(30)	1.386(12)	1.400(12)
Co(5)—Co(7)	2.496(2)	2.471(1)	O(5)—C(5)	1.163(11)	1.162(10)	C(30)—C(31)	1.412(11)	1.412(12)
Co(5)—Co(8)	2.503(2)	2.470(2)	O(6)—C(6)	1.185(10)	1.178(9)			

Table 2. Bond angles (ω) in the structure of **2**

Angle	ω/deg	
	2a	**2b**
Co(2)—Co(1)—Co(3)	59.7(1)	59.4(1)
Co(2)—Co(1)—Co(4)	58.7(1)	59.1(1)
Co(3)—Co(1)—Co(4)	59.2(1)	59.4(1)
Co(2)—Co(1)—C(19)	133.1(2)	122.9(2)
Co(3)—Co(1)—C(19)	156.8(2)	165.8(2)
Co(4)—Co(1)—C(19)	107.7(2)	108.6(2)
Co(2)—Co(1)—C(20)	166.5(2)	154.7(2)
Co(3)—Co(1)—C(20)	124.2(2)	133.3(2)
Co(4)—Co(1)—C(20)	110.8(2)	105.5(2)
C(19)—Co(1)—C(20)	38.3(3)	38.4(3)
Co(2)—Co(1)—C(21)	154.8(3)	166.5(3)
Co(3)—Co(1)—C(21)	104.6(3)	109.5(3)
Co(4)—Co(1)—C(21)	133.3(2)	124.0(2)
C(19)—Co(1)—C(21)	69.3(3)	69.8(3)
C(20)—Co(1)—C(21)	38.4(3)	38.5(4)
Co(2)—Co(1)—C(22)	122.3(3)	133.3(2)
Co(3)—Co(1)—C(22)	106.9(3)	105.4(3)
Co(4)—Co(1)—C(22)	164.5(3)	155.1(3)
C(19)—Co(1)—C(22)	82.8(3)	82.9(3)
C(20)—Co(1)—C(22)	70.3(3)	69.4(3)
C(21)—Co(1)—C(22)	39.1(4)	38.1(3)
Co(2)—Co(1)—C(23)	104.4(2)	109.1(3)
Co(3)—Co(1)—C(23)	130.5(3)	123.9(3)
Co(4)—Co(1)—C(23)	155.7(3)	165.6(3)
C(19)—Co(1)—C(23)	69.7(3)	69.8(3)
C(20)—Co(1)—C(23)	82.6(3)	82.2(3)
C(21)—Co(1)—C(23)	69.7(3)	69.5(3)
C(22)—Co(1)—C(23)	38.3(4)	39.0(4)
Co(2)—Co(1)—C(24)	109.1(2)	105.0(2)
Co(3)—Co(1)—C(24)	164.9(2)	154.8(2)
Co(4)—Co(1)—C(24)	125.7(2)	132.8(2)
C(19)—Co(1)—C(24)	38.2(3)	38.8(3)
C(20)—Co(1)—C(24)	69.2(3)	69.5(3)
C(21)—Co(1)—C(24)	82.0(3)	82.3(3)
C(22)—Co(1)—C(24)	69.5(4)	69.7(4)
C(23)—Co(1)—C(24)	38.6(3)	38.1(4)
Co(1)—Co(2)—Co(3)	59.9(1)	59.7(1)
Co(1)—Co(2)—Co(4)	60.2(1)	60.2(1)
Co(3)—Co(2)—Co(4)	59.8(1)	59.8(1)
Co(1)—Co(2)—C(1)	86.3(2)	78.8(2)
Co(3)—Co(2)—C(1)	50.3(3)	50.9(3)
Co(4)—Co(2)—C(1)	110.0(3)	110.3(3)
Co(1)—Co(2)—C(3)	71.0(2)	78.1(2)
Co(3)—Co(2)—C(3)	107.7(3)	109.8(3)
Co(4)—Co(2)—C(3)	50.4(3)	50.7(3)
C(1)—Co(2)—C(3)	155.3(4)	155.7(4)
Co(1)—Co(2)—C(7)	165.4(3)	163.7(3)
Co(3)—Co(2)—C(7)	114.0(3)	105.9(3)
Co(4)—Co(2)—C(7)	105.2(3)	107.1(3)
C(1)—Co(2)—C(7)	99.5(4)	98.2(4)
C(3)—Co(2)—C(7)	100.5(4)	102.1(4)
Co(1)—Co(2)—C(8)	95.5(3)	97.1(3)
Co(3)—Co(2)—C(8)	135.5(3)	140.2(3)
Co(4)—Co(2)—C(8)	142.1(3)	139.4(3)
C(1)—Co(2)—C(8)	95.5(4)	95.7(4)
C(3)—Co(2)—C(8)	96.1(4)	94.3(4)
C(7)—Co(2)—C(8)	97.3(4)	99.1(4)
Co(1)—Co(3)—Co(2)	60.5(1)	60.9(1)
Co(1)—Co(3)—Co(4)	60.2(1)	60.6(1)
Co(2)—Co(3)—Co(4)	59.2(1)	60.0(1)
Co(1)—Co(3)—C(1)	86.6(3)	79.0(3)
C(2)—Co(4)—C(11)	107.0(4)	104.5(4)
C(3)—Co(4)—C(11)	106.1(4)	102.6(4)
Co(1)—Co(4)—C(12)	109.6(3)	101.7(2)
Co(2)—Co(4)—C(12)	147.9(3)	144.9(3)
Co(3)—Co(4)—C(12)	145.0(3)	140.5(3)
C(2)—Co(4)—C(12)	94.7(4)	92.1(4)
C(3)—Co(4)—C(12)	96.7(4)	98.2(4)
C(11)—Co(4)—C(12)	99.0(4)	100.2(4)
Co(6)—Co(5)—Co(7)	59.5(1)	59.5(1)
Co(6)—Co(5)—Co(8)	59.2(1)	59.4(1)
Co(7)—Co(5)—Co(8)	58.9(1)	59.8(1)
Co(6)—Co(5)—C(26)	109.3(2)	109.0(2)
Co(7)—Co(5)—C(26)	123.6(2)	126.3(2)
Co(8)—Co(5)—C(26)	166.4(2)	163.9(2)
Co(6)—Co(5)—C(27)	105.9(2)	109.0(2)
Co(7)—Co(5)—C(27)	155.9(2)	160.3(2)
Co(8)—Co(5)—C(27)	133.3(2)	130.9(2)
C(26)—Co(5)—C(27)	38.9(3)	38.4(3)
Co(6)—Co(5)—C(28)	125.6(2)	129.1(3)
Co(7)—Co(5)—C(28)	165.3(2)	160.7(2)
Co(8)—Co(5)—C(28)	110.2(3)	107.4(3)
C(26)—Co(5)—C(28)	69.6(3)	70.2(3)
C(27)—Co(5)—C(28)	38.7(3)	39.0(3)
Co(6)—Co(5)—C(29)	156.3(3)	160.0(3)
Co(7)—Co(5)—C(29)	131.2(2)	126.8(2)
Co(8)—Co(5)—C(29)	105.6(3)	105.4(3)
C(26)—Co(5)—C(29)	82.7(3)	82.8(3)
C(27)—Co(5)—C(29)	70.2(3)	69.9(3)
C(28)—Co(5)—C(29)	38.3(3)	38.6(3)
Co(6)—Co(5)—C(30)	165.0(2)	160.4(2)
Co(7)—Co(5)—C(30)	107.9(2)	104.8(2)
Co(8)—Co(5)—C(30)	123.3(2)	125.4(3)
C(26)—Co(5)—C(30)	69.9(3)	69.5(3)
C(27)—Co(5)—C(30)	82.9(3)	82.2(3)
C(28)—Co(5)—C(30)	68.8(3)	69.7(3)
C(29)—Co(5)—C(30)	38.0(3)	38.5(3)
Co(6)—Co(5)—C(31)	132.6(2)	129.1(2)
Co(7)—Co(5)—C(31)	105.2(2)	104.5(2)
Co(8)—Co(5)—C(31)	155.0(2)	157.7(2)
C(26)—Co(5)—C(31)	38.0(3)	38.1(3)
C(27)—Co(5)—C(31)	69.4(3)	69.3(3)
C(28)—Co(5)—C(31)	81.3(3)	82.9(3)
C(29)—Co(5)—C(31)	69.1(3)	70.1(3)
C(30)—Co(5)—C(31)	38.7(3)	38.8(3)
Co(5)—Co(6)—Co(7)	61.3(1)	60.2(1)
Co(5)—Co(6)—Co(8)	61.6(1)	60.2(1)
Co(7)—Co(6)—Co(8)	60.3(1)	60.3(1)
Co(5)—Co(6)—C(4)	74.9(2)	75.7(2)
Co(7)—Co(6)—C(4)	50.7(3)	51.8(2)
Co(8)—Co(6)—C(4)	109.6(3)	110.8(2)
Co(5)—Co(6)—C(6)	68.8(3)	70.6(3)
Co(7)—Co(6)—C(6)	107.0(3)	107.8(2)
Co(8)—Co(6)—C(6)	50.1(3)	50.0(2)
C(4)—Co(6)—C(6)	143.6(4)	146.2(3)
Co(5)—Co(6)—C(13)	157.9(3)	156.6(3)
Co(7)—Co(6)—C(13)	101.3(3)	100.0(3)
Co(8)—Co(6)—C(13)	98.7(3)	100.0(3)
C(4)—Co(6)—C(13)	105.5(4)	102.9(3)
C(6)—Co(6)—C(13)	107.3(4)	107.7(4)
Co(5)—Co(6)—C(14)	100.6(3)	103.8(3)
Co(7)—Co(6)—C(14)	144.2(4)	145.9(3)
Co(7)—Co(8)—C(5)	50.6(2)	49.5(2)
Co(5)—Co(8)—C(6)	67.8(3)	71.0(3)
Co(6)—Co(8)—C(6)	50.8(2)	51.1(2)
Co(7)—Co(8)—C(6)	107.5(3)	108.4(2)
C(5)—Co(8)—C(6)	152.6(4)	148.2(4)
Co(5)—Co(8)—C(17)	160.6(3)	159.7(3)
Co(6)—Co(8)—C(17)	101.3(3)	100.9(3)
Co(7)—Co(8)—C(17)	111.7(3)	104.9(3)
C(5)—Co(8)—C(17)	103.1(4)	104.0(4)
C(6)—Co(8)—C(17)	100.8(4)	104.2(4)
Co(5)—Co(8)—C(18)	96.8(4)	100.3(3)
Co(6)—Co(8)—C(18)	143.7(3)	144.8(3)
Co(7)—Co(8)—C(18)	134.7(3)	139.1(3)
C(5)—Co(8)—C(18)	92.3(4)	93.3(4)
C(6)—Co(8)—C(18)	96.5(4)	96.1(3)
C(17)—Co(8)—C(18)	100.3(4)	99.9(4)
Co(2)—C(1)—Co(3)	79.7(3)	79.2(3)
Co(2)—C(1)—O(1)	141.4(8)	140.9(8)
Co(3)—C(1)—O(1)	138.9(8)	139.9(9)
Co(3)—C(2)—Co(4)	79.0(3)	78.9(3)
Co(3)—C(2)—O(2)	139.4(7)	142.2(8)
Co(4)—C(2)—O(2)	141.6(7)	138.9(8)
o(2)—C(3)—Co(4)	78.1(4)	78.6(4)
Co(2)—C(3)—O(3)	139.3(7)	140.3(7)
Co(4)—C(3)—O(3)	142.5(7)	141.1(7)
Co(6)—C(4)—Co(7)	78.7(3)	78.4(3)
Co(6)—C(4)—O(4)	140.5(7)	143.0(6)
Co(7)—C(4)—O(4)	140.7(7)	138.5(6)
Co(7)—C(5)—Co(8)	78.8(3)	79.3(3)
Co(7)—C(5)—O(5)	140.8(7)	141.9(6)
Co(8)—C(5)—O(5)	140.3(6)	138.8(6)
Co(6)—C(6)—Co(8)	79.1(3)	78.8(3)
Co(6)—C(6)—O(6)	141.0(7)	139.9(7)
Co(8)—C(6)—O(6)	139.8(7)	141.3(6)
Co(2)—C(7)—O(7)	179.8(9)	176.7(9)
Co(2)—C(8)—O(8)	177.5(9)	178.7(8)
Co(3)—C(9)—O(9)	178.8(8)	177.4(9)
Co(3)—C(10)—O(10)	177.0(8)	177.2(9)
Co(4)—C(11)—O(11)	175.8(8)	176.5(9)
Co(4)—C(12)—O(12)	175.4(8)	178.6(8)
Co(6)—C(13)—O(13)	177.6(9)	177.5(7)
Co(6)—C(14)—O(14)	179.7(9)	179.0(6)
Co(7)—C(15)—O(15)	178.0(9)	178.0(7)
Co(7)—C(16)—O(16)	177.5(9)	175.7(8)
Co(8)—C(17)—O(17)	177.5(9)	176.0(8)
Co(8)—C(18)—O(18)	177.1(9)	179.5(8)
Co(1)—C(19)—C(20)	70.6(5)	69.9(5)
Co(1)—C(19)—C(24)	69.8(5)	69.8(4)
C(20)—C(19)—C(24)	119.2(8)	118.0(8)
Co(1)—C(19)—C(25)	130.8(5)	130.4(5)
C(20)—C(19)—C(25)	119.1(7)	122.4(7)
C(24)—C(19)—C(25)	121.7(8)	119.6(8)
Co(1)—C(20)—C(19)	71.1(4)	71.7(4)
Co(1)—C(20)—C(21)	70.8(5)	70.6(5)
C(19)—C(20)—C(21)	120.1(8)	121.0(7)
Co(1)—C(21)—C(20)	70.7(5)	70.8(5)
Co(1)—C(21)—C(22)	70.5(5)	72.0(5)
C(20)—C(21)—C(22)	120.3(9)	121.0(9)
Co(1)—C(22)—C(21)	70.4(5)	69.9(5)
Co(1)—C(22)—C(23)	70.8(5)	70.3(5)
C(21)—C(22)—C(23)	119.1(9)	118.7(9)

Table 2 (continued)

Angle	ω/deg		Angle	ω/deg		Angle	ω/deg	
	2a	**2b**		**2a**	**2b**		**2a**	**2b**
Co(2)—Co(3)—C(1)	50.0(3)	49.9(3)	Co(8)—Co(6)—C(14)	141.4(3)	141.5(2)	Co(1)—C(23)—C(22)	70.9(5)	70.8(4)
Co(4)—Co(3)—C(1)	109.2(3)	109.5(3)	C(4)—Co(6)—C(14)	96.4(4)	96.6(4)	Co(1)—C(23)—C(24)	69.8(4)	70.4(4)
Co(1)—Co(3)—C(2)	70.6(2)	71.5(3)	C(6)—Co(6)—C(14)	92.3(4)	92.4(3)	C(22)—C(23)—C(24)	119.4(8)	119.9(8)
Co(2)—Co(3)—C(2)	107.4(3)	108.9(3)	C(13)—Co(6)—C(14)	101.2(5)	99.6(4)	Co(1)—C(24)—C(19)	72.0(5)	71.4(4)
Co(4)—Co(3)—C(2)	50.6(3)	51.3(3)	Co(5)—Co(7)—Co(6)	59.2(1)	60.3(1)	Co(1)—C(24)—C(23)	71.6(5)	71.5(5)
C(1)—Co(3)—C(2)	154.9(4)	150.1(4)	Co(5)—Co(7)—Co(8)	60.7(1)	60.1(1)	C(19)—C(24)—C(23)	122.0(8)	121.3(8)
Co(1)—Co(3)—C(9)	93.4(3)	97.2(3)	Co(6)—Co(7)—Co(8)	59.7(1)	59.8(1)	C(19)—C(25)—C(26)	111.9(6)	112.7(7)
Co(2)—Co(3)—C(9)	132.8(3)	137.2(3)	Co(5)—Co(7)—C(4)	73.6(2)	74.8(2)	Co(5)—C(26)—C(25)	132.1(6)	129.8(6)
Co(4)—Co(3)—C(9)	142.7(3)	143.5(3)	Co(6)—Co(7)—C(4)	50.6(3)	49.8(2)	Co(5)—C(26)—C(27)	68.8(5)	69.9(5)
C(1)—Co(3)—C(9)	93.6(4)	92.2(4)	Co(8)—Co(7)—C(4)	109.0(2)	108.3(2)	C(25)—C(26)—C(27)	121.7(7)	120.4(7)
C(2)—Co(3)—C(9)	97.9(4)	95.9(4)	Co(5)—Co(7)—C(5)	85.7(2)	78.2(2)	Co(5)—C(26)—C(31)	70.1(5)	70.1(5)
Co(1)—Co(3)—C(10)	163.9(3)	160.2(3)	Co(6)—Co(7)—C(5)	110.3(2)	110.4(2)	C(25)—C(26)—C(31)	120.4(7)	120.3(7)
Co(2)—Co(3)—C(10)	113.1(3)	105.9(3)	Co(8)—Co(7)—C(5)	50.6(2)	51.3(2)	C(27)—C(26)—C(31)	117.9(7)	119.2(7)
Co(4)—Co(3)—C(10)	103.6(3)	100.4(3)	C(4)—Co(7)—C(5)	157.1(3)	152.4(3)	Co(5)—C(27)—C(26)	72.4(4)	71.7(4)
C(1)—Co(3)—C(10)	100.2(4)	104.2(4)	Co(5)—Co(7)—C(15)	166.9(3)	165.2(3)	Co(5)—C(27)—C(28)	71.9(5)	70.9(5)
C(2)—Co(3)—C(10)	99.4(4)	102.0(4)	Co(6)—Co(7)—C(15)	107.8(3)	108.3(3)	C(26)—C(27)—C(28)	120.2(7)	121.1(7)
C(9)—Co(3)—C(10)	100.7(4)	102.2(5)	Co(8)—Co(7)—C(15)	113.1(3)	106.7(3)	Co(5)—C(28)—C(27)	69.4(4)	70.1(4)
Co(1)—Co(4)—Co(2)	61.1(1)	60.7(1)	C(4)—Co(7)—C(15)	99.4(4)	105.7(3)	Co(5)—C(28)—C(29)	70.5(4)	70.0(4)
Co(1)—Co(4)—Co(3)	60.6(1)	60.0(1)	C(5)—Co(7)—C(15)	98.9(4)	98.8(4)	C(27)—C(28)—C(29)	120.4(7)	118.6(7)
Co(2)—Co(4)—Co(3)	61.0(1)	60.2(1)	Co(5)—Co(7)—C(16)	91.4(3)	96.2(3)	Co(5)—C(29)—C(28)	71.3(4)	71.4(5)
Co(1)—Co(4)—C(2)	70.8(2)	70.6(2)	Co(6)—Co(7)—C(16)	139.3(3)	134.9(3)	Co(5)—C(29)—C(30)	69.7(5)	70.6(5)
Co(2)—Co(4)—C(2)	108.9(2)	107.7(3)	Co(8)—Co(7)—C(16)	132.6(2)	143.7(3)	C(28)—C(29)—C(30)	119.2(7)	120.2(8)
Co(3)—Co(4)—C(2)	50.4(3)	49.9(3)	C(4)—Co(7)—C(16)	96.8(4)	88.8(4)	Co(5)—C(30)—C(29)	72.3(5)	70.9(6)
Co(1)—Co(4)—C(3)	71.9(2)	78.4(2)	C(5)—Co(7)—C(16)	93.2(4)	99.9(4)	Co(5)—C(30)—C(31)	72.0(5)	71.0(5)
Co(2)—Co(4)—C(3)	51.4(3)	50.7(2)	C(15)—Co(7)—C(16)	100.5(4)	98.6(4)	C(29)—C(30)—C(31)	121.1(8)	120.7(8)
Co(3)—Co(4)—C(3)	109.8(3)	110.2(2)	Co(5)—Co(8)—Co(6)	59.2(1)	60.3(1)	Co(5)—C(31)—C(26)	71.9(5)	71.8(5)
C(2)—Co(4)—C(3)	142.7(3)	148.8(3)	Co(5)—Co(8)—Co(7)	60.4(1)	60.1(1)	Co(5)—C(31)—C(30)	69.3(5)	70.2(5)
Co(1)—Co(4)—C(11)	151.3(3)	157.7(3)	Co(6)—Co(8)—Co(7)	60.1(1)	59.9(1)	C(26)—C(31)—C(30)	121.0(7)	120.2(7)
Co(2)—Co(4)—C(11)	94.6(3)	102.3(3)	Co(5)—Co(8)—C(5)	85.5(3)	77.4(3)			
Co(3)—Co(4)—C(11)	95.3(3)	99.7(3)	Co(6)—Co(8)—C(5)	110.6(2)	108.8(2)			

Crystals of **2** suitable for X-ray structural study were grown by slow evaporation of a solution of complex **2** in a CH_2Cl_2—heptane mixture in a refrigerator.

The structure of complex **2** is shown in Fig. 1; the bond lengths and bond angles are given in Tables 1 and 2. The structures of clusters containing the $Co_4(CO)_9$ fragment bonded to the arene ligand were studied in considerable detail (see, for example, Refs. 4 and 5). The essential features of the structures of these clusters are typical also of complex **2**. Thus, the Co—Co distances in the base of the pyramid are shortened compared to the side edges of the pyramid (the average values for two independent molecules (**a** and **b**) in **2** are 2.454 and 2.481 Å, respectively), which is apparently determined by the contracting action of the bridging CO groups. In all cases, the plane of the aromatic nucleus is parallel to the plane of the base of the metal cluster: the dihedral angle is 1.6° (average). This makes it possible to consider the (η^6-arene)$Co_4(CO)_9$ compounds as sandwich systems, in which the central Co atom is bonded, on the one hand, to the arene ligand and, on the other hand, to the tricobalt metal cycle $Co_3(CO)_9$, which is in agreement with the difference in Co—Co distances. Similarly to the results obtained previously,[5] a slight but rather marked elongation of the axial terminal Co—C(O) bonds (average 1.804 Å) in all independent $Co_4(CO)_9$ fragments compared to the equatorial bonds (average 1.785 Å) is observed in complex **2**. The dihedral angles formed by the planes of the bridging carbonyl CoCCo groups with the basal Co_3 plane is one more important characteristic of the analogous fragments. As in all structures studied previously, the bridging CO groups in **2** deviate from this plane toward the fourth Co atom occupying the vertex of the pyramid. The values of the dihedral angles in **2** vary over a wide range from 0.2° to 23.4°, which is indicative of a high flexibility of the whole system and, apparently, is determined both by the effect of internal steric factors related to volumes of ligands at the fourth Co atom (*cf.* Ref. 4) and the effects of the crystal field.

In the crystal, the bicluster derivative of diphenylmethane **2** has an *s-trans-s-trans* conformation, which was unexpected because in the literature an *anti* conformation (*s-cis-s-trans*) of the **A** type was assigned *a priori* to the analog of **2**, the bis-chromium tricarbonyl complex $Ph_2CH_2[Cr(CO)_3]_2$ (**3**).[8,9] Besides, for the corresponding derivative of biphenyl, $Ph_2[Cr(CO_3]_2$, the *anti* structure was actually established.[11] However, diphenylmethane is a more flexible system; therefore, we performed X-ray structural analysis for complex **3**. For this purpose, complex **3** was prepared (as a mixture with a monomolecular product) according to the conventional procedure (see Experimental):

$$\mathrm{Ph_2CH_2 + Co_2(CO)_6 \longrightarrow [\eta^6\text{-}PhCr(CO)_3]CH_2Ph\ +}$$

$$\mathrm{+\ [\eta^6\text{-}PhCr(CO)_3]_2CH_2}$$

3

The crystals of **3** suitable for X-ray structural analysis were grown in the same manner as described for **2**.

It was found that complex **3** (Fig. 2), unlike the biphenyl derivative, adopts an *s-trans-s-trans* conformation of one of the *syn* rotamers (of the **C** type) rather than an *anti* conformation of the **A** type. Therefore, the sterically less hindered conformation occurs in the crystal regardless of the size of the metal-containing group [$Cr(CO)_3$ or $Co_4(CO)_9$].

The geometry of the diphenylmethane fragment in molecules **2** and **3** (bond lengths and bond angles in molecule **3** are given in Tables 3 and 4) is close to that observed for the free Ph_2CH_2 ligand.[12] The tilt angle of the phenyl ring is 75.3° and 68.7° in two independent molecules of complex **2**, 71.7° in **3**, and 80.5° in the free diphenylmethane (the observed differences result, apparently, from packing effects of the molecules in the crystal).

The conformation of the $Cr(CO)_3$ group in **3** with respect to benzene rings is close to the staggered conformation (the C(13)—C(7)—Cr(1)—C(2) and C(13)—

Table 3. Bond lengths (*d*) in the structure of **3**

Bond	*d*/Å	Bond	*d*/Å
Cr(1)—C(1)	1.846(2)	O(2)—C(2)	1.152(3)
Cr(1)—C(2)	1.834(2)	O(3)—C(3)	1.148(2)
Cr(1)—C(3)	1.843(2)	O(4)—C(4)	1.148(3)
Cr(1)—C(7)	2.236(2)	O(5)—C(5)	1.149(3)
Cr(1)—C(8)	2.209(2)	O(6)—C(6)	1.149(2)
Cr(1)—C(9)	2.219(2)	C(7)—C(8)	1.415(3)
Cr(1)—C(10)	2.207(2)	C(7)—C(12)	1.399(3)
Cr(1)—C(11)	2.206(2)	C(7)—C(13)	1.512(3)
Cr(1)—C(12)	2.212(2)	C(8)—C(9)	1.395(3)
Cr(2)—C(4)	1.846(2)	C(9)—C(10)	1.399(3)
Cr(2)—C(5)	1.848(2)	C(10)—C(11)	1.379(3)
Cr(2)—C(6)	1.837(2)	C(11)—C(12)	1.438(4)
Cr(2)—C(14)	2.218(2)	C(13)—C(14)	1.515(3)
Cr(2)—C(15)	2.207(2)	C(14)—C(15)	1.418(3)
Cr(2)—C(16)	2.208(2)	C(14)—C(19)	1.397(3)
Cr(2)—C(17)	2.210(2)	C(15)—C(16)	1.402(3)
Cr(2)—C(18)	2.217(2)	C(16)—C(17)	1.408(3)
Cr(2)—C(19)	2.203(2)	C(17)—C(18)	1.387(4)
O(1)—C(1)	1.148(3)	C(18)—C(19)	1.423(3)

Table 4. Bond angles (ω) in the structure of **3**

Angle	ω/deg	Angle	ω/deg
C(1)—Cr(1)—C(2)	87.7(1)	C(15)—Cr(2)—C(18)	78.7(1)
C(1)—Cr(1)—C(3)	87.9(1)	C(16)—Cr(2)—C(18)	66.4(1)
C(2)—Cr(1)—C(3)	87.3(1)	C(17)—Cr(2)—C(18)	36.5(1)
C(1)—Cr(1)—C(7)	156.3(1)	C(4)—Cr(2)—C(19)	151.6(1)
C(2)—Cr(1)—C(7)	91.1(1)	C(5)—Cr(2)—C(19)	90.8(1)
C(3)—Cr(1)—C(7)	115.6(1)	C(6)—Cr(2)—C(19)	118.9(1)
C(1)—Cr(1)—C(8)	119.2(1)	C(14)—Cr(2)—C(19)	36.8(1)
C(2)—Cr(1)—C(8)	90.6(1)	C(15)—Cr(2)—C(19)	66.5(1)
C(3)—Cr(1)—C(8)	152.7(1)	C(16)—Cr(2)—C(19)	78.8(1)
C(7)—Cr(1)—C(8)	37.1(1)	C(17)—Cr(2)—C(19)	66.9(1)
C(1)—Cr(1)—C(9)	92.6(1)	C(18)—Cr(2)—C(19)	37.5(1)
C(2)—Cr(1)—C(9)	116.1(1)	Cr(1)—C(1)—O(1)	178.1(2)
C(3)—Cr(1)—C(9)	156.6(1)	Cr(1)—C(2)—O(2)	179.5(2)
C(7)—Cr(1)—C(9)	66.8(1)	Cr(1)—C(3)—O(3)	178.9(2)
C(8)—Cr(1)—C(9)	36.7(1)	Cr(2)—C(4)—O(4)	179.6(2)
C(1)—Cr(1)—C(10)	91.2(1)	Cr(2)—C(5)—O(5)	177.1(2)
C(2)—Cr(1)—C(10)	152.8(1)	Cr(2)—C(6)—O(6)	178.5(2)
C(3)—Cr(1)—C(10)	119.8(1)	Cr(1)—C(7)—C(8)	70.4(1)
C(7)—Cr(1)—C(10)	79.2(1)	Cr(1)—C(7)—C(12)	70.7(1)
C(8)—Cr(1)—C(10)	66.4(1)	C(8)—C(7)—C(12)	118.1(2)
C(9)—Cr(1)—C(10)	36.8(1)	Cr(1)—C(7)—C(13)	128.9(1)
C(1)—Cr(1)—C(11)	116.2(1)	C(8)—C(7)—C(13)	120.6(2)
C(2)—Cr(1)—C(11)	156.1(1)	C(12)—C(7)—C(13)	121.3(2)
C(3)—Cr(1)—C(11)	93.0(1)	Cr(1)—C(8)—C(7)	72.5(1)
C(7)—Cr(1)—C(11)	67.2(1)	Cr(1)—C(8)—C(9)	72.0(1)
C(8)—Cr(1)—C(11)	78.3(1)	C(7)—C(8)—C(9)	121.6(2)
C(9)—Cr(1)—C(11)	65.9(1)	Cr(1)—C(9)—C(8)	71.2(1)
C(10)—Cr(1)—C(11)	36.4(1)	Cr(1)—C(9)—C(10)	71.1(1)
C(1)—Cr(1)—C(12)	154.1(1)	C(8)—C(9)—C(10)	119.9(2)
C(2)—Cr(1)—C(12)	118.1(1)	Cr(1)—C(10)—C(9)	72.0(1)
C(3)—Cr(1)—C(12)	90.9(1)	Cr(1)—C(10)—C(11)	71.7(1)
C(7)—Cr(1)—C(12)	36.7(1)	C(9)—C(10)—C(11)	120.2(2)
C(8)—Cr(1)—C(12)	66.2(1)	Cr(1)—C(11)—C(10)	71.8(1)
C(9)—Cr(1)—C(12)	78.6(1)	Cr(1)—C(11)—C(12)	71.2(1)
C(10)—Cr(1)—C(12)	67.1(1)	C(10)—C(11)—C(12)	120.1(2)
C(11)—Cr(1)—C(12)	38.0(1)	Cr(1)—C(12)—C(7)	72.6(1)
C(4)—Cr(2)—C(5)	88.8(1)	Cr(1)—C(12)—C(11)	70.8(1)
C(4)—Cr(2)—C(6)	89.4(1)	C(7)—C(12)—C(11)	120.1(2)
C(5)—Cr(2)—C(6)	86.2(1)	C(7)—C(13)—C(14)	112.0(2)
C(4)—Cr(2)—C(14)	156.8(1)	Cr(2)—C(14)—C(13)	128.7(1)
C(5)—Cr(2)—C(14)	114.4(1)	Cr(2)—C(14)—C(15)	70.9(1)
C(6)—Cr(2)—C(14)	91.3(1)	C(13)—C(14)—C(15)	120.1(2)
C(4)—Cr(2)—C(15)	119.4(1)	Cr(2)—C(14)—C(19)	71.0(1)
C(5)—Cr(2)—C(15)	151.5(1)	C(13)—C(14)—C(19)	121.3(2)
C(6)—Cr(2)—C(15)	90.0(1)	C(15)—C(14)—C(19)	118.5(2)
C(14)—Cr(2)—C(15)	37.4(1)	Cr(2)—C(15)—C(14)	71.7(1)
C(4)—Cr(2)—C(16)	91.6(1)	Cr(2)—C(15)—C(16)	71.5(1)
C(5)—Cr(2)—C(16)	158.5(1)	C(14)—C(15)—C(16)	120.7(2)
C(6)—Cr(2)—C(16)	115.3(1)	Cr(2)—C(16)—C(15)	71.5(1)
C(14)—Cr(2)—C(16)	67.2(1)	Cr(2)—C(16)—C(17)	71.5(1)
C(15)—Cr(2)—C(16)	37.0(1)	C(15)—C(16)—C(17)	119.9(2)
C(4)—Cr(2)—C(17)	89.4(1)	Cr(2)—C(17)—C(16)	71.4(1)
C(5)—Cr(2)—C(17)	121.4(1)	Cr(2)—C(17)—C(18)	72.0(1)
C(6)—Cr(2)—C(17)	152.4(1)	C(16)—C(17)—C(18)	120.2(2)
C(14)—Cr(2)—C(17)	79.4(1)	Cr(2)—C(18)—C(17)	71.4(1)
C(15)—Cr(2)—C(17)	66.8(1)	Cr(2)—C(18)—C(19)	70.7(1)
C(16)—Cr(2)—C(17)	37.2(1)	C(17)—C(18)—C(19)	119.8(2)
C(4)—Cr(2)—C(18)	114.2(1)	Cr(2)—C(19)—C(14)	72.2(1)
C(5)—Cr(2)—C(18)	93.9(1)	Cr(2)—C(19)—C(18)	71.8(1)
C(6)—Cr(2)—C(18)	156.4(1)	C(14)—C(19)—C(18)	120.9(2)
C(14)—Cr(2)—C(18)	67.1(1)		

Table 5. Atomic coordinates (×10^4) and equivalent isotropic temperature parameters (×10^3) in the structure of **2**

Atom	x	y	z	U_{eq}/Å^2	Atom	x	y	z	U_{eq}/Å^2
Co(1a)	4362(1)	8438(1)	1134(1)	18(1)	Co(1b)	−639(1)	13476(1)	6226(1)	18(1)
Co(2a)	5802(1)	8706(1)	2086(1)	21(1)	Co(2b)	934(1)	13554(1)	7139(1)	20(1)
Co(3a)	4370(1)	9667(1)	1737(1)	21(1)	Co(3b)	−195(1)	14680(1)	6897(1)	24(1)
Co(4a)	6596(1)	9618(1)	1328(1)	22(1)	Co(4b)	1813(1)	14495(1)	6395(1)	21(1)
Co(5a)	6627(1)	6678(1)	−976(1)	17(1)	Co(5b)	1698(1)	11809(1)	4123(1)	17(1)
Co(6a)	8647(1)	6411(1)	−361(1)	23(1)	Co(6b)	3580(1)	11311(1)	4693(1)	20(1)
Co(7a)	9218(1)	7296(1)	−1162(1)	22(1)	Co(7b)	4331(1)	12464(1)	4071(1)	20(1)
Co(8a)	8120(1)	5787(1)	−1319(1)	22(1)	Co(8b)	3185(1)	11039(1)	3669(1)	20(1)
O(1a)	3285(8)	8714(4)	2691(3)	53(3)	O(1b)	−1688(7)	13496(4)	7681(3)	48(3)
O(2a)	4601(7)	10356(4)	627(3)	36(2)	O(2b)	21(7)	15469(4)	5815(3)	41(2)
O(3a)	7820(6)	8180(4)	1404(3)	38(2)	O(3b)	2936(7)	13026(4)	6460(3)	42(3)
O(4a)	9243(6)	8194(4)	−98(3)	34(2)	O(4b)	4186(6)	12960(3)	5241(2)	29(2)
O(5a)	8666(7)	6696(4)	−2347(3)	44(3)	O(5b)	3507(7)	12356(4)	2858(2)	37(2)
O(6a)	6395(7)	4796(4)	−508(3)	40(2)	O(6b)	1347(6)	9754(3)	4300(2)	32(2)
O(7a)	7956(7)	9385(4)	3068(3)	46(3)	O(7b)	2927(7)	14188(5)	8166(3)	53(3)
O(8a)	5125(8)	6977(4)	2395(3)	61(3)	O(8b)	131(8)	11772(4)	7339(3)	55(3)
O(9a)	1223(7)	9440(4)	1450(3)	51(3)	O(9b)	−3162(9)	14859(6)	6738(3)	72(4)
O(10a)	5275(8)	11290(4)	2356(3)	47(3)	O(10b)	1424(8)	16108(4)	7656(3)	57(3)
O(11a)	8511(7)	10946(4)	2103(3)	41(2)	O(11b)	4223(7)	15775(4)	7031(3)	45(2)
O(12a)	8174(8)	9958(5)	331(3)	58(3)	O(12b)	2753(7)	14612(4)	5266(3)	47(3)
O(13a)	11449(7)	6036(4)	−67(3)	56(3)	O(13b)	6390(7)	10924(4)	4937(3)	45(3)
O(14a)	7454(10)	6292(5)	716(3)	72(4)	O(14b)	2237(8)	10762(4)	5716(3)	50(3)
O(15a)	12417(7)	7813(5)	−1161(3)	60(3)	O(15b)	7482(7)	12776(5)	3997(3)	64(3)
O(16a)	8454(7)	8738(4)	−1651(3)	52(3)	O(16b)	4139(7)	14172(4)	4081(3)	49(3)
O(17a)	10350(8)	4867(5)	−1316(3)	62(3)	O(17b)	5648(8)	10338(5)	3523(3)	57(3)
O(18a)	5830(8)	4762(5)	−2141(3)	58(3)	O(18b)	1072(7)	10194(4)	2723(3)	41(2)
C(1a)	4088(10)	8917(5)	2351(3)	30(3)	C(1b)	−781(9)	13764(6)	7388(3)	31(3)
C(2a)	4991(9)	10030(4)	1020(3)	24(3)	C(2b)	344(10)	15080(5)	6185(4)	32(3)
C(3a)	7101(9)	8615(5)	1526(3)	25(3)	C(3b)	2265(9)	13468(5)	6596(3)	25(3)
C(4a)	9111(8)	7610(5)	−387(4)	27(3)	C(4b)	4096(7)	12480(5)	4879(3)	20(3)
C(5a)	8677(9)	6629(5)	−1862(4)	27(3)	C(5b)	3646(8)	12104(5)	3305(3)	24(3)
C(6a)	7261(9)	5385(5)	−656(4)	29(3)	C(6b)	2240(8)	10381(5)	4242(3)	23(3)
C(7a)	7126(9)	9122(5)	2690(4)	28(3)	C(7b)	2184(9)	13927(6)	7777(4)	32(3)
C(8a)	5375(10)	7636(6)	2264(4)	36(3)	C(8b)	428(9)	12467(5)	7258(3)	29(3)
C(9a)	2444(10)	9537(5)	1562(4)	31(3)	C(9b)	−1999(11)	14809(6)	6800(4)	39(4)
C(10a)	4896(10)	10651(5)	2125(4)	32(3)	C(10b)	773(10)	15557(6)	7373(4)	36(3)
C(11a)	7808(9)	10438(5)	1788(4)	29(3)	C(11b)	3318(10)	15274(5)	6773(3)	31(3)
C(12a)	7529(9)	9791(5)	715(4)	33(3)	C(12b)	2390(9)	14556(5)	5700(4)	29(3)
C(13a)	10386(11)	6185(6)	−167(4)	40(4)	C(13b)	5308(9)	11057(5)	4851(3)	29(3)
C(14a)	7925(11)	6341(6)	290(4)	42(4)	C(14b)	2767(9)	10983(5)	5319(4)	30(3)
C(15a)	11172(9)	7598(5)	−1165(4)	31(3)	C(15b)	6247(9)	12666(5)	4033(4)	27(3)
C(16a)	8770(9)	8179(5)	−1470(4)	32(3)	C(16b)	4206(8)	13515(5)	4055(4)	26(3)
C(17a)	9494(10)	5234(6)	−1327(4)	38(3)	C(17b)	4702(10)	10622(5)	3561(3)	32(3)
C(18a)	6712(10)	5146(6)	−1811(4)	38(3)	C(18b)	1899(10)	10521(5)	3092(4)	31(3)
C(19a)	4557(8)	7771(4)	381(3)	19(2)	C(19b)	−640(8)	12639(5)	5532(3)	20(3)
C(20a)	3625(8)	8283(5)	250(3)	25(3)	C(20b)	−1126(8)	13318(5)	5336(3)	22(3)
C(21a)	2413(9)	8232(6)	553(4)	32(3)	C(21b)	−2267(9)	13541(6)	5566(4)	27(3)
C(22a)	2140(10)	7672(6)	1003(4)	41(3)	C(22b)	−2968(9)	13090(6)	5993(4)	32(3)
C(23a)	3080(10)	7164(5)	1130(4)	32(3)	C(23b)	−2485(9)	12400(5)	6199(4)	33(3)
C(24a)	4282(9)	7228(5)	820(3)	22(3)	C(24b)	−1339(9)	12188(5)	5973(3)	26(3)
C(25a)	5856(9)	7839(5)	50(4)	25(3)	C(25b)	609(10)	12396(6)	5305(4)	30(3)
C(26a)	5431(8)	7322(4)	−489(3)	18(2)	C(26b)	342(8)	12199(4)	4678(3)	19(2)
C(27a)	4815(8)	6440(5)	−498(3)	20(3)	C(27b)	−337(8)	11377(5)	4464(3)	24(3)
C(28a)	4358(9)	5974(5)	−1019(4)	27(3)	C(28b)	−560(8)	11175(6)	3873(4)	31(3)
C(29a)	4619(8)	6364(5)	−1532(3)	28(3)	C(29b)	−65(9)	11815(6)	3503(4)	30(3)
C(30a)	5279(9)	7214(5)	−1521(3)	26(3)	C(30b)	613(9)	12630(6)	3717(4)	29(3)
C(31a)	5651(8)	7696(5)	−1009(4)	24(3)	C(31b)	830(8)	12822(5)	4303(3)	23(3)

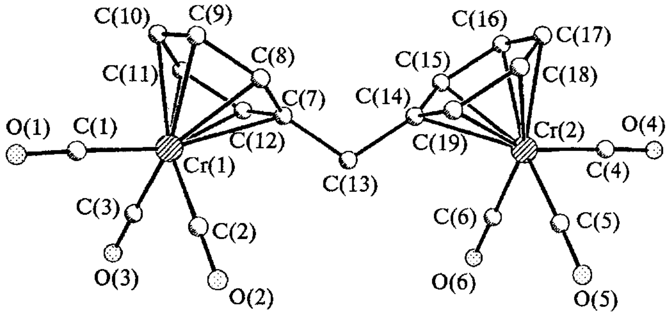

Fig. 2. Structure of molecule **3**.

Table 6. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature parameters ($\times 10^3$) in the structure of **3**

Atom	x	y	z	$U_{eq}/Å^2$
Cr(1)	969(1)	1535(1)	8745(1)	32(1)
Cr(2)	4382(1)	−1503(1)	6315(1)	32(1)
O(1)	−546(1)	4288(3)	9222(1)	80(1)
O(2)	2361(2)	4580(2)	8399(1)	75(1)
O(3)	1872(1)	1667(2)	10276(1)	59(1)
O(4)	5988(1)	−3695(3)	5582(1)	80(1)
O(5)	5595(2)	1788(2)	5970(1)	76(1)
O(6)	5634(1)	−1556(2)	7715(1)	58(1)
C(1)	22(2)	3212(3)	9039(1)	48(1)
C(2)	1822(2)	3405(3)	8529(1)	44(1)
C(3)	1521(2)	1600(3)	9690(1)	39(1)
C(4)	5370(2)	−2858(3)	5862(1)	49(1)
C(5)	5117(2)	531(3)	6085(1)	47(1)
C(6)	5155(2)	−1560(3)	7174(1)	39(1)
C(7)	1772(1)	−249(2)	7954(1)	35(1)
C(8)	961(2)	657(3)	7582(1)	39(1)
C(9)	−43(2)	573(3)	7828(1)	49(1)
C(10)	−260(2)	−397(3)	8465(1)	53(1)
C(11)	511(2)	−1298(3)	8843(1)	54(1)
C(12)	1546(2)	−1222(3)	8590(1)	43(1)
C(13)	2856(2)	−119(3)	7683(1)	44(1)
C(14)	2966(1)	−984(3)	6933(1)	36(1)
C(15)	3115(2)	−2860(3)	6876(1)	40(1)
C(16)	3241(2)	−3671(3)	6186(1)	45(1)
C(17)	3215(2)	−2620(3)	5541(1)	49(1)
C(18)	3057(2)	−785(3)	5586(1)	51(1)
C(19)	2942(2)	37(3)	6287(1)	45(1)

C(14)—Cr(2)—C(6) torsion angles are 24.5° and 25.5°, respectively). The conformation of the Co_4 fragments in **2** with respect to phenyl ligands can be considered in a similar manner: the C(25)—C(19)—Co(1)—Co(4) and C(25)—C(26)—Co(5)—Co(6) torsion angles are 10.8° and 22.4°, respectively, in molecule **2a** and 24.2° and 16.5°, respectively, in molecule **2b**. Obviously, in this case none of the conformations can be considered preferable.

The effect of different metal-containing groups on the geometry of the diphenylmethane ligand manifests itself in the orientation of the planes of the benzene rings with respect to the plane passing through the central carbon atom and two key atoms of the phenyl substituents. The corresponding torsion angles are: C(20a)—C(19a)—C(25a)—C(26a) 84.1° and C(19a)—C(25a)—C(26a)—C(27a) 60.0° in molecule **2a**; C(20b)—C(19b)—C(25b)—C(26b) 58.4° and C(19b)—C(25b)—C(26b)—C(27b) 91.0° in molecule **2b**; and C(8)—C(7)—C(13)—C(14) 65.6° and C(7)—C(13)—C(14)—C(15) 83.1° in molecule **3**. Therefore, in all three molecules (**2a**, **2b**, and **3**), one of the torsion angles is close to 90°, and the second torsion angle is close to 60°, while in uncoordinated diphenylmethane, the difference in the values of both torsion angles is substantially smaller (63.5° and 71.8°).

Experimental

Complexes **1** and **2** were prepared according to the known procedure.[6]

Preparation of $Ph_2CH_2[Cr(CO)_3]_2$ (3). A mixture of $Cr(CO)_6$ (1 g, 4.65 mmol) and diphenylmethane (0.5 g, 3 mmol) refluxed for 6 h in an argon flow in a mixture of diglyme (50 mL) and heptane (10 mL). After cooling, the solvent was removed *in vacuo*. The residue was chromatographed on a column packed with Al_2O_3 with a 1:1 CH_2Cl_2—petroleum ether mixture. $Ph_2CH_2Cr(CO)_3$ (325 mg, 60 %) was isolated from the first yellow band, and $Ph_2CH_2[Cr(CO)_3]_2$ (**3**) (180 mg, 14 %) was isolated from the second yellow band. Complex **3** was recrystallized from a 1:10 CH_2Cl_2—heptane mixture, m.p. 143—145 °C (with decomposition). Found (%): C, 51.69; H, 2.81; Cr, 23.69. $C_{19}H_{12}Cr_2O_6$. Calculated (%): C, 51.83; H, 2.75; Cr, 23.62.

X-ray structural study. Crystals of **2** are triclinic, at −115 °C, a = 9.544(3), b = 16.699(5), c = 23.881(7) Å, α = 91.01(2), β = 95.98(2), γ = 105.77(2)°, V = 3638(2) Å^3, d_{calc} = 2.088 g cm^{-3}, Z = 4, space group $P\bar{1}$. Crystals of **3** are monoclinic, at 20 °C, a = 13.050(3), b = 7.464(2), c = 18.132(4) Å, β = 91.36(3)°, V = 1765.7(9) Å^3, d_{calc} = 1.656 g cm^{-3}, Z = 4, space group $P2_1/c$. The unit-cell parameters and intensities of 12483 and 5437 independent reflections were measured on an automated Siemens P3/PC diffractometer (−115 °C, λ(Mo-$K\alpha$) radiation, graphite monochromator, $\theta/2\theta$ scanning technique, $\theta \le 25°$) and a CAD-4 Enraf-Nonius diffractometer (20 °C, λ(Mo-Kα) radiation, graphite monochromator, ω/θ = 1.2, $\theta \le 31°$) for **2** and **3**, respectively.

The structures were solved by the direct method and refined by the full-matrix least-squares method, first isotropically and then anisotropically. Hydrogen atoms were located from the electron density syntheses and included in the refinement with isotropic thermal parameters. The final values of R factors are as follows: R = 0.0584 and 0.0306, R_w = 0.0723 and 0.0379 using 8576 and 3645 reflections with $I > 3\sigma(I)$ (for **2** and **3**, respectively). All calculations were performed on an IBM PC computer using the SHELXTL PLUS program package (PC version).[13] The coordinates for nonhydrogen atoms are given in Tables 5 and 6.

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