

## Metal Vapour Syntheses of some Bis( $\eta^6$ -arene)chromium(0) Compounds

PAAVO LUMME, PETER VON BAGH, JUHA KAHIMA and HELEENA KARRUS

*Department of Inorganic Chemistry, University of Helsinki, SF-00100 Helsinki 10, Finland*

Received September 3, 1982

*Bis(2-chloro-1,4-dimethylbenzene)chromium(0), bis(4-chloro-1,2-dimethylbenzene)chromium(0), bis(2,4-dichloro-1-methylbenzene)chromium(0), bis(2,6-dichloro-1-methylbenzene)chromium(0) and bis(1,4-dichlorobenzene)chromium(0) were prepared by co-condensation of vaporized chromium with the corresponding organic ligand at 77 K. The compositions and sandwich structures of the complexes were confirmed through mass spectra, the major fragmentation patterns of which are discussed, and the IR spectra. On the basis of symmetry considerations and IR absorption spectra, a cis-structure is suggested for the first and last mentioned compounds and a trans-structure for the others. The UV absorption spectra were also recorded.*

### Introduction

The arene chromium complexes have been one of the most studied organometallic groups. There are rather few possibilities left to find a primary arene chromium compound which had not been synthesized so far. From the dimethylbenzene chromium compounds bis(1,2-, 1,3- or 1,4-dimethylbenzene)-chromium(0) have been made [1], but chloro-dimethylbenzene derivatives seem not to have been an object, except one of those discussed here. Similarly several bis(monohalobenzene)chromium complexes are known [1–3], but not dihalobenzene complexes. We have prepared several bis(chloroarene)-chromium(0) compounds using the method to co-condense vaporized metal atoms with organic ligands at liquid nitrogen temperature and high vacuum [1–9]. The syntheses and spectroscopic properties of the studied compounds are reported in this paper.

### Experimental

#### Reagents

Chromium (puriss., 99.995%, Fluka AG) was supplied as pellets. 2-chloro-1,4-dimethylbenzene (purum, Fluka AG), 4-chloro-1,2-dimethylbenzene (pract., Fluka AG), 2,4-dichloro-1-methylbenzene

(purum, Fluka AG), 2,6-dichloro-1-methylbenzene (purum, Fluka AG) and 1,4-dichlorobenzene (pract., Merck) were used as such. The other reagents used were of guaranteed quality products.

#### Methods

For syntheses the metal atom reactor [10] of Kontes/Martin was used. The pressure in the system was reduced with a mechanical and oil diffusion pump to 0.5 Pa. After this the reaction vessel immersed in liquid nitrogen in a Dewar-flask was glazed with the oxygen-derived freed organic component (the oxygen was removed from organics by the refrigeration-melting method). The metal was vaporized through electric heating from a molybdenum bath, with Al<sub>2</sub>O<sub>3</sub> coated molybdenum wire cup, or an aluminium oxide cup (1.5 cm<sup>3</sup>) wired with tungsten wire. When the metal vaporized the organic component was diluted 1:4 (in the first and third case) or 1:5, cyclohexane was added continuously keeping the pressure under 6 Pa. After the reaction nitrogen gas was introduced into the system because of possible pyrophoric metals being left, and also to avoid contact with air. The product was dissolved in acetone or absolute ethanol and filtered. The yields reported are based on metal vaporized, and are corrected by assuming that only 70% of the metal vapour reaches the reaction zone.

From the filtrate the electron-impact mass spectra were run immediately with a JEOL JMS-01SG-2 Mass spectrometer equipped with a Texas Instruments 980 B computer. The electron beam ionization energy was generally 70–80 eV and the probe temperature 60–70 °C.

For other experiments solvents and impurities were removed through vacuum distillation. From the residue the UV spectra were recorded on Perkin-Elmer 402 Ultraviolet spectrophotometer and the IR spectra on a Perkin-Elmer 577 Grating infrared spectrophotometer.

#### *Bis(2-chloro-1,4-dimethylbenzene)chromium(0)*

The yield of the yellow-brown, waxlike solid compound was about 7%. Upon heating it decomposes, leaving chromium oxides [11]. The UV spectrum was

TABLE I. Main Peaks Owing to Chromium in the Mass Spectra of the Synthesized Bis( $\eta^6$ -arene)chromium(0) Compounds.

m/e	Assignment	100I/ $\Sigma$ I	m/e	Assignment	100I/ $\Sigma$ I
<b>Bis(2-chloro-1,4-dimethylbenzene)chromium(0)</b>			<b>Bis(4-chloro-1,2-dimethylbenzene)chromium(0)</b>		
334/332	C <sub>16</sub> H <sub>18</sub> Cl <sub>2</sub> Cr <sup>+</sup>	2/5	334/332	C <sub>16</sub> H <sub>18</sub> Cl <sub>2</sub> Cr <sup>+</sup>	1/5
297	C <sub>16</sub> H <sub>18</sub> ClCr <sup>+</sup>	1	297	C <sub>16</sub> H <sub>18</sub> ClCr <sup>+</sup>	1
194/193/192	C <sub>8</sub> H <sub>9</sub> ClCr <sup>+</sup>	3/5/8	194/193/192	C <sub>8</sub> H <sub>9</sub> ClCr <sup>+</sup>	2/3/5
162	C <sub>6</sub> H <sub>3</sub> ClCr <sup>+</sup>	4	156	C <sub>8</sub> H <sub>8</sub> Cr <sup>+</sup>	9
157	C <sub>8</sub> H <sub>9</sub> Cr <sup>+</sup>	1	155	C <sub>8</sub> H <sub>7</sub> Cr <sup>+</sup>	7
156	C <sub>8</sub> H <sub>8</sub> Cr <sup>+</sup>	3	53/52/50	Cr <sup>+</sup>	8/48/11
155	C <sub>8</sub> H <sub>7</sub> Cr <sup>+</sup>	3			
52	Cr <sup>+</sup>	65			
<b>Bis(2,4-dichloro-1-methylbenzene)chromium(0)</b>			<b>Bis(1,4-dichlorobenzene)chromium(0)</b>		
376/374/372	C <sub>14</sub> H <sub>12</sub> Cl <sub>4</sub> Cr <sup>+</sup>	2/4/6	348/347/346	C <sub>12</sub> H <sub>8</sub> Cl <sub>4</sub> Cr <sup>+</sup>	3/1/6
339/337	C <sub>14</sub> H <sub>12</sub> Cl <sub>3</sub> Cr <sup>+</sup>	2/2	345/344	C <sub>12</sub> H <sub>8</sub> Cl <sub>4</sub> Cr <sup>+</sup>	1/5
214/212	C <sub>7</sub> H <sub>6</sub> Cl <sub>2</sub> Cr <sup>+</sup>	7/11	309	C <sub>12</sub> H <sub>8</sub> Cl <sub>3</sub> Cr <sup>+</sup>	3
53/52/50	Cr <sup>+</sup>	6/57/3	202/200/199/	C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> Cr <sup>+</sup>	2/9/3
			198	C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> Cr <sup>+</sup>	13
			89/87	ClCr <sup>+</sup>	4/9
			53/52/50	Cr <sup>+</sup>	4/31/6
<b>Bis(2,6-dichloro-1-methylbenzene)chromium(0)</b>					
376/375/374	C <sub>14</sub> H <sub>12</sub> Cl <sub>4</sub> Cr <sup>+</sup>	10/3/15			
373/372	C <sub>14</sub> H <sub>12</sub> Cl <sub>4</sub> Cr <sup>+</sup>	5/10			
341/340/339/	C <sub>14</sub> H <sub>12</sub> Cl <sub>3</sub> Cr <sup>+</sup>	7/7/19			
338/337	C <sub>14</sub> H <sub>12</sub> Cl <sub>3</sub> Cr <sup>+</sup>	2/19			
53	Cr <sup>+</sup>	3			

taken in a 0.1% solution in acetone. The IR spectrum of the complex was run in a KBr disk (complex: KBr = 1:300 mg), and for the ligand between two KBr disks.

In this connection it should be noted that after the completion of the present work in 1979 we found that Klabunde *et al.* [11a] recently synthesized bis-(2-chloro-1,4-dimethylbenzene)chromium(0) using metal atom reactor techniques; the compound not being stable in air. This is in agreement with our results.

#### *Bis(4-chloro-1,2-dimethylbenzene)chromium(0)*

The dilution ratio of ligand to cyclohexane was 1:5. The brown-yellow green product was dissolved in acetone and the mass spectrum was taken on this. When acetone was evaporated an orange powder was left which decomposed at 396–398 K. The UV and IR spectra of the powder were recorded as above. The yield was about 8%.

#### *Bis(2,4-dichloro-1-methylbenzene)chromium(0)*

The dark green/black solid decomposed slowly when heated. Spectroscopic measurements were performed as described, except that 0.1% solution in abs. ethanol was used. The yield was 10%.

#### *Bis(2,6-dichloro-1-methylbenzene)chromium(0)*

The yellow-green solid was obtained with very low yield and because of instability only mass spectra

were run. The IR spectrum was run in KBr for the hydrolyzed complex bis(2,6-dichloro-1-methylbenzene)(OH)Cr(I).

#### *Bis(1,4-dichlorobenzene)chromium(0)*

The compound was prepared as above, or by covering the reaction vessel first with 1,4-dichlorobenzene. The spectra of the compound were obtained as in the first case above, except that for the IR spectra a disk of 1:400 mg KBr was used. The yellow solid decomposes by heating. The yield was 5%. This complex is stable for a half hour in air, 10 hours in benzene, 4 hours in acetone, but unstable in CHCl<sub>3</sub> or CCl<sub>4</sub>. The hydrolyzed compound is stable several days, decomposes at 416 K, dissolves in benzene, and remains undissolved in acetone.

## Results and Discussion

The mass, UV and IR spectroscopic measurements for the synthesized four complexes are listed in Tables I–III, respectively, except for bis(2,6-dichloro-1-methylbenzene)chromium(0) where the mass spectrum only is given.

In Table I the relative abundances of the Cr-containing ions only are considered in per cent from the sum of their ion-intensities. The mass peaks of the most fragmented ligands are not considered due to

TABLE II. UV Absorption Maxima of the Prepared Bis( $\eta^6$ -arene)chromium(0) Compounds in  $\text{cm}^{-1}$ . (s = strong, m = medium, w = weak).

Bis(2-chloro-1,4-dimethylbenzene)chromium(0)	Bis(4-chloro-1,2-dimethylbenzene)chromium(0)	Assignment
47 620 w	46 950 s	Metal–ligand
–	35 460 m	Ligand
29 760 s	28 250 w	Metal–ligand
Bis(2,4-dichloro-1-methylbenzene)chromium(0)	Bis(1,4-dichlorobenzene)chromium(0)	Assignment
47 620 s	47 620 w	Metal–ligand
35 715 w	–	Ligand
28 170 m	30 120 s	Metal–ligand

their frequency and to avoid confusion with the adjacent chromium compounds. The observed main fragments of the mass spectra not containing chromium are, however, noted in connection with the suggested fragmentation schemes of the complexes in Figs. 1–4. The multiple parent ions of the molecular peaks are mainly due to the isotopes of chlorine ( $^{35}\text{Cl}$  75.53,  $^{37}\text{Cl}$  24.47%) and chromium ( $^{50,52-54}\text{Cr}$  4.31, 83.76, 9.55, 2.38%). Because the mass spectra should be taken on very dilute solutions, not all mass peaks of the decomposition products were observable.

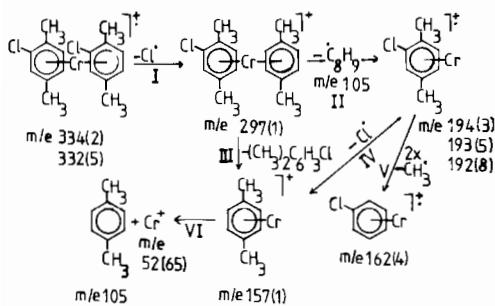


Fig. 1. The major fragmentation routes of bis(2-chloro-1,4-dimethylbenzene)chromium(0). The relative percentual abundances of the ions in parenthesis.

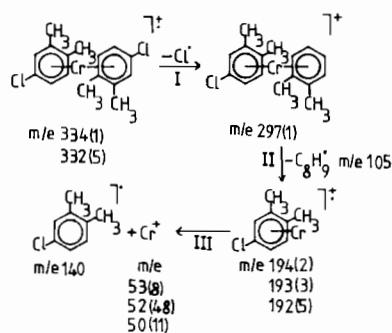


Fig. 2. The main fragmentation routes of bis(4-chloro-1,2-dimethylbenzene)chromium(0).

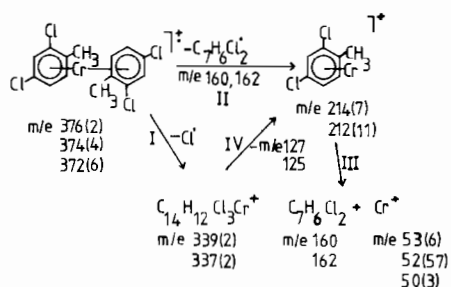


Fig. 3. The main fragmentation routes of bis(2,4-dichloro-1-methylbenzene)chromium(0).

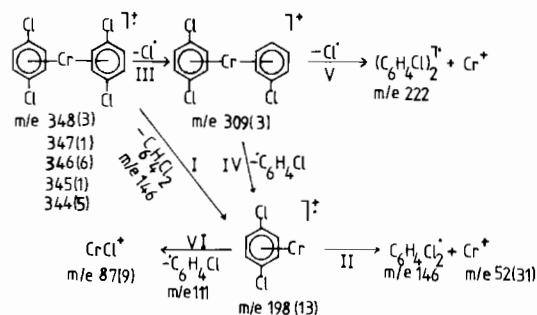


Fig. 4. The main fragmentation routes of bis(1,4-dichlorobenzene)chromium(0).

The recorded IR data for the ligand compounds are also included for comparison in Table III. The results are examined especially to respect to the degree in which they confirm the sandwich character of the prepared complexes and the arrangement of the ligand molecules to each other in the complexes.

#### Bis(2-chloro-1,4-dimethylbenzene)chromium(0)

To ascertain the composition of the compound its mass spectrum was taken immediately after the synthesis, because the solid compound is unstable as such and decomposes to chromium oxides at higher temperatures. The molecular peaks at  $m/e$  334, 332

TABLE III. Wave Lengths ( $\text{cm}^{-1}$ ), Intensities and Assignments of the IR Absorption Maxima of the Synthesized Bis( $\eta^6$ -arene)chromium Complexes and Ligands.

2-Chloro-1,4-dimethylbenzene		4-Chloro-1,2-dimethylbenzene		2,4-Dichloro-1-methylbenzene		1,4-Dichloro-benzene		2,6-Dichloro-1-methylbenzene		Assignment
Complex	Ligand	Complex	Ligand	Complex	Ligand	Complex	Ligand	OH-Complex	Ligand	
3050w	3020m	3020w	3025m	3060w	3065s	3090w	3090w	3380vs, br	3040m	$\nu(\text{OH})$
	2970vs	2970s	2975vs	2960s	3025m					$\nu(\text{CH})$
2955m	2945vs		2950vs		2985vs			2940m		$\nu_{\text{as}}(\text{CH}_3)$
2920m	2920vs	2920m	2925vs	2920s	2930vs			2910s		$\nu_{\text{as}}(\text{CH}_3)$
2860w	2860vs		2870vs	2880s	2860m			2820m		$\nu_{\text{s}}(\text{CH}_3)$
	2730m		2740m		2740m					$\delta_{\text{as}}(\text{CH}_3)$
	1882m		1870m		1880s		1883m		1910m	$\delta_{\text{s}}(\text{CH}_3)$
	1840vw				1850vw				1835m	$\pi(\text{CH}), \nu(\text{CC})$
	1810vw				1810vw					$\pi(\text{CH})$
1725m	1745m		1735m		1780s		1750vw		1765m	$\pi(\text{CH})$
										$\pi(\text{CH})$
1620m	1680w	1620w		1700vw	1700vw		1625w	1720m	1650m	$\delta(\text{OH}), \delta(\text{MOH})$
					1625m					$\nu(\text{CC})$
1595vw	1608vs		1600vs		1590vs			1615m, br		$\nu(\text{CC})$
1540vw	1575m		1570s		1560vs					$\nu(\text{CC})$
1495m	1555m								1550vs	$\nu(\text{CC})$
1450m	1495vs		1485vs	1470m	1480s		1475vs		1475sh	$\nu(\text{CC}), \delta_{\text{as}}(\text{CH}_3)$
	1445vs	1450vs	1450vs	1440m	1440s		1418w		1425vs	$\nu(\text{CC}), \delta_{\text{as}}(\text{CH}_3)$
	1390vs	1392vs	1398s	1380m	1380s		1390s		1373w	$\nu(\text{CC}), \delta_{\text{s}}(\text{CH}_3)$
1380s	1378vs		1375s		1375s					$\delta_{\text{s}}(\text{CH}_3)$
		1340w		1320vw						$\nu(\text{CC})$
1280m	1280s		1285w		1278s		1268w		1290w	$\nu(\text{C-Cl}), \text{ring}$
1255m		1257w	1272m	1260m	1265vs				1260s	$\nu(\text{C-Cl}), \text{ring}$
1208vw	1218vs	1210w	1225m		1220m					$\nu(\text{CC})$
					1208m				1195vs	$\nu(\text{CC})$
1115m	1148m	1185s	1183vs		1175w					$\nu(\text{CC}), \delta(\text{CH})$
		1110m	1140m		1150s				1145m	$\nu(\text{CC}), \delta(\text{CH})$
			1128vs		1130vs		1122w			$\nu(\text{CC}), \delta(\text{CH})$
			1102vs	1095m	1110vs		1108vw		1110sh	$\nu(\text{CC}), \delta(\text{CH})$
		1082s	1082m		1087vs		1087vs		1078vs	$\nu(\text{CC}), \delta(\text{CH})$
1055vw	1090vw	1032s	1050w	1050s	1055vs				1065sh	$\delta(\text{CH})$
	1050vs	1010s	1035vs		1040vs	1060vs			1020m	$\delta(\text{CH})$
		985vs	997vs	990vw	1000vs				993vs	$\delta(\text{CH}), \rho_{\text{r}}(\text{CH}_3)$
		947vw	942w		946w		1017vs		883m	$\delta(\text{CH})$
		885vs	885vs		885vs		950w			$\rho_{\text{r}}(\text{CH}_3)$



Also the specially strong  $\nu(\text{C-Cl})$  stretching vibrations at 695, 688 and 545  $\text{cm}^{-1}$  of the ligand are missing from the spectrum of the complex (Table III). Likewise the  $\rho_r(\text{CH}_3)$  rocking bands at 885 and 870  $\text{cm}^{-1}$ .

The above mentioned weakening or absence of  $\text{CH}_3$  and  $\text{C-Cl}$  vibrations in the spectrum of the complex may support the *cis*-arrangement of the ligands with respect of each others around the central chromium atom. The suggested structure of the complex gets further support from the weakening or lack of the strong  $\phi(\text{CC})$  (out-of-plane skeleton deformation) vibrations at 473, 440 and 402  $\text{cm}^{-1}$  of the ligand and appearing of the weak  $\nu(\text{MR})$  vibration at 430  $\text{cm}^{-1}$  in the complex spectrum (Table III).

#### *Bis(4-chloro-1,2-dimethylbenzene)chromium(0)*

The fragmentation behaviour of this compound is simpler than that described above. The complex releases first one of the chloro atoms giving the fragment at  $m/e$  297 (Fig. 2). Cleavage of  $\text{C}_8\text{H}_9$  from this leaves the fragment at mass number  $m/e$  192 which finally decomposes to chromium and ligand ( $m/e$  140). Also in this case the parent ions at mass numbers  $m/e$  332 and 334 support the sandwich complex structure (Table I and Fig. 1).

The chloro substitution of dimethylbenzenes seems to effect considerably the colour of their bis-(arene)chromium complexes. Although bis(1,2-dimethylbenzene)chromium(0) is reported to be a black solid [1], the bis(4-chloro-1,2-dimethylbenzene)chromium(0) described here is an orange solid. Both are, however, oxidized in air and decomposed by heating.

The UV absorption maxima at 46 950 and 28 250  $\text{cm}^{-1}$  of this complex are of the same origin and interpretation as for the former complex. The spectrum, however, shows an additional medium band at 35 460  $\text{cm}^{-1}$  due to the ligands.

In the present complex the  $\text{CH}_3$  vibrations are further enhanced leading at the range 2970–2740  $\text{cm}^{-1}$  to the appearance of  $\nu_{\text{as}}(\text{CH}_3)$  at 2970  $\text{cm}^{-1}$  and  $\nu_{\text{s}}(\text{CH}_3)$  at 2920  $\text{cm}^{-1}$  only in the spectrum of the complex (Table III).

The weakening or absence of the  $\text{CH}$  bending and  $\text{CC}$  stretching vibrations in the range 1900–1500  $\text{cm}^{-1}$  (Table III) in the spectrum of the complex may be interpreted as for the preceding complex.

On the contrary, the vibration changes in the ranges 1500–1000 and 1000–300  $\text{cm}^{-1}$  of the complex spectrum compared with the ligand's are not so radical as for the preceding complex. This may be explained by a more loose sandwich structure and weaker effect of the  $\text{CH}_3$  and  $\text{C-Cl}$  vibrations of the studied complex. Therefore, the ligands may be arranged *trans*-like to each other around the chromium atom. The mass spectral behaviour of the

complex (Fig. 1 and Table I) points also to this direction. The reinforcing of the  $\nu(\text{MR})$  vibrations at 430 and 420  $\text{cm}^{-1}$  in the complex spectrum (Table III) is also noteworthy.

#### *Bis(2,4-dichloro-1-methylbenzene)chromium(0)*

The bis-( $\eta^6$ -arene)chromium(0) complexes of methylbenzene and its monochlorosubstituents are very like each other, being black or green-black solids [1, 2] which oxidize in air. The insertion of a second chloro atom in the benzene ring does not change the situation. However, the chloro substitution lowers the yield of the sandwich complex radically from 50–60 to 5–10 per cent.

The main cleavage schemes of bis(2,4-dichloro-1-methylbenzene)chromium(0) in the mass spectrometer may be presented on the basis of the mass spectrum (*cf.* Table I) as given in Fig. 3. For this complex, however, the prevailing fragmentation route seems to be the cleavage of one ligand molecule giving the ion at  $m/e$  212/214 which at last leaves ligand and metal. On the contrary the route to cleavage first one chloro atom (route I, Fig. 3) is left in background.

The UV spectrum of this compound (Table II) shows corresponding maxima as the preceding complex and their interpretation and meanings are similar.

From the IR spectrum of the complex compared with that of the ligand at the ranges 3100–2740 and 1900–1380  $\text{cm}^{-1}$  similar conclusions may be drawn as for the two preceding complexes. In the range 1250–1130  $\text{cm}^{-1}$  the strong  $\text{C}=\text{C}$  stretching vibrations of the ligand are missing from the complex spectrum, pointing again to the bonding of the chromium atom to the benzene rings *via* their carbon atoms. Within 1100–550  $\text{cm}^{-1}$  the complex shows general weakening of  $\text{C}=\text{C}$  stretching and  $\text{CH}$  bending vibrations compared with the ligand, confirming further the sandwich structure of the complex.

In the range 550–300  $\text{cm}^{-1}$  the most conspicuous differences between the spectra of the complex and ligand are the appearance of a strong  $\nu(\text{MR})$  stretching vibration at 430  $\text{cm}^{-1}$  and the missing of the strong  $\nu(\text{C-Cl})$  stretching vibrations of the ligand at 405, 385 and 318  $\text{cm}^{-1}$  in the spectrum of the complex. The former property strengthens the opinion about the sandwich character of the complex and the latter the *trans*-arrangement of the ligands with respect to each other around the chromium atom. This is also supported through the mass spectrum of the complex (*cf.* Table I and Fig. 3).

#### *Bis(2,6-dichloro-1-methylbenzene)chromium(0)*

The situation with all three substituents in adjacent positions in the benzene ring seems to make the chromium complex even more unstable. The yield is poor.

The cleavage scheme is similar to that presented in Fig. 3, except that the prevailing fragmentation seems

to be the escape of one chloro atom first. No ion at  $m/e$  212/214 was observed. The isotope patterns, however, are clear and confirm the composition (Table I).

The infrared spectrum of the hydrolyzation product, bis(2,6-dichloro-1-methylbenzene)(OH)-Cr(I), confirms the bonding of chromium with organic ligands through the carbon atoms of the benzene rings ( $\eta$ -bonding). The CH bending or C=C stretching bands of the benzene ring observed at 1910, 1835, 1765, 1650, 1550, 1195, 1145 and 487  $\text{cm}^{-1}$  in the spectrum of the ligand are missing when compared with the hydroxyl complex. The bands at 2950–2820, 1475–1370 and 1100–993  $\text{cm}^{-1}$  are due to symmetric or asymmetric vibrations of the  $\text{CH}_3$  groups. The CCl stretching vibrations are observed at 1290–1250, 795–530 and 397–367  $\text{cm}^{-1}$ . The OH stretching vibrations are seen at 3380  $\text{cm}^{-1}$  and deformation bands at 1720 and 1615  $\text{cm}^{-1}$  (Table III).

On the basis of the frequency of the IR absorption bands a *trans*-arrangement to respect of each others of the organic ligands in this and bis(2,6-dichloro-1-methylbenzene)chromium(0) complexes is suggested (cf. Tables III and IV).

#### Bis(1,4-dichlorobenzene)chromium(0)

In this case also the main fragmentation route seems to be the cleavage of one ligand molecule (route I, Fig. 4) followed by decomposition to metal and ligand (route II, Fig. 4). The cleavage of one chloro atom first directs to branched decomposition (routes III–V, Fig. 4). According to these the mass

spectrum shows major peaks at  $m/e$  344 ( $\text{M}^+$ ), 198 ( $(\text{M}-\text{C}_6\text{H}_4\text{Cl}_2)^+$ ), 146 ( $\text{C}_6\text{H}_4\text{Cl}_2^+$ ), 87 ( $\text{CrCl}^+$ ) and 52 ( $\text{Cr}^+$ ), (cf. Table I).

The UV spectrum of this compound shows absorption maxima at 47 620 and 30 120  $\text{cm}^{-1}$ , typical for a sandwich complex, but no maximum characteristic for ligands only (Table II). In this respect the compound resembles the first one discussed here.

The infrared spectrum of the complex lacks practically all the CH bending and CH and C=C stretching vibrations shown by the ligand spectrum at 3100–3000 and 1900–1500  $\text{cm}^{-1}$  (Table III). The spectrum of the complex compared with the ligand's in the spectral range 1500–550  $\text{cm}^{-1}$  also shows considerable absences or transitions of absorption peaks. The  $\nu(\text{MR})$  vibration at 430  $\text{cm}^{-1}$  is in this case rather weak.

However, in any case the spectral changes are to be interpreted to support a sandwich structure of the complex. This may have according to the IR spectrum a *cis*-arrangement of the ligands which seems to be in agreement with the UV spectrum.

#### Cis-Trans-Structure of the Chromium Complexes

In Table IV we have considered from an approximate symmetry point of view the number of the theoretically possible normal vibrations (without lattice vibrations) of the studied chromium complexes, assuming the ligands around the chromium atom to be planar and to accept a *cis*- or *trans*-arrangement to respect of each others. These are the two extreme symmetry configurations possible

TABLE IV. Structure of the Chromium(0) Complexes and Symmetry Vibrations.

Structure	Bis(2-chloro-1,4-dimethylbenzene)-chromium(0)		Bis(4-chloro-1,2-dimethylbenzene)-chromium(0)		Bis(2,4-dichloro-1-methylbenzene)-chromium(0)	
	<i>Cis</i>	<i>Trans</i>	<i>Cis</i>	<i>Trans</i>	<i>Cis</i>	<i>Trans</i>
Point group	$\text{C}_s$	$\text{C}_2$	$\text{C}_s$	$\text{C}_i$	$\text{C}_s$	$\text{C}_i$
IR active vibrations	53A' + 52A''		53A' + 52A''		44A' + 43A''	
IR active vibrations	105	105	105	54	87	45
Bands observed	20		25		20	
Structure (suggested)	<i>Cis</i>		<i>Trans</i>		<i>Trans</i>	
					Bis(1,4-dichlorobenzene)-chromium(0)	
Structure	<i>Cis</i>		<i>Trans</i>		<i>Cis</i>	
Point group	$\text{D}_{2h}$		$\text{D}_2$		$\text{C}_{2v}$	
IR active vibrations	10B <sub>1u</sub> + 8B <sub>2u</sub> + 10B <sub>3u</sub>		17B <sub>1</sub> + 17B <sub>2</sub> + 17B <sub>3</sub>		25A <sub>1</sub> + 19B <sub>1</sub> + 24B <sub>2</sub>	
IR active vibrations	28		51		68	
Bands observed	8				—	
Structure (suggested)	<i>Cis</i>				<i>Trans</i>	

for the complexes if they are considered to be of the usual sandwich type molecules. The real structures may naturally deviate from these to some extent.

The theoretically possible numbers of IR active vibrations of the different structures compared with the practical spectra (Table III) led us to the suggested *cis*- or *trans*-structures of the compounds (Table IV). These are also in agreement with the appearance of the absorption maxima observed in the UV spectra of the complexes (Table II) and their discussion above. The ligand band at about 35 714  $\text{cm}^{-1}$  is less typical of a *trans*-structure and is to be expected more in the case of a *cis*-structure.

Urey-Bradley force field calculations with normal coordinate analyses of the complex spectra would possibly only sharpen the suggested assignments (Table III) of the IR absorptions but not judge the micro structure of the complexes, because the number of the theoretically implied IR active vibrations to the observed is about 2–5:1 (Tables III and IV). This is certainly achieved only through a single crystal X-ray or neutron diffraction structure analysis of the complexes or their crystalline derivatives.

#### Acknowledgement

The authors are indebted to Miss Hilka Kenttämä, M. Ph. for recording the mass spectra.

#### References

- 1 V. Graves and J. J. Lagowski, *Inorg. Chem.*, **15**, 577 (1976).
- 2 P. S. Skell, D. L. Williams-Smith and M. J. McGlinchey, *J. Am. Chem. Soc.*, **95**, 3337 (1973).
- 3 K. J. Klabunde, 'Chemistry of Free Atoms and Particles', Academic Press, New York, 1980.
- 4 P. S. Skell, L. D. Wescott, Jr., J.-P. Goldstein and R. R. Engel, *J. Am. Chem. Soc.*, **87**, 2829 (1965).
- 5 P. L. Timms, *Chem. Commun.*, 1033 (1969).
- 6 P. L. Timms, *Adv. Inorg. Chem. Radiochem.*, **14**, 121 (1972).
- 7 P. L. Timms, *Angew. Chem.*, **87**, 295 (1975).
- 8 G. A. Domrachev and V. D. Zino'ev, *Russ. Chem. Rev.*, **47**, 354 (1978).
- 9 J. R. Blackborow and D. Young, 'Metal Vapour Synthesis in Organometallic Chemistry', Vol. 9, in series 'Reactivity and Structure Concepts in Organic Chemistry', Eds. K. Hafner *et al.*, Springer-Verlag, Berlin, 1979.
- 10 'Instruction Manual for Kontes Metal Atom Reactor', Kontes/Martin, Evanston, Illinois, U.S.A.
- 11 V. M. Fomin, Yu. A. Alexandrov and V. A. Umilin, *J. Organometal. Chem.*, **61**, 267 (1973).
- 11 (a) P. M. Treichel, G. P. Essenmacher, H. F. Efner and K. J. Klabunde, *Inorg. Chim. Acta*, **48**, 41 (1981).
- 12 (a) P. O. Lumme and M.-L. Korvola, *Thermochim. Acta*, **13**, 419 (1975).
- (b) P. O. Lumme and J. Korvola, *Thermochim. Acta*, **9**, 109 (1974).
- 13 (a) J. Müller, K. Öfele and G. Krebs, *J. Organometal. Chem.*, **82**, 383 (1974).
- (b) H. O. Van Oven, C. J. Groenenboom and H. J. De Liefde Meijer, *J. Organometal. Chem.*, **81**, 379 (1974).
- (c) J. Müller, *Angew. Chem.*, **84**, 725 (1972).
- 14 D. G. Carroll and S. P. McGlynn, *Inorg. Chem.*, **7**, 1285 (1968).
- 15 S. Yamada, H. Nakamura and R. Tsuchida, *Bull. Chem. Soc. Japan*, **30**, 647 (1957).
- 16 S. Yamada, H. Yamazaki, H. Nishikawa and R. Tsuchida, *Bull. Chem. Soc. Japan*, **33**, 481 (1960).
- 17 J. H. S. Green, D. J. Harrison and W. Kynaston, *Spectrochim. Acta*, **27 A**, 807 (1971).
- 18 J. R. Scherer and J. C. Evans, *Spectrochim. Acta*, **19**, 1739 (1963).
- 19 A. Stojiljković and D. H. Whiffen, *Spectrochim. Acta*, **12**, 47 (1958).
- 20 J. W. Boyd, J. M. Lavoie and D. M. Green, *J. Chem. Phys.*, **60**, 4088 (1974).