Organometallic Chemistry

Mononuclear and binuclear tricarbonylchromium complexes of aryl-substituted [2.2]paracyclophanes

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The complexation reactions of monoaryl- and diaryl-substituted [2.2]paracyclophanes with $(NH_3)_3Cr(CO)_3$ have been studied. The aromatic rings of [2.2]paracyclophane are more favorable for coordination than aryl substituents. This leads to the regioselective formation of the corresponding mono- or binuclear tricarbonylchromium complexes. In some cases, the tricarbonylchromium group is coordinated to the aryl ring of the substituent to form (in low yields) the corresponding mononuclear complex or binuclear complexes with both the aromatic ring of paracyclophane and the aryl ring of the substituent involved in coordination. The structure of such complex, namely, [4-(η^6-2,4,6-trimethylphenyl)-11-16-η^6-[2.2]paracyclophane]bis[tricarbonylchromium(0)], was confirmed by X-ray diffraction study.

Key words: aryl-substituted [2.2]paracyclophanes, tricarbonylchromium complexes; complexation, regioselectivity; X-ray diffraction study.

Much research has been devoted to the peculiarities of complexation of the $Cr(CO)_3$ group with simple aromatic and polyaromatic ligands that contain several different aromatic rings, which are able to participate in coordination.[1—6] The reactivities and methods for the synthesis of arenetricarbonylchromium complexes of condensed and noncondensed aromatic compounds (including heterocyclic compounds), such as diphenyl,[2] 1,3,5-triphenylbenzene,[3] 9-mono- and 9,10-diphenylanthracenes,[4] di- and triphenyl-substituted pyridines,[5] triphenylphosphine,[6] *etc.*, were studied in detail. The use of the electron-withdrawing $Cr(CO)_3$ group made it possible to develop an efficient procedure for revealing the difference in the π-donor ability of aromatic rings, in particular, its decrease in the series triphenylphosphine > benzene ≫ pyridine.[3] It was also noted that the stability of arenetricarbonylchromium complexes decreases in the series C_6Me_6 > Mes > $Me_2NC_6H_5$ ≫ xylene > toluene ≈ benzene > chlorobenzene ≫ naphthalene.[1]

[2.2]Paracyclophane (1) is a conformationally rigid macrocycle, which consists of two benzene rings fixed by two ethylene bridges, due to which the steric strain of the molecule occurs. The steric strain causes a distortion of the aromatic nuclei, bond angles, and bond lengths and leads to an interaction between the π-electron clouds of the aromatic rings. In this connection, [2.2]paracyclophane is an attractive model for studying interactions with acceptors. However, the reactivities of the aromatic rings of [2.2]paracyclophane compared to those of ordinary arenes have not been studied systematically within the framework of the unified molecular

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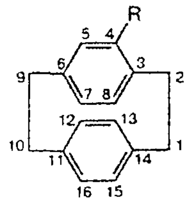
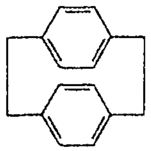
system. Our work was devoted to solution of this problem. The preliminary results have been reported previously.[7,8]

The mononuclear tricarbonylchromium complex **2** of [2.2]paracyclophane[9,10] and complexes of some its derivatives, such as polymethyl-,[11] carboxymethyl-,[12] and 4,7-dialkoxy[2.2]paracyclophanes,[12] have been reported in the literature. The formation of binuclear complexes was observed only in the case of unsubstituted [2.2]paracyclophane (complex **3**) as well as in going to more layered (polydeck) cyclophanes.[10]





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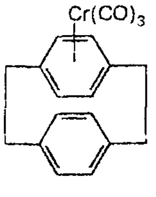

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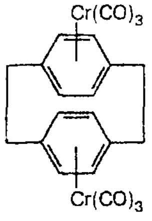
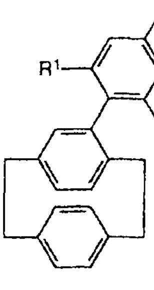


3

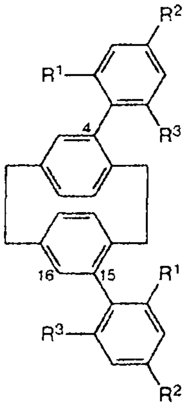
The complexation reactions have been studied also for derivatives of [2.2]paracyclophane-1,9-diene whose aromatic rings are even more substantially distorted than those in paracyclophane, which contains saturated bridges. The reactions of 4,7-dimethoxy- or 4,7-di-(*tert*-butoxy)[2.2]paracyclophane-1,9-dienes yielded two mononuclear aryl complexes. The complex coordinated through the unsubstituted ring predominates.[13] Studies of the regioselectivity of complexation of 1,2:9,10-dibenzo[2.2]paracyclophane-1,9-diene and its 4′,5′,4″,5″-tetrakis(*p*-*tert*-butylphenyl) derivative demonstrated[14] that predominantly monocoordination to the ring of cyclophane occured (the yields of the resulting complexes were 44 and 38%, respectively). For all the compounds under study, the reactions with the use of the threefold excess of $(Et_3CN)_3Cr(CO)_3$ afforded binuclear complexes with the participation of both rings of cyclophane (the yields were 36 and 5%, respectively). In none of the cases reported in Ref. 14 was complexation with the participation of the aromatic rings of the substituents observed.[14]

Results and Discussion

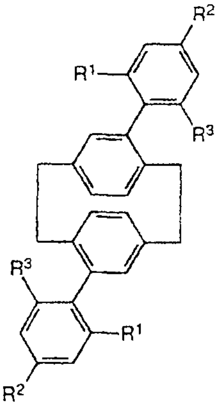
It was of interest to study complexation of derivatives of [2.2]paracyclophane, which contain several centers to which the electron-withdrawing $Cr(CO)_3$ group could be coordinated. For this purpose, we synthesized ligands **4—6**, **7a**, **8a,b**, and **9b**, which contain different aryl substituents, using a convenient procedure we developed[15] for the introduction of one or two aryl groups into the [2.2]paracyclophane molecule by cross-coupling.



4—6



7a, 8a



8b, 9b

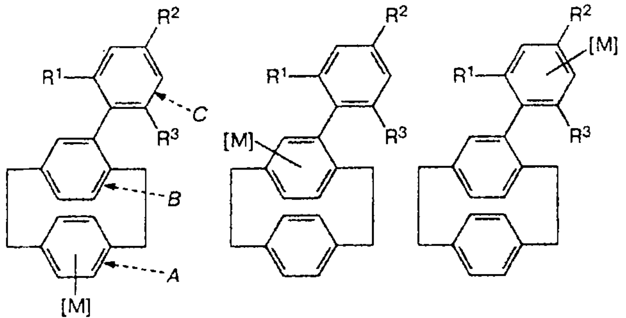
4, 7a: $R^1 = R^3 = H$, $R^2 = Me$
5, 8a,b: $R^1 = R^3 = H$, $R^2 = OMe$
6, 9b: $R^1 = R^2 = R^3 = Me$

Regioselectivity of complexation of [2.2]paracyclophane derivatives with $(NH_3)_3Cr(CO)_3$. Several methods are known for the preparation of tricarbonylchromium complexes of [2.2]paracyclophane. An analysis of these methods demonstrated that the use of $Cr(CO)_6$ (in diglyme,[10,12] in a Bu_2O/THF mixture,[13] or in ligroin under irradiation[16]) makes it possible to prepare predominantly mononuclear complexes with the unsubstituted ring of paracyclophane involved in coordination. The use of $(Et_3CN)_3Cr(CO)_3$ allows one to obtain mono- and binuclear complexes with the participation of the substituted or unsubstituted ring of paracyclophane.[13,14]

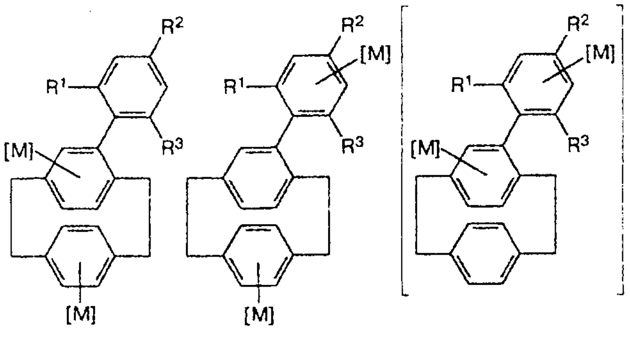
In this work, we used $(NH_3)_3Cr(CO)_3$ for introducing the $Cr(CO)_3$ group. The reactions were carried out in boiling dioxane. It appeared that the reaction of $(NH_3)_3Cr(CO)_3$ with [2.2]paracyclophane **1** afforded mononuclear complex **2** (the yield was 8.5%) and binuclear complex **3** (the yield was 80%). According to the published data,[8] the reaction, which was carried out with the use of $Cr(CO)_6$, afforded complex **3** in a yield of no more than 8% even when the duration of the reaction was increased or a large excess of $Cr(CO)_6$ was used.

To study the regularities of complexation in the series of aryl-substituted paracyclophanes, we used initially monoaryl derivatives **4—6**. These compounds contain three fragments, which are potentially able to participate in coordination, namely, the unsubstituted ring of paracyclophane (*A*), the substituted ring of paracyclophane (*B*), and the aryl ring of the substituent (*C*).

Therefore, different modes of coordination of one or two tricarbonylchromium groups are possible due to which several types of mononuclear (**A**, **B**, and **C**) and binuclear (**AB**, **AC**, and **BC**) complexes (**10**—**12**) can be formed (Table 1).



A **B** **C**



AB **AC** **BC**

(was not detected)

[M] = $Cr(CO)_3$
10A, **10AB**: $R^1 = R^3 = H$, $R^2 = Me$
11A, **11AB**, **11B**: $R^1 = R^3 = H$, $R^2 = OMe$
12A, **12AB**, **12AC**, **12C**: $R^1 = R^2 = R^3 = Me$

It was established that in the case of compound **4**, the reaction yielded two complexes, namely, mononuclear complex **10A** and binuclear complex **10AB**. The coordination of one $Cr(CO)_3$ group occurs regioselectively to the unsubstituted ring of [2.2]paracyclophane. In binuclear complex **10AB**, chromium is coordinated to both rings of cyclophane. The reaction products with the participation of the aryl ring of the substituent were not detected.

In going to compound **5**, we also found that the reaction with $(NH_3)_3Cr(CO)_3$ yielded the corresponding mononuclear and binuclear π-complexes (**11A** and **11AB**, respectively). However, in this case we also succeeded in isolating mononuclear complex **11B** in which the metal atom is coordinated to the substituted ring of paracyclophane. In this reaction, we also did not detect products of coordination of $Cr(CO)_3$ to the *exo*-aryl ring. It should be noted that complex **11A** predominated over the second mononuclear complex. This regioselectivity of complexation with the participation of the unsubstituted ring was observed previously for 4,7-dialkyloxy[2.2]paracyclophanes.[13] The yields of the corresponding binuclear complexes **10AB** and **11AB** were increased substantially as the excess of $(NH_3)_3Cr(CO)_3$ was increased.

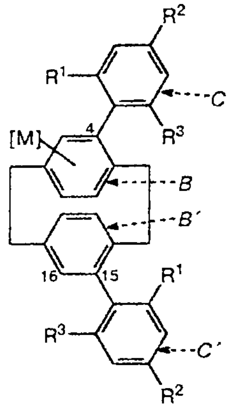
Table 1. Conditions of the reactions of monoaryl-substituted [2.2]paracyclophanes **4**—**6** (L) with $(NH_3)_3Cr(CO)_3$ ("Cr") (dioxane, 100 °C) and the yields of the mononuclear and binuclear complexes

L	«Cr»/L	Duration of the reaction/h	Product	Yields of complexes of different types (%)				
				A	AB	B	AC	C
4	1 : 1	4	**10**	46	24	—	—	—
	2 : 1	0.5		45	45	—	—	—
	3 : 1	1		17	63	—	—	—
5	1 : 1	0.5	**11**	29	9	14	—	—
	2 : 1	0.5		38	33	19	—	—
	3 : 1	0.3		10	64	6	—	—
6	2 : 1	0.5	**12**	53	1.6	—	2.7	—
	3 : 1	0.3		45	0.9	—	3.6	—
	2 : 1	1		66	4.6	—	5.1	0.76

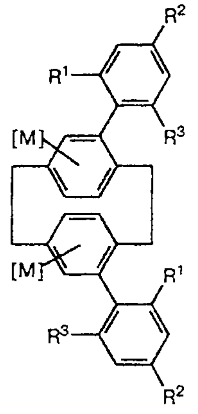
The reaction of compound **6** with $(NH_3)_3Cr(CO)_3$ yielded predominantly mononuclear complex **12A** with the $Cr(CO)_3$ group coordinated to the unsubstituted ring along with three other complexes. One of the two binuclear complexes (**12AB**) has a structure similar to the structures observed in the above-considered cases. However, complex **12AB** was obtained in a substantially lower yield due to steric hindrances caused by bulky mesityl substituents. In addition, complexes with the participation of the aryl substituent, namely, mononuclear complex **12C** and binuclear complex **12AC** in which the second $Cr(CO)_3$ group is coordinated to the unsubstituted ring of paracyclophane, were isolated. The yields of the binuclear complexes, **12AB** and **12AC**, were no more than 3—5%. The yield of mononuclear complex **12C** was less than 1%. It should be noted that, unlike the reactions with ligands **4** and **5**, the yields of the binuclear complexes remained unchanged when a larger excess of $(NH_3)_3Cr(CO)_3$ was used.

The general character of the regularities we observed was confirmed using the reaction of isomeric 4,15- and 4,16-diaryl derivatives of [2.2]paracyclophane as examples. These compounds have only two types of aromatic rings (*B* and *C*) due to high symmetry and, therefore, they can form mononuclear complexes (**13**—**16**) of types **B** and **C** and binuclear complexes (**13**) of types **BB′**, **BC**, and **BC′** (the 4,15-isomers are shown below). The data on the reactivities of the diaryl-substituted ligands with $(NH_3)_3Cr(CO)_3$ are given in Table 2.

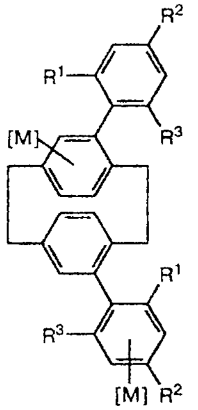
The reaction of *p*-tolyl derivative **7a** with $(NH_3)_3Cr(CO)_3$ yielded mononuclear complex **13B** in which the $Cr(CO)_3$ group is coordinated to the cyclophane ring. Two $Cr(CO)_3$ fragments are also coordinated predominantly to the aromatic rings of paracyclophane to form product **13BB′**. In addition, bi-



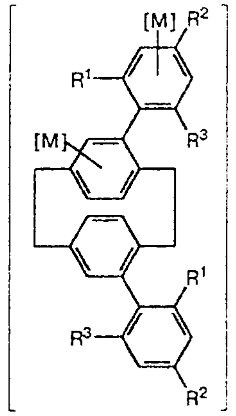
B



BB′



BC′



BC

(was not detected)

[M] = $Cr(CO)_3$

4,15-isomers:

13B, **13BBr′**, **13BCr′**: R¹ = R³ = H, R² = Me

14B: R¹ = R³ = H, R² = OMe

4,16-isomers:

15B: R¹ = R³ = H, R² = OMe

16B: R¹ = R² = R³ = Me

nuclear complex **13BC′**, which contains the chromium atom in the *exo*-aryl ring, was isolated in low yield.

Unfortunately, we failed to identify unambiguously a number of products of the reaction of compounds **8a,b** with $(NH_3)Cr(CO)_3$ because of their very poor solubility. Products isolated in pure form are mononuclear complexes **14B** and **15B** in which the $Cr(CO)_3$ group is coordinated to the ring of paracyclophane.

In the case of dimesityl-substituted derivative **9b**, several different complexes were formed in low yields. However, we succeeded in isolating only mononuclear complex **16B** in which the $Cr(CO)_3$ group is coordinated to the ring of paracyclophane. The structure of this complex was established based on the data of ¹H NMR spectroscopy.

Table 2. Conditions of the reactions of diaryl-substituted [2.2]paracyclophanes **7a**, **8a**,**b**, and **9a** (L) with $(NH_3)_3Cr(CO)_3$ ("Cr") (dioxane, 100 °C) and the yields of the mononuclear and binuclear complexes

L	«Cr»/L	Duration of the reaction/h	Product	Yields of complexes of different types (%)		
				B	**BB′**	**BC′**
7a	2 : 1	2	**13**	21	50	3
8a	3 : 1	6	**14**	43	*	—
	5 : 1	1		53	*	—
8b	3 : 1	0.5	**15**	31	*	—
	5 : 1	7		Traces	*	—
9b	3 : 1	1	**16**	37	Traces	Traces

* In the reaction mixture, poorly soluble product were formed. We suggested that they are binuclear complexes with the **BB′** type of coordination.

It was found that the mononuclear and binuclear complexes in which the $Cr(CO)_3$ fragment is coordinated to the aromatic rings of [2.2]paracyclophane are more stable to light and atmospheric oxygen both in solutions and in the solid state and have a deeper color compared to the complexes in which the $Cr(CO)_3$ group is coordinated to the aryl ring of the substituent.

Based on the data obtained, it can be concluded that the $Cr(CO)_3$ group exhibits higher affinity for the aromatic system of paracyclophane than for ordinary arene. Apparently, a distortion of the molecule (as suggested previously[9,10,16]) affects substantially the coordinating ability. A comparative study of mononuclear complexes of various polyarenes (including [2.2]paracyclophane) demonstrated[17] that an analogous dependence was observed also for η^6-arene complexes of nickel.

Apparently, the complexation is regioselective due to the spatial proximity of the two aromatic rings of cyclophane, *i.e.*, due to the fact that a trans-annular interaction between their HOMOs can occur. In this case, perturbation of the above-mentioned orbitals occurs, which leads to the formation of two new levels, the higher of which (HOMO of paracyclophane) corresponds to an inter-ring interaction between π-orbitals in the antiphase, *i.e.*, to antibonding. In our subsequent work,[18] the results of the theoretical analysis of the donor properties of the arene rings of [2.2]paracyclophane with respect to the $Cr(CO)_3$ fragment are discussed.

Determination of the structures of mononuclear and binuclear complexes by ¹H NMR spectroscopy. The complexes obtained were isolated in the individual form and were characterized by the data of elemental analysis and ¹H NMR spectra. ¹H NMR spectroscopy is a very convenient and informative method for identifying these complexes. The signals of the aromatic protons of paracyclophane are observed at higher field (δ ~6.5) than the signals of the ordinary aromatic protons due to mutual shielding. In addition, the protons of each aromatic ring manifest themselves in characteristic multip-

Table 3. ^{1}H NMR spectra of mononuclear and binuclear tricarbonylchromium complexes of monoaryl-substituted paracyclophanes

Complex	Solvent	δ (*J*)				
		R$_n$ (s, 3 H)	–CH$_2$–CH$_2$– (m)	Ring *A*	Ring *B*	Ring *C*
10A	Acetone-d$_6$	2.37	3.0–3.50 (7 H); 3.50–3.80 (1 H)	4.87 (dd, 1 H, ^3J, ^4J)*; 5.08 (m, 2 H); 5.15 (dd, 1 H, ^3J, ^4J)	6.90 (dd, 1 H, ^3J, ^4J); 7.00 (d, 1 H, ^4J); 7.05 (d, 1 H, ^3J)	7.32, 7.50 (both d, 2 H each)
10AB	Acetone-d$_6$	2.41	2.50–3.75 (8 H)	5.08 (dd, 1 H, ^3J, ^4J); 5.48–5.56 (m, 2 H); 5.64 (dd, 1 H, ^3J, ^4J)	5.43 (dd, 1 H, ^3J, ^4J); 5.57 (d, 1 H, ^3J); 5.76 (d, 1 H, ^4J)	7.34, 7.58 (both d, 2 H each)
11A	Acetone-d$_6$	3.86	2.20–3.30 (7 H); 3.63 (1 H)	4.85 (dd, 1 H); 5.03–5.12 (m, 2 H); 5.20 (dd, 1 H)	6.89 (dd, 1 H, ^3J, ^4J); 6.96 (d, 1 H, ^4J); 7.01 (d, 1 H, ^3J)	7.08, 7.54 (both d, 2 H each)
11AB	Acetone-d$_6$	3.90	2.28–3.57 (8 H)	5.08 (dd, 1 H, ^3J, ^4J); 5.48–5.58 (m, 2 H); 5.62 (dd, 1 H, ^3J, ^4J)	5.41 (dd, 1 H, ^3J, ^4J); 5.55 (d, 1 H, ^3J); 5.74 (d, 1 H, ^4J)	7.09, 7.63 (both d, 2 H each)
11B	Acetone-d$_6$	3.85	2.65–3.40 (8 H)	6.70 (m, 2 H); 6.97 (m, 2 H)	4.97 (dd, 1 H, ^3J, ^4J); 5.06 (d, 1 H, ^3J); 5.31 (d, 1 H, ^4J)	7.05, 7.50 (both d, 2 H each)
12A	CDCl$_3$	1.85, 2.34, 2.75	2.62–3.50 (8 H)	4.60 (d, 1 H); 4.70 (d, 1 H); 4.95 (dd, 2 H)	6.70 (dd, 1 H, ^3J, ^4J); 6.80 (d, 1 H, ^4J); 6.84 (d, 1 H, ^3J)	6.92, 7.08 (both s, 1 H each)
12AB	CDCl$_3$	2.32, 2.39, 2.82	2.55–3.38 (8 H)	4.59 (d, 1 H, ^3J); 5.05 (d, 1 H, ^3J); 5.28 (dd, 2 H)	4.92 (d, 1 H); 5.15 (d, 1 H); 5.55 (d, 1 H)	7.00, 7.08 (both s, 1 H each)
12C	CDCl$_3$	1.65, 2.24, 2.72	2.56–3.47 (8 H)	6.25–6.40 (m, 4 H)	6.65 (s, 1 H); 6.82 (d, 2 H)	4.95, 5.05 (both s, 1 H each)
12AC	CDCl$_3$	1.70, 2.27, 2.71	2.62–3.53 (8 H)	4.49 (d, 1 H); 4.57 (d, 1 H); 4.98 (dd, 2 H)	6.64 (s, 2 H); 6.90 (s, 1 H)	5.00, 5.05 (both s, 1 H each)

* For all the complexes listed, the spin-spin coupling constants between the aromatic protons have standard values: ^3J = 7.8–8.0 Hz; and ^4J = 1.8–2.0 Hz.

lets. Complexation leads to the upfield shift of the protons of the coordinated ring by 1.5–2.0 ppm, which is typical of arenes and was observed previously in the case of derivatives of [2.2]paracyclophane. The signals of the second ring of paracyclophane undergo only a slight downfield shift (by 0.1–0.2 ppm). Both effects have been observed previously for derivatives of [2.2]paracyclophane.[10,13,16,19]

A change in the chemical shifts and multiplicity of the signals of the aromatic protons can be observed for a series of mono- and binuclear complexes **12** of 4-mesitylene[2.2]paracyclophane (Table 3). For example, when the first Cr(CO)$_3$ group was introduced into the unsubstituted ring of paracyclophane (type **A**), the signals of its protons are observed at δ 4.6–5.0. In the region of the signals of aromatic protons, two singlets from the protons of the mesitylene rings and the ABX system of the substituted ring of paracyclophane are clearly observed. When the second Cr(CO)$_3$ group was introduced into the second ring of paracyclophane (type **AB**), only the signals of the two aromatic hydrogen atoms of the substituent persist in the region of aromatic protons, whereas the signals of the protons of the rings of paracyclophane shift upfield (at δ 4.5–5.5). Based on the values of the spin-spin coupling constants and the data on double homonuclear resonance, the complete assignment of all the signals of this group was made. When the Cr(CO)$_3$ group is coordinated to the mesitylene substituent (type **C**), only two singlets of the mesitylene aromatic protons are observed at high field, whereas the signals of the protons of the rings of paracyclophane are observed in the typical region. In the spectrum of the binuclear complex with the participation of the unsubstituted ring of cyclophane and the aryl substituent (type **AC**), two singlets and the signals of the protons of the unsubstituted ring are clearly seen at higher field, whereas a somewhat different pattern, which corresponds to the ABX system of the substituted ring, is observed in the region of aromatic protons. The ^{1}H NMR spectra of complexes **10**–**16** are given in Tables 3 and 4.

Crystal structure of [4-(η^6-2,4,6-trimethylphenyl)-11-16-η^6-[2.2]paracyclophane]bis[tricarbonylchromium(0)] (12AC). The structure of molecule **12AC** is shown in Fig. 1. The bond lengths and the principal bond angles are listed in Table 5. On the whole, the geometric charac-

Table 4. ^{1}H NMR spectra of mononuclear and binuclear tricarbonylchromium complexes of diaryl-substituted [2.2]paracyclophanes

Complex	Solvent	δ (*J*)				
		R_n (s)	$-CH_2-CH_2-$ (m, 8 H)	Ring *B*	Ring *B'*	Ring *C* (*C'*)
13B	Acetone-d_6	2.43 (6 H)	2.50—3.50	4.95 (d, 1 H, ^3J); 5.28 (dd, 1 H, ^3J, ^4J); 5.49 (d, 1 H, ^4J)	6.85 (d, 1 H, ^3J); 7.10 (dd, 1 H, ^3J, ^4J); 7.19 (d, 1 H, ^4J)	7.33, 7.50 (both d, 4 H each)
13BB'	Acetone-d_6	2.42 (6 H)	2.50—3.40	5.14 (d, 2 H, ^3J); 5.66 (dd, 2 H, ^3J); 5.89 (d, 2 H, ^4J)		7.34, 7.56 (both d, 4 H each)
13BC'	Acetone-d_6	2.28 (3 H); 2.43 (3 H)	2.54—3.65	5.09 (d, 1 H, ^3J); 5.30 (dd, 1 H, ^3J, ^4J); 5.48 (d, 1 H, ^4J)	6.79 (d, 1 H, ^3J); 7.10 (dd, 1 H, ^3J, ^4J); 7.20 (d, 1 H, ^4J)	5.62 (dd, 1 H, ^3J, ^4J); 5.77 (dd, 1 H, ^3J, ^4J); 5.90 (dd, 1 H, ^3J, ^4J); 6.53 (dd, 1 H, ^3J, ^4J); 7.33 (d, 2 H); 7.50 (d, 2 H)
14B	C_6D_6	3.37 (3 H); 3.45 (3 H)	1.92—3.22	4.15 (dd, 1 H, ^3J, ^4J); 4.65 (d, 1 H, ^3J); 4.69 (d, 1 H, ^4J)	6.35 (dd, 1 H, ^3J, ^4J); 6.65 (d, 1 H, ^3J); 6.70 (d, 1 H, ^4J)	6.82, 6.95, 7.20, 7.25 (all d, 2 H each)
15B	C_6D_6	3.37 (3 H); 3.45 (3 H)	1.88—3.47	4.26 (d, 1 H, ^3J); 4.50 (dd, 1 H, ^3J, ^4J); 4.65 (d, 1 H, ^4J)	6.45 (d, 1 H, ^3J); 6.55 (dd, 1 H, ^3J, ^4J); 6.67 (d, 1 H, ^4J)	6.85, 6.97, 7.22, 7.26 (all d, 2 H each)
16B	C_6D_6	2.08 (3 H); 2.24 (3 H); 2.38 (3 H); 2.53 (3 H); 2.61 (3 H); 2.70 (3 H)	1.80—2.90	4.56 (dd, 1 H); 4.75 (d, 1 H); 5.29 (s, 1 H)	6.15 (br.s, 2 H); 6.50 (d, 1 H)	6.75—7.06 (m, 4 H)

* For all the complexes listed, the spin-spin coupling constants between the aromatic protons have standard values: ^3J = 7.8—8.0 Hz; and ^4J = 1.8—2.0 Hz.

teristics of the aromatic rings of the paracyclophane fragment are close to the corresponding values in noncoordinated paracyclophanes[20,21] and in tricarbonyl(3-8-η^6-[2.2]paracyclophane)chromium(0).[22] The C(3)—C(8) and C(11)—C(16) rings adopt a flattened boat conformation. The C(3), C(6), C(11), and C(14) atoms deviate from the corresponding four-atom planar bases of the rings toward the inner cavity of the paracyclophane skeleton by 0.200, 0.154, 0.145, and 0.179 Å, respectively. The deviations are close to the corresponding values for noncoordinated paracyclophanes.

A peculiarity of the geometric structure of molecule **12AC** is the difference in the torsion angles about the dimethylene bridges (the C(3)—C(2)—C(1)—C(14) and C(6)—C(9)—C(10)—C(11) angles are 10.7° and 0.1°, respectively), which is, apparently, due to the presence of the mesityltricarbonylchromium substituent. This, in turn, leads to a substantial increase in the C(5)—C(4)—C(7)—C(8)/C(12)—C(13)—C(15)—C(16) dihedral angle, which is formed by the planar four-atom bases of the aromatic rings. As a result, this angle is equal to 6.4°, *i.e.*, it is substantially larger than the analogous values observed previously in the molecules of paracyclophane derivatives that contain two bridges and do not contain substituents in the dimethylene chains. According to the published data (see, for example, Refs. 20 and 21), this

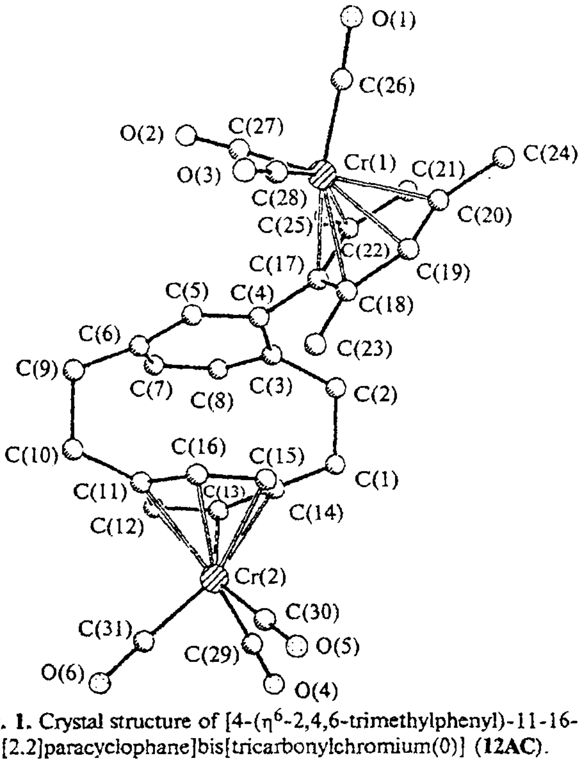


Fig. 1. Crystal structure of [4-(η^6-2,4,6-trimethylphenyl)-11-16-η^6-[2.2]paracyclophane]bis[tricarbonylchromium(0)] (**12AC**).

Table 5. Bond lengths (*d*) and principal bond angles (ω) in molecule **12AC**

Bond	*d*/Å	Angle	ω/deg	Bond	*d*/Å	Angle	ω/deg
Cr(1)—C(17)	2.247(9)	C(26)—Cr(1)—C(27)	88.3(5)	C(2)—C(3)	1.507(15)	C(12)—C(13)—C(14)	120.6(8)
Cr(1)—C(18)	2.241(11)	C(26)—Cr(1)—C(28)	87.4(5)	C(3)—C(4)	1.416(12)	C(1)—C(14)—C(13)	122.1(9)
Cr(1)—C(19)	2.214(12)	C(27)—Cr(1)—C(28)	88.2(5)	C(3)—C(8)	1.396(13)	C(1)—C(14)—C(15)	120.3(9)
Cr(1)—C(20)	2.264(11)	C(29)—Cr(2)—C(30)	87.5(5)	C(4)—C(5)	1.384(15)	C(13)—C(14)—C(15)	116.8(9)
Cr(1)—C(21)	2.227(10)	C(29)—Cr(2)—C(31)	88.1(5)	C(4)—C(17)	1.502(12)	C(14)—C(15)—C(16)	120.1(9)
Cr(1)—C(22)	2.226(8)	C(30)—Cr(2)—C(31)	88.1(5)	C(5)—C(6)	1.405(13)	C(11)—C(16)—C(15)	120.8(8)
Cr(1)—C(26)	1.823(12)	C(2)—C(1)—C(14)	111.7(10)	C(6)—C(7)	1.388(12)	C(4)—C(17)—C(18)	125.8(9)
Cr(1)—C(27)	1.806(12)	C(1)—C(2)—C(3)	113.3(9)	C(6)—C(9)	1.505(15)	C(4)—C(17)—C(22)	115.6(8)
Cr(1)—C(28)	1.842(11)	C(2)—C(3)—C(4)	123.5(8)	C(7)—C(8)	1.398(16)	C(18)—C(17)—C(22)	118.6(8)
Cr(2)—C(11)	2.357(11)	C(2)—C(3)—C(8)	118.7(8)	C(9)—C(10)	1.574(17)	C(17)—C(18)—C(19)	119.2(9)
Cr(2)—C(12)	2.198(11)	C(4)—C(3)—C(8)	116.9(9)	C(10)—C(11)	1.513(16)	C(17)—C(18)—C(23)	122.2(8)
Cr(2)—C(13)	2.173(11)	C(3)—C(4)—C(5)	119.0(8)	C(11)—C(12)	1.412(12)	C(19)—C(18)—C(23)	118.6(8)
Cr(2)—C(14)	2.329(10)	C(3)—C(4)—C(17)	118.6(9)	C(11)—C(16)	1.386(14)	C(18)—C(19)—C(20)	124.0(9)
Cr(2)—C(15)	2.197(10)	C(5)—C(4)—C(17)	122.4(8)	C(12)—C(13)	1.399(15)	C(19)—C(20)—C(21)	117.1(9)
Cr(2)—C(16)	2.231(10)	C(4)—C(5)—C(6)	122.2(8)	C(13)—C(14)	1.412(14)	C(19)—C(20)—C(24)	123.5(9)
Cr(2)—C(29)	1.826(12)	C(5)—C(6)—C(7)	116.3(9)	C(14)—C(15)	1.411(13)	C(21)—C(20)—C(24)	119.4(9)
Cr(2)—C(30)	1.840(13)	C(5)—C(6)—C(9)	122.6(8)	C(15)—C(16)	1.415(15)	C(20)—C(21)—C(22)	121.9(9)
Cr(2)—C(31)	1.829(14)	C(7)—C(6)—C(9)	119.9(8)	C(17)—C(18)	1.417(13)	C(17)—C(22)—C(21)	119.2(8)
O(1)—C(26)	1.174(14)	C(6)—C(7)—C(8)	120.9(9)	C(17)—C(22)	1.451(14)	C(17)—C(22)—C(25)	123.3(8)
O(2)—C(27)	1.169(14)	C(3)—C(8)—C(7)	120.6(8)	C(18)—C(19)	1.420(14)	C(21)—C(22)—C(25)	117.5(9)
O(3)—C(28)	1.157(13)	C(6)—C(9)—C(10)	114.7(9)	C(18)—C(23)	1.498(14)	Cr(1)—C(26)—O(1)	176.5(11)
O(4)—C(29)	1.168(14)	C(9)—C(10)—C(11)	110.9(9)	C(19)—C(20)	1.376(16)	Cr(1)—C(27)—O(2)	178.2(10)
O(5)—C(30)	1.158(15)	C(10)—C(11)—C(12)	121.9(9)	C(20)—C(21)	1.428(14)	Cr(1)—C(28)—O(3)	179.0(10)
O(6)—C(31)	1.162(17)	C(10)—C(11)—C(16)	119.2(8)	C(20)—C(24)	1.498(14)	Cr(2)—C(29)—O(4)	178.9(10)
C(1)—C(2)	1.575(16)	C(12)—C(11)—C(16)	117.8(9)	C(21)—C(22)	1.417(13)	Cr(2)—C(30)—O(5)	178.6(10)
C(1)—C(14)	1.496(14)	C(11)—C(12)—C(13)	120.4(9)	C(22)—C(25)	1.497(13)	Cr(2)—C(31)—O(6)	177.2(11)

angle is generally less than 2°, and it is never more than 3°. The increase in the dihedral angle in the molecule of complex **12AC** is, apparently, caused by the steric repulsion between the Me group (the C(23) atom) and the coordinated ring of paracyclophane. The C(15)...C(23) nonbonded interatomic distance is 3.393 Å.

The C(3)—C(2) and C(6)—C(9) vectors are inclined to the C(4)C(5)C(7)C(8) plane at angles of 24.9° and 22.2°, respectively. The C(1)—C(14) and C(10)—C(11) vectors are inclined to the C(12)C(13)C(15)C(16) plane at almost the same angles (22.4° and 22.0°, respectively). However, the bond angles at the C(2) (113.3(9)°) and C(9) atoms (114.7(9)°) are somewhat larger than the angles at the C(1) and C(10) atoms (111.7(10)° and 110.9(9)°, respectively) although these differences are close to the experimental error.

The coordinated mesityl ring is planar (to within 0.01 Å) and forms the dihedral angle of 122.4° with the C(4)C(5)C(7)C(8) plane. The C(3)—C(4)—C(17)—C(18) torsion angle is 116.7°.

Experimental

The ^{1}H NMR spectra were recorded on Bruker WP-200-SY and Bruker AMX-400 spectrometers (200.13 and 400.13 MHz, respectively). $SiMe_4$ or the signals from the residual protons of the solvents with the known chemical shifts were used as the internal standard. The compositions of the reaction mixtures were analyzed by TLC on Silufol UV-254 plates with the use of a luminescence indicator. Silpearl UV-254, Chemapol L 40/100, and Kieselgel 60 (Merck) silica gels were used for preparative chromatographic separation of the mixtures.

Dioxane was boiled with HCl (100 mL of HCl per liter of dioxane), shaken over KOH, and twice distilled over Na in the presence of benzophenone under a stream of argon. Benzene was boiled for 3 h and distilled over Na in the presence of benzophenone under a stream of argon. Diethyl ether was kept over KOH for 2—3 days, boiled over metallic Na in the presence of benzophenone, and distilled under a stream of argon. Chloroform was successively distilled over Na_2CO_3 and P_2O_5. Pentane and hexane were boiled over metallic Na for 5 h and distilled under a stream of argon.

Reaction of [2.2]paracyclophane (1) with $(NH_3)_3Cr(CO)_3$. $(NH_3)_3Cr(CO)_3$ (0.41 g, 2.2 mmol) was added to a suspension of compound **1** (0.21 g, 1 mmol) in dioxane (5 mL). The reaction mixture was boiled for 0.5 h (TLC control). A yellow precipitate formed. The reaction mixture was filtered off and the precipitate was treated with warm benzene (2×10 mL). A benzene-insoluble precipitate (0.38 g, 80%) of (3-8-η^6;11-16-η^6-[2.2]paracyclophane)bis[tricarbonylchromium(0)] (**3**) was isolated as a finely crystalline yellow compound, m.p. 180 °C (with decomp.) (published data:[10] m.p. 183 °C (with decomp.)). The filtrates were combined. The solvent was evaporated. The residue was reprecipitated from benzene with pentane, and tricarbonyl(3-8-η^6-[2.2]paracyclophane)chromium(0) (**2**) was obtained as a crystalline yellow compound in a yield of 0.036 g (8.5%), m.p. 185—187 °C (with decomp.) (published data:[9] m.p. 188 °C (with decomp.)).

Reaction of 4-(4-methylphenyl)[2.2]paracyclophane (4) with $(NH_3)_3Cr(CO)_3$. $(NH_3)_3Cr(CO)_3$ (0.39 g, 2.1 mmol) was added to a solution of compound **4** (0.26 g, 0.87 mmol) in boiling dioxane (17 mL). The reaction mixture was boiled for 0.5 h. The course of the reaction was monitored by TLC. The reaction mixture was concentrated. An oily orange residue was separated by column chromatography on SiO_2 (a 3 : 1 benzene—pentane mixture as the eluent). Evaporation of the solvent and reprecipitation of the residue from benzene with pentane gave tricarbonyl[4-(4-methylphenyl)-11-16-η^6-[2.2]paracyclophane]chromium(0) (**10A**) as orange crystals in a yield of 0.166 g (43.9%), m.p. 137—139 °C (with decomp.). Found (%): C, 72.30; H, 4.44; Cr, 12.08. $C_{26}H_{22}CrO_3$. Calculated (%): C, 72.63; H, 4.21; Cr, 12.08. After elution with a 1 : 1 benzene—pentane mixture and evaporation of the solvent, the residue was reprecipitated from THF with pentane, and [4-(4-methylphenyl)-3-8-η^6;11-16-η^6-[2.2]paracyclophane]bis[tricarbonylchromium(0)] (**10AB**) was obtained as a finely crystalline yellow compound in a yield of 0.207 g (41.7%), m.p. 162—164 °C (with decomp.).

Reaction of 4-(4-methoxyphenyl)[2.2]paracyclophane (5) with $(NH_3)_3Cr(CO)_3$. $(NH_3)_3Cr(CO)_3$ (0.206 g, 1.1 mmol) was added to a solution of compound **5** (0.165 g, 0.5 mmol) in dioxane (12 mL). The reaction mixture was boiled for 0.5 h. The course of the reaction was monitored by TLC. Then the reaction mixture was filtered off. The solvent was removed *in vacuo*. The solid residue was treated with $CHCl_3$. The insoluble residue was filtered off. The filtrate was concentrated and chromatographed on silica gel (a 4 : 3 ether—pentane mixture as the eluent). A mixture of two mononuclear complexes was obtained. Found (%): C, 69.25; H, 4.89; Cr, 11.23. $C_{26}H_{22}CrO_4$. Calculated (%): C, 69.32; H, 4.92; Cr, 11.55. Successive recrystallization from benzene—pentane and $CHCl_3$—heptane mixtures gave tricarbonyl[4-(4-methoxyphenyl)-3-8-η^6-[2.2]paracyclophane]chromium(0) (**11B**) as orange crystals in a yield of 0.043 g (19%). The filtrate was concentrated. The oily orange residue was dissolved in benzene. Reprecipitation with pentane gave tricarbonyl[4-(4-methoxyphenyl)-11-16-η^6-[2.2]paracyclophane]chromium(0) (**11A**) as pale-yellow needles in a yield of 0.078 g (38%), m.p. 182—183 °C (with decomp.). The precipitate, which was insoluble in $CHCl_3$, was reprecipitated from dioxane with pentane, and [4-(4-methoxyphenyl)-3-8-η^6;11-16-η^6-[2.2]paracyclophane]bis[tricarbonylchromium(0)] (**11AB**) was obtained as a finely crystalline yellow compound in a yield of 0.107 g (34%), m.p. 175—176 °C (with decomp.).

Reaction of 4-(2,4,6-trimethylphenyl)[2.2]paracyclophane (6) with $(NH_3)_3Cr(CO)_3$. $(NH_3)_3Cr(CO)_3$ (0.21 g, 1.1 mmol) was added to a solution of compound **6** (0.15 g, 0.46 mmol) in dioxane (7 mL). The reaction mixture was boiled for 1 h (TLC control) and filtered off. The filtrate was concentrated. The solid residue was chromatographed on silica gel (a 3 : 4 benzene—pentane mixture as the eluent). The solvent was evaporated. The residue was reprecipitated from benzene with pentane, and tricarbonyl[(2,4,6-trimethylphenyl)-11-16-η^6-[2.2]paracyclophane]chromium(0) (**12A**) was obtained as orange crystals in a yield of 0.136 g (65.6%), m.p. 186—187 °C (with decomp.). Found (%): C, 72.08; H, 5.37; Cr, 11.86. $C_{28}H_{26}CrO_3$. Calculated (%): C, 72.71; H, 5.67; Cr, 11.24. Subsequent elution with a 1 : 1 benzene—pentane mixture gave a mixture of three complexes, which were separated by preparative TLC on Silpearl plates (a 10 : 1 $CHCl_3$—hexane mixture as the eluent). After reprecipitation from benzene with pentane, the fractions with R_f 0.21 gave [4-(η^6-2,4,6-trimethylphenyl)-11-16-η^6-[2.2]paracyclophane]bis[tricarbonylchromium(0)] (**12AC**) as pale-yellow crystals in a yield of 0.014 g (5.1%), m.p. 182—183 °C (with decomp.). After reprecipitation of the residue from benzene with pentane, the fractions with R_f 0.15 gave [4-(2,4,6-trimethylphenyl)-3-8-η^6;11-16-η^6-[2.2]paracyclophane]bis[tricarbonylchromium(0)] (**12AB**) as orange crystals in a yield of 0.012 g (4.6%), m.p. 125—127 °C (with decomp.). After evaporation of the solvent, the fractions with R_f 0.10 gave tricarbonyl[(η^6-2,4,6-trimethylphenyl)[2.2]paracyclophane]chromium(0) (**12C**) as bright-yellow crystals in a yield of 0.0016 g (0.76%).

Reaction of 4,15-di(4-methylphenyl)[2.2]paracyclophane (7a) with $(NH_3)_3Cr(CO)_3$. $(NH_3)_3Cr(CO)_3$ (0.53 g, 2.82 mmol) was added to a solution of compound **7a** (0.5 g, 1.28 mmol) in dioxane (40 mL). The reaction mixture was boiled for 1 h and filtered off. The precipitate, which was formed from the hot solution, was separated and extracted with dioxane in a Soxlet apparatus under an inert atmosphere. Pentane was added to the extract, and [4,15-di(4-methylphenyl)-3-8-η^6;11-16-η^6-[2.2]paracyclophane]bis[tricarbonylchromium(0)] (**13BB′**) was obtained as a finely crystalline orange compound in a yield of 0.30 g (35%). The combined filtrates were concentrated. The residue was chromatographed on silica gel (a 1 : 1 benzene—heptane mixture as the eluent). The solvent was evaporated. The residue was reprecipitated from benzene with pentane, and tricarbonyl[4,15-di(4-methylphenyl)-3-8-η^6-[2.2]paracyclophane]chromium(0) (**13B**) was obtained as orange crystals in a yield of 0.135 g (21%), m.p. 148—150 °C (with decomp.). Found (%): C, 75.79; H, 5.41; Cr, 9.82. $C_{33}H_{28}CrO_3$. Calculated (%): C, 75.55; H, 5.38; Cr, 9.91. Subsequent elution with a 1.0 : 1.0 : 0.1 benzene—heptane—ether mixture followed by evaporation of the solvent and reprecipitation of the residue from benzene with pentane gave [4-(4-methylphenyl),15-(4-η^6-methylphenyl)-3-8-η^6-[2.2]paracyclophane]bis[tricarbonylchromium(0)] (**13BC′**) as yellow crystals in a yield of 0.04 g (5%). The crystals are fairly stable to light and in air.

Reaction of 4,15-di(4-methoxyphenyl)[2.2]paracyclophane (8a) with $(NH_3)_3Cr(CO)_3$. $(NH_3)_3Cr(CO)_3$ (0.28 g, 1.5 mmol) was added to a solution of compound **8a** (0.21 g, 0.50 mmol) in dioxane (4 mL). The reaction mixture was boiled for 6 h and filtered off. The filtrate was concentrated and chromatographed on silica gel (a 1 : 1 pentane—ether mixture as the eluent). The solvent was evaporated. The residue was reprecipitated from benzene with pentane, and tricarbonyl[4,15-di(4-methoxyphenyl)-3-8-η^6-[2.2]paracyclophane]chromium(0) (**14B**) was obtained in a yield of 0.12 g (43%). Found (%): C, 70.99; H, 5.09; Cr, 9.14. $C_{33}H_{28}CrO_5$. Calculated (%): C, 71.21; H, 5.07; Cr, 9.34.

Reaction of 4,16-di(4-methoxyphenyl)[2.2]paracyclophane (8b) with $(NH_3)_3Cr(CO)_3$. The reaction was carried out by a procedure analogous to that described above, starting from compound **8b** (0.021 g) and $(NH_3)_3Cr(CO)_3$ (0.028 g) for 0.5 h. Tricarbonyl[4,16-di(4-methoxyphenyl)-3-8-η^6-[2.2]paracyclophane]chromium(0) (**15B**) was obtained in a yield of 0.085 g (31%), m.p. 180—182 °C (with decomp.).

Reaction of 4,16-di(2,4,6-trimethylphenyl)[2.2]paracyclophane (9b) with $(NH_3)_3Cr(CO)_3$. $(NH_3)_3Cr(CO)_3$ (0.09 g, 0.47 mmol) was added to a solution of compound **9b** (0.05 g, 0.13 mmol) in dioxane (2 mL). The reaction mixture was boiled for 1 h and filtered off. The filtrate was concentrated and chromatographed on silica gel (a 1 : 1 hexane—$CHCl_3$ mixture as the eluent). The solvent was evaporated. The residue was reprecipitated from benzene with pentane, and tricarbonyl[4,16-di(2,4,6-trimethylphenyl)-3-8-η^6-[2.2]paracyclophane]chromium(0) (**16B**) was obtained in a yield of 0.085 g (31%).

X-ray structural analysis of crystal solvate 12AC · $1.5C_6H_6$. Crystals are monoclinic, at −85 °C: a = 10.423(3) Å, b = 23.911(6) Å, c = 14.130(4) Å, β = 107.54(2)°, V = 3358(2) Å^3, Z = 4, d_{calc} = 1.416 g cm^{-3}, space group $P2_1/c$. The unit cell parameters and intensities of 4099 independent reflections were measured on an automated four-circle Syntex $P2_1$ diffractometer (−85 °C, Mo-Kα radiation, graphite monochromator, $\theta/2\theta$ scanning technique, $\theta \le 22°$). The structure was solved by the direct method and refined first isotropically and then anisotropically by the full-matrix least-squares method.

Table 6. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($U_{eq} \times 10^3$) in the structure of **12AC** · 1.5 C_6H_6

Atom	*x*	*y*	*z*	U_{eq}/Å^2
Cr(1)	988(2)	6844(1)	3989(1)	22(1)
Cr(2)	7537(2)	8796(1)	4688(1)	25(1)
O(1)	−1605(7)	6226(3)	3683(5)	42(3)
O(2)	639(7)	7310(3)	5848(5)	38(3)
O(3)	−698(7)	7796(3)	2903(5)	42(3)
O(4)	10457(7)	8590(3)	4949(5)	43(3)
O(5)	7111(8)	8888(4)	2499(6)	69(4)
O(6)	8170(9)	10018(4)	4801(7)	69(5)
C(1)	7328(11)	7281(4)	5110(9)	41(5)
C(2)	6238(9)	6931(4)	5421(8)	29(4)
C(3)	5335(10)	7286(4)	5832(7)	22(4)
C(4)	4001(9)	7431(4)	5285(7)	17(4)
C(5)	3481(10)	7936(4)	5481(7)	26(4)
C(6)	4193(10)	8288(4)	6257(6)	21(4)
C(7)	5319(10)	8059(5)	6941(7)	31(5)
C(8)	5895(10)	7565(4)	6730(7)	24(4)
C(9)	3948(10)	8909(4)	6253(7)	33(5)
C(10)	4877(10)	9270(5)	5796(8)	37(5)
C(11)	5835(9)	8902(4)	5457(7)	21(4)
C(12)	7090(9)	8734(4)	6108(7)	24(4)
C(13)	7699(10)	8239(5)	5934(8)	29(4)
C(14)	7060(10)	7896(4)	5114(8)	25(5)
C(15)	5995(10)	8137(4)	4359(7)	23(4)
C(16)	5378(10)	8635(4)	4546(8)	28(4)
C(17)	3202(9)	7032(4)	4509(7)	18(4)
C(18)	2707(9)	7141(4)	3477(7)	20(4)
C(19)	1993(9)	6715(5)	2831(7)	25(4)
C(20)	1765(9)	6189(4)	3141(7)	24(4)
C(21)	2255(9)	6077(4)	4181(7)	25(4)
C(22)	2958(8)	6486(4)	4870(7)	18(4)
C(23)	2871(9)	7698(4)	3044(7)	25(4)
C(24)	1027(10)	5740(4)	2451(7)	31(4)
C(25)	3454(10)	6321(4)	5941(7)	26(4)
C(26)	−571(12)	6452(5)	3799(8)	32(5)
C(27)	761(9)	7120(4)	5117(8)	25(4)
C(28)	−49(10)	7426(5)	3314(8)	29(5)
C(29)	9315(11)	8665(4)	4842(8)	29(5)
C(30)	7289(10)	8848(5)	3345(9)	39(5)
C(31)	7921(11)	9544(6)	4780(8)	37(5)
C(32)	185(18)	9054(7)	2005(22)	97(12)
C(33)	1138(26)	9189(10)	2913(17)	109(12)
C(34)	2004(18)	9598(9)	2924(12)	85(9)
C(35)	1992(13)	9886(6)	2142(15)	65(7)
C(36)	1109(17)	9764(7)	1283(12)	63(8)
C(37)	200(16)	9351(8)	1178(13)	73(8)
C(38)	5694(24)	9679(7)	−464(24)	94(12)
C(39)	6098(16)	9712(8)	562(22)	87(11)
C(40)	5420(23)	10025(9)	1039(13)	79(9)

All H atoms were placed in geometrically calculated positions (C—H is 0.96 Å) and refined with a common refinable isotropic temperature factor U_{iso} = 0.069(7) Å^2 using the riding model. The final values of the *R* factors were as follows: R = 0.0623 and R_w = 0.0571 using 2084 observed reflections with $I > 2\sigma(I)$. All calculations were carried out using the SHELXTL PLUS program (PC version).[23] The atomic coordinates are given in Table 6.

References

1. T. G. Traylor, K. J. Stewart, and M. J. Goldberg, *J. Am. Chem. Soc.*, 1984, **106**, 4445.
2. Yu. F. Oprunenko, I. A. Shaposhnikova, Yu. A. Ustynyuk, and D. N. Kravtsov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 703 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36**, 644 (Engl. Transl.)].
3. J. Deberitz and H. Nöth, *J. Organomet. Chem.*, 1973, **55**, 153.
4. S. D. Cunningham, K. Ofele, and B. R. Willeford, *J. Am. Chem. Soc.*, 1983, **105**, 3724.
5. J. Deberitz and H. Nöth, *J. Organomet. Chem.*, 1973, **61**, 271.
6. J. Deberitz and H. Nöth, *Chem. Ber.*, 1970, 2541.
7. V. I. Rozenberg, V. G. Kharitonov, E. V. Yatsenko, and O. A. Reutov, in *Abstrs. of Papers of XV Int. Conf. on Organometallic Chemistry*, Warsawa, 1992, 176.
8. V. I. Rozenberg, E. V. Sergeeva, E. V. Vorontsov, F. M. Dolgushin, A. I. Yanovsky, Yu. T. Struchkov, and K. P. Butin, in *Abstrs. of Papers of 8th Int. Sympos. on Novel Aromatic Compounds*, Braunshweig, 1995, 157.
9. D. J. Cram and D. I. Wilkinson, *J. Am. Chem. Soc.*, 1960, **82**, 5721.
10. H. Ohno, H. Horita, T. Otsuba, Y. Jakata, and S. Misumi, *Tetrahedron Lett.*, 1977, 265.
11. A. F. Mourad and H. Hopf, *Tetrahedron Lett.*, 1979, 1209.
12. E. Langer and H. Lehner, *Tetrahedron*, 1973, **29**, 375.
13. M. Stobbe, O. Reiser, T. Thiemann, R. G. Daniels, and A. de Meijere, *Tetrahedron Lett.*, 1986, **27**, 2353.
14. O. Reiser and A. de Meijere, *J. Organomet. Chem.*, 1991, **413**, 137.
15. V. I. Rozenberg, E. V. Sergeeva, V. G. Kharitonov, N. V. Vorontsova, E. V. Vorontsov, and V. V. Mikul'shina, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1081 [*Russ. Chem. Bull.*, 1994, **43**, 1018 (Engl. Transl.)].
16. F. Cristani, D. De Filippo, P. Deplano, F. Devillanova, A. Dias, E. F. Trogu, and G. Verani, *Inorg. Chim. Acta*, 1975, **12**, 119.
17. S.-B. Choe and K. J. Klabunde, *J. Organomet. Chem.*, 1989, **12**, 119.
18. G. A. Papoyan, K. P. Butin, R. Hoffmann, and V. I. Rozenberg, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 151 [*Russ. Chem. Bull.*, 1998, **47**, 152 (Engl. Transl.)].
19. N. Mori, M. Takamori, and T. Takemura, *J. Chem. Soc., Dalton Trans.*, 1985, 1065.
20. S. V. Lindeman, Yu. T. Struchkov, and V. N. Guryshev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 2007 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **35**, 1825 (Engl. Transl.)].
21. P. G. Jones, P. Bubenitschek, H. Hopf, and Z. Pechliranidis, *Z. Kristallogr.*, 1993, **208**, 136.
22. Y. Kai, N. Yasuoka, and N. Kasai, *Acta Crystallogr.*, 1978, **34B**, 2840.
23. W. Robinson and G. M. Sheldrick, *SHELX* in *Crystallographic Computing-Techniques and New Technologies*, Eds. N. M. Isaacs and M. R. Taylor, Oxford Univ. Press, Oxford (England), 1988, 366.

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