π-Compression in [2.2]Paracyclophanes: Structural and Spectroscopic Effects in Tricarbonyl([2.2]paracyclophane-1,9-diene)chromium(0) Complexes

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Crystal structures of the four complexes tricarbonyl(3-8-η-[2.2]-paracyclophane-1,9-diene)chromium(0) (**3**), (μ-3-8-η:11-16-η-[2.2]-paracyclophane-1,9-diene)bis[tricarbonylchromium(0)] (**4**), tricarbonyl(4,7-dimethoxy-11-16-η-[2.2]paracyclophane-1,9-diene)chromium(0) (**5**) and tricarbonyl[1,10-bis(trimethylsilyl)-11-16-η-[2.2]-paracyclophane-1,9-diene]chromium(0) (**6**), containing differently substituted [2.2]paracyclophane-1,9-diene ligands have been determined by X-ray diffraction. The most interesting differences are observed in the interannular distances and the widths across the skeleton between the two bridges. The two benzene decks move more closely together as the π-electron density is withdrawn from the cyclophane ligand. The shrinkage of the interannular distances *a* and *b* of up to 12 pm for the dinuclear complex **4** is more pronounced for the whole series of diene complexes **3**–**6** than for the [2.2]paracyclophane complex **1**-$Cr(CO)_3$, and it correlates with the electron-withdrawing power of the substituents. ^1H and ^{13}C NMR, and UV and IR spectroscopic properties of **3**–**6** are in accord with previous obervations for complexation effects in such systems. An interesting correlation was detected for the aryl one-bond C–H coupling constants ($^1J_{C,H}$) in this self-consistent series, **3**–**6**. $^1J_{C,H}$ varies from 157.9 to 161.9 Hz for an uncomplexed and from 172.5 to 177.6 Hz for a complexed aryl moiety, and can thus be used as a sensitive and easily accessible probe for structural and electronic changes in such systems.

Dedicated to Professor Otto Bastiansen on his 70th birthday

[2.2]Paracyclophane (**1**), its diene **2** and their derivatives are fascinating molecules, because the short C_2 bridges force the two benzene rings into such close proximity that their π-electron densities acually interpenetrate.[1] The distances between the benzene decks in **1** (309 pm)[2] and [2.2]paracyclophane-1,9-diene (**2**) (314 pm)[3] are actually shorter than the sum of the van der Waals thicknesses of the benzene rings. As pointed out early by Cram,[4] the π-electron clouds of **1** (and consequently of **2**) are pushed outward from the center, causing an increased π-density on the outer faces of the molecule. Compared to benzene, **1** thereby is a better π-donor and exhibits a higher tendency to form π-complexes with acceptor molecules such as tetracyanoethylene (TCNE).[4] This π-repulsion apparently enhances the boat-like deformation of the benzene rings in **1** (as well as **2**) and should be attended by a change in hybridization for the aromatic carbon atoms toward sp^3. The expected decrease in *s*-character of the aromatic C–H bonds, however,

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has not been found to be expressed in the corresponding ^{13}C, H coupling constants ($^1J_{C,H}$) of [2*n*]cyclophanes.[5]

Because of our interest in new materials with strong intramolecular charge transfer[6,7] we synthesized a series of tricarbonylchromium(0) complexes with [2.2]paracyclophane-1,9-diene ligands and studied their chemical as well as physical properties. Not only can these complexes serve as precursors for functionalized [2.2]paracyclophanes with predetermined substitution patterns,[7] but they themselves also constitute systems with intramolecular charge-transfer properties. The tricarbonylchromium group exhibits a strong electron-withdrawing effect, comparable to that of a nitro group[8] – on an arene ligand. Due to the well-known electronic nature of the [2.2]paracyclophane skeleton,[1,9] this effect should be transmitted to the second, opposite arene deck as well. In order to determine the nature and the extent of the expected changes induced by such effects, we investigated a series of tricarbonyl([2.2]paracyclophane-1,9-diene) chromium(0) complexes by X-ray crystallography and by NMR, IR and UV/VIS spectroscopy.

Crystal structure analyses of chromium complexes 3–6[10]

The series of complexes formed from [2.2]paracyclophane-1,9-diene (**2**) was chosen rather than the corresponding ones formed from the parent [2.2]paracyclophane (**1**) because the benzene rings in **2** are more severely bent,[3] and consequently larger structural changes could be expected upon complexation. We had complexes **3**–**6** at our disposal in connection with an investigation of their chemical properties,[7,11] the crystal structure of tricarbonyl(3-8-η-[2.2]paracyclophane)chromium(0) [**1**-$Cr(CO)_3$] has been determined previously[12] and thus can be used as a basis for comparison. **3** not only served to confirm the known shrinkage of the interannular distance upon tricarbonylchromium complexation,[12] but also as a calibration to determine additional transannular effects resulting from donor substitution, as in **5**, quasi-acceptor substitution, as

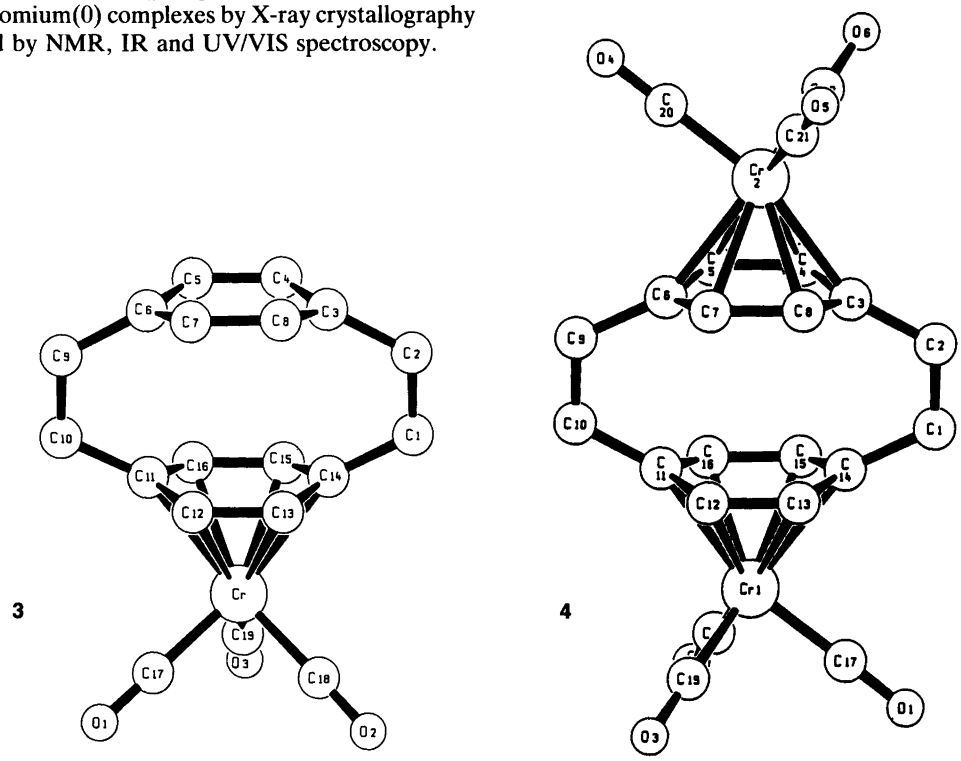


Fig. 1. SCHAKAL plots for mononuclear (**3**) and dinuclear (**4**) tricarbonylchromium(0) complexes of [2.2]paracyclophane-1,9-diene.

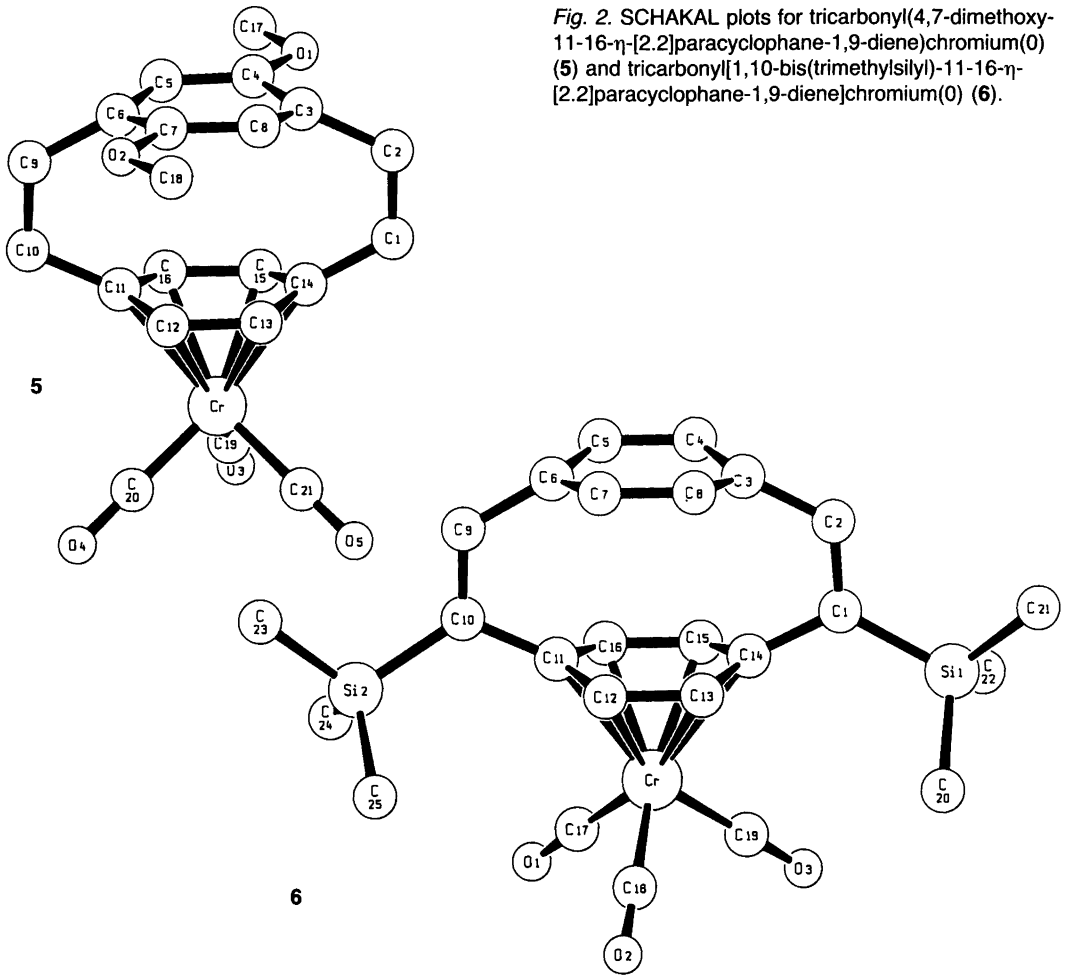


Fig. 2. SCHAKAL plots for tricarbonyl(4,7-dimethoxy-11-16-η-[2.2]paracyclophane-1,9-diene)chromium(0) (**5**) and tricarbonyl[1,10-bis(trimethylsilyl)-11-16-η-[2.2]paracyclophane-1,9-diene]chromium(0) (**6**).

in the dinuclear complex **4**, and the effects of substituents on the bridges, as in **6**.

Standard procedures were used to grow crystals of complexes **3**–**6** and to analyse their structures (see Experimental).[13–15] The resulting geometries are depicted in Figs. 1 and 2, and relevant bonding parameters are summarized in Table 1. Except for bond angles and interannular distances (*vide infra*) there are no obvious systematic changes in bonding parameters significantly exceeding the limits of error within this series. The differences between the mononuclear complex **3** and the diene ligand **2**[3] are about the same as those between **1**-$Cr(CO)_3$[12] and [2.2]paracyclophane (**1**).[2] The surprising distortion of the dimethoxy derivative **5** with the observed cross-wise differences of corresponding bridge bond angles ($C^1-C^2-C^3/C^6-C^9-C^{10}$: 115.7/119.8 and $C^2-C^1-C^{14}/C^9-C^{10}-C^{11}$: 118.5/113.2) might be due to intermolecular interactions in the crystal. Indeed, the crystal symmetry is lower than the molecular symmetry, and the precision of this structure analysis with $R = 6.1\,\%$ is poorer than for **3** ($R = 3.7\,\%$), **4** ($R = 4.4\,\%$) and **6** ($R = 3.8\,\%$).

The orientation for the tricarbonylchromium group relative to the [2.2]paracyclophane skeleton is the same in all three mononuclear complexes **3**, **5** and **6**, and identical to the preferred orientation in other tricarbonylchromium complexes of *para*-disubstituted arenes[16] (Fig. 3). In the dinuclear complex **4**, however, the $Cr(CO)_3$

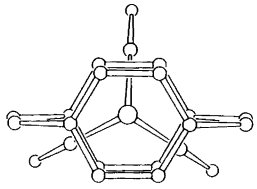
Table 1. Comparison of bond distances (in pm) and bond angles (in degrees) in [2.2]paracyclophane-1,9-diene (**2**)[a] and its complexes **3**–**6** (standard deviations in parentheses).

	2	**3**	**4**	**5**	**6**
C^1-C^2/ C^9-C^{10}	133.6/ 133.6	134.0(7)/ 133.9(6)	133.1(5)/ 133.1(5)	134.7(8)/ 136.5(8)	134.6(3)/ 133.6(3)
C^2-C^3/ C^6-C^9	151.6/ 150.7	149.3(6)/ 150.0(6)	148.6(5)/ 150.8(6)	152.4(8)/ 150.9(8)	149.4(4)/ 149.6(3)
C^3-C^4/ C^6-C^7	140.4/ 139.2	140.0(6)/ 139.3(7)	141.5(5)/ 138.4(5)	139.0(7)/ 138.5(8)	138.9(4)/ 139.1(4)
C^3-C^8/ C^5-C^6	138.8/ 141.4	140.0(7)/ 139.6(6)	139.4(5)/ 140.3(5)	138.0(7)/ 139.7(8)	138.9(4)/ 139.3(4)
C^4-C^5/ C^7-C^8	139.2/ 140.0	139.6(6)/ 137.4(8)	139.5(5)/ 142.0(5)	137.7(8)/ 139.5(8)	139.0(4)/ 138.7(4)
C^1-C^{14}/ $C^{10}-C^{11}$	150.7/ 151.6	148.8(6)/ 149.5(6)	150.8(5)/ 148.6(5)	149.1(8)/ 150.6(7)	151.2(3)/ 150.5(3)
$C^{11}-C^{12}$/ $C^{14}-C^{15}$	140.4/ 139.2	138.9(6)/ 141.2(6)	141.5(5)/ 138.4(5)	141.9(7)/ 139.0(7)	139.5(3)/ 141.1(3)
$C^{11}-C^{16}$/ $C^{13}-C^{14}$	138.8/ 141.4	141.2(6)/ 139.2(6)	139.4(5)/ 140.3(5)	141.4(7)/ 140.6(7)	140.5(3)/ 138.7(3)
$C^{12}-C^{13}$/ $C^{15}-C^{16}$	139.2/ 140.0	140.8(6)/ 139.9(6)	139.5(5)/ 142.0(5)	140.0(7)/ 142.2(7)	141.7(3)/ 139.6(3)
$Cr-C^{12}$/ $Cr-C^{15}$	–	222.4(4)/ 218.7(4)	217.7(4)/ 224.2(3)	219.0(6)/ 220.8(5)	221.6(2)/ 219.5(2)
$Cr-C^{13}$/ $Cr-C^{16}$	–	222.2(5)/ 219.0(4)	220.9(4)/ 220.1(4)	218.1(5)/ 224.5(5)	225.0(2)/ 217.2(2)
$Cr-C^{11}$/ $Cr-C^{14}$	–	243.2(4)/ 234.7(4)	234.1(4)/ 236.9(4)	225.3(5)/ 232.5(5)	234.4(2)/ 239.3(2)
C^4-O^1/ C^7-O^2	–	–	–	137.4(6)/ 137.7(7)	–
O^1-C^{17}/ O^2-C^{18}	–	–	–	139.2(8)/ 142.0(9)	–
Si^1-C^1/ Si^2-C^{10}	–	–	–	–	188.5(2)/ 188.9(2)
Si^1-C^{20}/ Si^1-C^{21}	–	–	–	–	185.1(4)/ 186.4(5)
Si^1-C^{22}/ Si^2-C^{23}	–	–	–	–	185.5(4)/ 186.2(5)
Si^2-C^{24}/ Si^2-C^{25}	–	–	–	–	185.7(4)/ 185.6(3)

[a]Ref. 3.

orientation is different; interestingly, the two $Cr(CO)_3$ groups on the same ligand are staggered with respect to each other, thereby yielding an overall centrosymmetric structure.

The crystal packing of **4** and of all the mononuclear $Cr(CO)_3$ complexes with [2.2]paracyclophane-1,9-diene ligands is very similar. The molecules are packed in zig-zag layers with parallel molecular axes within each layer, but perpendicular orientation of all the axes in the next (Fig. 4). Only in crystalline **4** do the stacks of molecules alternate with stacks of incorporated benzene molecules (Fig. 4).



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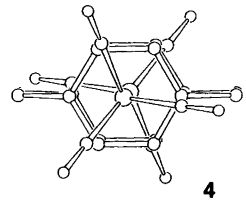

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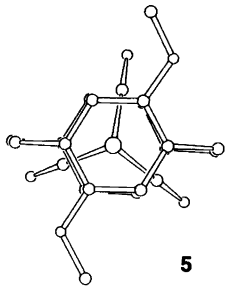

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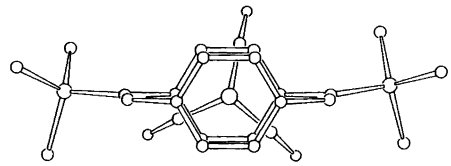

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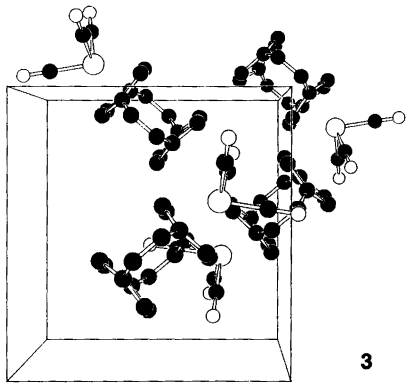
Fig. 3. Top view of complexes **3–6** depicting the relative orientation (conformation) of the tricarbonylchromium unit.



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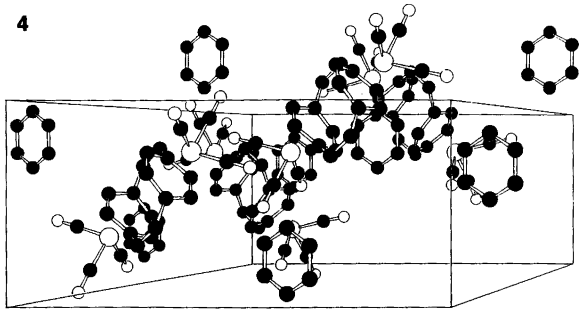

Fig. 4. Packing of molecules in crystalline tricarbonyl(11-16-η-[2.2]paracyclophane-1,9-diene)chromium(0) (**3**) and (μ-3-8-η: 11-16-η-[2.2]paracyclophane-1,9-diene)bis(tricarbonyl) chromium(0) (**4**).

Discussion of structural consequences of complexation in 3–6

Upon complexation of [2.2]paracyclophane-1,9-diene (**2**), the interannular distances *a* and *b* shrink by 9 and 8 pm, respectively. This is slightly more pronounced than the shrinkage of 7 and 6 pm, respectively, upon going from **1** to **1**-Cr$(CO)_3$, and it is in line with the expectation that withdrawal of π-electron density on one side of a [2.2]paracyclophane should also decrease the electron density between the two decks (A and B in Scheme 1) and thereby diminish the repulsive π-interaction. With the two π-donating methoxy groups on the opposite deck B in **5**, electron withdrawal on A by the $Cr(CO)_3$ group can be more successful, as indicated by the shrinkage of 11 and 9 pm in distances *a* and *b*, respectively (Table 2). Furthermore, the π-electron attracting $SiMe_3$ groups on the bridges in **6** appear to prevent the two decks from moving as closely together as in **3** and **5**.

The geometrical changes occur predominantly on the complexed side of the molecule. While the bending angle α_2 (Fig. 5) stays about the same as in the free ligand (Table 2) or even increases, the overall unit of the complexed ring with its two exocyclic C–C bonds is flattened with significantly smaller (> 2.5° on the average) angles β_2, and even the bond angles γ_2 are an average of 4.4° smaller than in **2**, while γ_1 is about the same in **3**, **5**, **6** and **2**.

The complex **6** with the two bulky $SiMe_3$ groups on the bridge positions adjacent to the complexed ring A shows a unique kind of deformation: The distance *d* between C^1 and C^{10} across the skeleton is significantly larger than in all the other compounds – which is in line with the smallest value of β_2 – and this must be due to some sort of steric interaction between the $SiMe_3$ groups and the $Cr(CO)_3$ unit. This repulsion between the bulky groups may also be responsible for the observation that the chromium center in **6** lies about 27 pm away from the plane $C^1–C^2–C^9–C^{10}$ bisecting the molecule, although this deformation may also be caused by a crystal disorder phenomenon. In spite of these indications, however, no sign of slowing down of the tricarbonylchromium rotation (the so-called chromium carousel[17]) could be seen in the ^{13}C NMR spectrum of **6**, even upon cooling the sample down to −90 °C.[18]

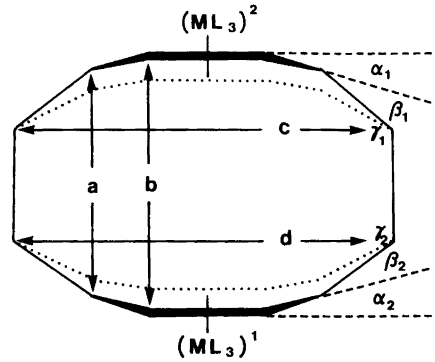

Fig. 5. Side view of [2.2]paracyclophane skeleton to visualize geometrical features of the free ligands **1**, **2** (solid lines) as well as the tricarbonylchromium(0) complexes **3**, **4**, **5** and **6** (dotted lines).

Table 2. Comparison of selected geometrical features (interannular distances etc., see Fig. 1) of the [2.2]paracyclophane skeleton in **1** and **2** as well as the complexes **3**, **4**, **5** and **6** (Fig. 5).

Compound	Distance/pm				Angle/°					
	a	*b*	*c*	*d*	α_1	β_1	γ_1	α_2	β_2	γ_2
1[a]	278	309	559	559	12.6	11.2	113.7	12.6	11.2	113.7
1–$Cr(CO)_3$[b]	272	302	562	564	11.4	11.2	112.8	12.2	8.9	110.9
2[c]	280	314	546	546	13.1	15.4	118.7	13.1	15.4	119.0
3	272	305	544	546	13.5	13.9	119.7	14.0	12.8	115.6
4	268	302	549	549	14.6	13.6	116.4	14.6	13.6	117.3
5	271	303	547	549	12.1	15.3	119.2	13.8	12.5	114.5
6	271	306	543	554	13.6	14.2	120.9	14.6	11.2	113.4

[a]Ref. 2. [b]Ref. 12. [c]Ref. 3.

In the dinuclear complex **4**, electron-withdrawing $Cr(CO)_3$ groups act on both sides of the hydrocarbon ligand, which thereby necessitates that the angle changes be the same on both sides. As in the mononuclear complexes **3**, **5** and **6**, the α-bending increases while the β-bending and the bond angles decrease. The interannular distances *a* and *b* are even smaller (by 3 to 4 pm) than in **3**; this shrinkage, however, is not as large as upon going from **2** to **3**, yet significant (Table 2). There appears to be a limit as to how much the two benzene decks can be pressed together by electron-withdrawing groups on the outsides.

Interesting spectroscopic properties of complexes 3–6

All new complexes were characterized by ^1H and ^{13}C NMR, and by UV and IR spectroscopy. As usual for arenetricarbonylchromium complexes,[19] the aryl proton signals of the complexed ring (deck A in **3**, **5** and **6**) are shifted upfield (Table 3) due to the back-bonding effect of the metal.[20] The protons on the opposite, uncomplexed ring (deck B in **3**, **5** and **6**), however, experience a smaller, but significant (0.30 to 0.34 ppm) downfield shift. This is a definite indication of an effective transannular charge transfer: the $Cr(CO)_3$ group not only withdraws π-electron density from the proximal ring, but also from the opposite side by through-bond[9] and probably through-space interaction[1,9] (see discussion of structural consequences above). While the adjacent ring is more than replenished by the back-bonding of the chromium, the opposite ring must experience a net loss of π-density, as the back-bonding cannot have an effect there. As the shift differences on the uncomplexed side are rather small, the importance of complexation-induced changes in transannular charge transfer has been questioned.[21]

The ^{13}C NMR data (Table 3) demonstrate the

Table 3. Comparison of ^1H and ^{13}C NMR chemical shifts (δ_{TMS} in ppm) of aromatic rings in [2.2]paracyclophane (**1**), diene **2** and their complexes **1**-$Cr(CO)_3$, **3**–**6**.

Compound	^1H NMR ($CDCl_3$)				^{13}C NMR ($CDCl_3$)			
	δA	δB	Δδ[a]A	ΔδB	δA $C^{12(13,15,16)}/C^{11(14)}$	δB $C^{4(5,7,8)}/C^{3(6)}$	ΔδA	ΔδB
1	6.48		–		132.7/139.0		–	
		6.48		–		132.7/139.0		–
1-$Cr(CO)_3$[b]	4.64		−1.83		94.0/122.4		−38.7/	−16.6
		6.77		0.30		133.3/139.4		0.6/0.45
2	6.48		–		130.8/137.7		–	
		6.48		–		130.8/137.7		–
3	4.76		−1.72		91.5/118.6		−39.3/	−19.1
		6.78		0.30		131.9/138.0		1.4/1.4
4[c]	5.03		−1.45		90.7/119.9[b]		−39.2/	−18.4
		5.03		−1.45	91.6/124.3		−38.4/	−18.6
						90.7/119.9	−39.2/	−18.4
						91.6/124.3	−38.4/	−18.6
	4.71/							
5	5.04		−1.76/	−1.76	89.2/118.5		−38.2/	−19.6
		6.12	0.34		91.6		−39.6	
						119.5/127.3		0.4/0.4
						154.6		1.9
6	4.58		−1.71		91.0/125.5		−38.7/	−16.7
		6.72		0.33		131.1/139.1		0.9/0.2

[a] Δδ = δ(complex)-δ(hydrocarbon). [b] Ref. 22. [c] For reasons of solubility ^{13}C NMR data were recorded for **4**-$SiMe_3$.

same trends. All carbon signals for the uncomplexed ring (deck B in **3**, **5** and **6**) show a downfield shift by ~1 ppm with respect to the corresponding signals of the free ligands. In the complexed ring (deck A) the signals for the four central carbons experience a high-field shift by about 40 ppm, while that for the bow and stern carbons C^{11} and C^{14} is only about 20 ppm because the chromium is much closer to the central carbon atoms of the six-membered ring in its shallow boat form. The same kind of geometry-related, but smaller, ^{13}C chemical shift differences were reported and interpreted for **1**-$Cr(CO)_3$.[21]

In the ^1H NMR spectrum of **4**, of course, all the aryl proton signals are shifted upfield, although less so than for the complexed side of **3**. **4**-$SiMe_3$, which is far more soluble than **4**, is the first dinuclear complex with a [2.2]paracyclophane ligand for which ^{13}C NMR data have been recorded.[22] All the aryl carbon signals of **4**-$SiMe_3$ show an upfield shift which is almost as large as that for the complexed ring in the mononuclear **3**. At first glance this is surprising, as the two Cr $(CO)_3$ groups should counteract each other, at least as far as the electron withdrawal is concerned. The back-bonding, however, which is responsible for the upfield shift,[20] apparently is as strong in **4**-$SiMe_3$ on both sides as it is in **3** on one side.

The different intramolecular charge transfer properties of the complexes **3**–**6** in comparison to **1**-$Cr(CO)_3$[23] and the ligands **2** and **1** are clearly expressed in their electronic spectra (Table 4). The UV spectra of **3**–**6** as well as of **1**-$Cr(CO)_3$ are all characterized by an intense absorption in the region 338–357 nm with a long-wavelength shoulder often extending into the visible region. The bathochromic shift of the main band as well as the shoulder in the spectrum of the dinuclear complex **4** has to be taken to indicate a more effective charge transfer from the metal to the arene.[24] The magnitude of this effect in the series **2**, **3** and **4** is virtually identical with that in the series **1**, **1**-$Cr(CO)_3$ and bis-complex of **1**.[22] Alkoxy substituents as in **5**, and other examples,[7,25] appear to cause a slight transannular destabilization of the excited states, as the most intense absorption maximum shows a hypsochromic shift. The two trimethylsilyl groups in **6**, on the other hand, cause a small, but significant bathochromic shift (Table 4).

Similar conclusions can be drawn from the carbonyl stretching frequencies in the IR spectra of these complexes (Table 4). As is generally accepted,[26] a shift to lower wavenumbers of the symmetric (a_1) and antisymmetric (e) ($\nu_{C=O}$) in $ArCr(CO)_3$ spectra accounts for increased π-basicity of the arene ligand and vice versa.

Table 4. Comparison of spectroscopic data evidencing transannular electronic interactions in [2.2]paracyclophane (**1**), diene **2** and its complexes **3**–**6**.

Compound	UV (CH_2Cl_2) λ_{max}/nm (log ε)	IR [KBr(CH_2Cl_2)] $(\nu_{C=O})_{a_1}/(\nu_{C=O})_e$ [cm^{-1}]	^{13}C NMR ($CDCl_3$) $\delta_{C=O}$ ppm	$^1J_{C,H}$/Hz A/B
1	288 (2.54)[a]	–	–	156
1-$Cr(CO)_3$	343 (4.04)[b]	1959/1878[b]	–	171/158
2	301 (2.10)	–	–	161.2
3	342 (3.97)	1951/1864	234.81	177.6/158.1
	sh 426 (3.12)	(1960/1881)		
4	357 (4.26)	1938/1875	233.90[c]	176.7[c]
	sh 440 (3.48)	(1962/1877)		
5	338 (4.13)	1950/1860	234.75	176.7/157.9
	sh 413 (3.33)	(1963/1883)		172.5
6	345 (3.97)	1948/1872	235.18	176.2/161.9
	sh 434 (3.09)	(1952/1876)		

[a] In ethanol. [b] In THF.[23] [c] For solubility reasons, data for bistrimethylsilyl derivative **4**-$SiMe_3$.

Surprisingly, for the bis-$Cr(CO)_3$ complex **4** $(\nu_{C=O})_{a_1}$ decreases, while $(\nu_{C=O})_e$ increases. The same phenomenon is observed for **1**-$Cr(CO)_3$ and the corresponding bis-complex.[22] Small differences in the carbonyl group bond-orders are also visible in their ^{13}C chemical shifts (Table 4).

A very interesting regularity was discovered for the one-bond aromatic C–H coupling constants ($^1J_{C,H}$) in the series **2**–**6**. While $^1J_{C,H}$ increases from 161.2 Hz in **2** to 171.6 Hz in the complexed ring A of **3**, it decreases to 158.1 Hz in the uncomplexed ring B of **3** (Table 4). The increase of $^1J_{C,H}$ upon complexation is generally known.[19a,21] Although various explanations have been offered,[27,28] the most recent one[20] definitely ascribes this effect to the rehybridization of the carbon atoms associated with the back-bonding from the chromium to the ligand.[29] This is supported by an "*ab initio*" theoretical study,[30] which showed that the C(2*p*)–H(1*s*) overlap integral in an $ArCr(CO)_3$ complex is smaller than in benzene, and this corresponds to a higher *s* character and thus a larger $^1J_{C,H}$.

Accordingly, within the self-consistent series **2**–**6** one may take variations of $^1J_{C,H}$ as indicative of hybridization changes. In accordance with the observed differences in ring geometries, especially their boat-type out-of-plane deformations in **2**–**6** (see above), the $^1J_{C,H}$ varies from 157.9 to 161.9 Hz for an uncomplexed and from 172.5 to 177.6 Hz for a complexed aryl moiety (Table 4). The fact that all $^1J_{C,H}$ values for the diene **2** and its complexes **3**–**6** are larger than the corresponding values fo **1** and **1**-$Cr(CO)_3$ is also in accord with the structural differences between **2** and **1**.

Conclusion

The tricarbonylchromium complexation of [2.2]paracyclophane-1,9-diene (**2**) and its derivatives induces significanct structural changes in the skeleton. The shrinkage of the interannular distances *a* and *b* on going from **2** to its complex **3** and further to its bis-complex **4** is more pronounced than the previously observed difference between **1** and **1**-$Cr(CO)_3$.[12] In general, the electron-withdrawing effect of the $Cr(CO)_3$ group, which is larger than that of a tetracyanoethylene (TCNE) unit in a **1**-TCNE complex,[31,32] results in a decrease in electron density between the decks of the [2.2]paracyclophane unit. In essence, this is equivalent to a reduction of the space between the two decks.

The complexation-induced changes of the geometrical as well as the spectroscopic features are further influenced by substituents, as evidenced within the series of complexes **3**–**6**. While chemical shifts in ^1H and ^{13}C NMR spectra, UV absorption maxima and carbonyl absorptions in IR spectra have previously been correlated with charge-transfer phenomena in such complexes, the above-mentioned correlations of one-bond C–H coupling constants ($^1J_{C,H}$) with geometrical and electronic features has not been seen as clearly before. The determination of $^1J_{C,H}$ within a consistent series of [2.2]paracyclophane derivatives can thus be used as a convenient and sensitive tool for detecting structural variations,[33] including those caused by changes of hydrogen positions which are not accurately determined by the X-ray structural analysis.

Experimental

Detailed procedure for the preparation of complexes **3**–**6**[7,11] will be reported elsewhere in another context.[25]

Crystal structure analysis of tricarbonyl(3-8-η-[2.2]paracyclophane-1,9-diene)chromium(0) (**3**). A crystal of **3**, grown from a solution in hexane/benzene (1:1), was sealed in a thin-walled quartz capillary in an inert atmosphere. The orthorombic crystal had space group $P2_12_12_1$ with a = 1065.7(6), b = 1106.6(7), c = 1261.1(7) pm, D = 1.46 g·cm^{-3}, μ = 0.75 cm^{-1}, V = 1497.7·10^6 pm^3, Z = 4. 1813 reflections with $2\theta < 50°$ [1380 with $I > 3\sigma(I)$] were recorded on a four-circle automated Huber diffractometer equipped with a closed-cycle low-temperature device, scan rate 4.5°·min^{-1}, Mo$K\bar{\alpha}$ radiation (71.07 pm), temperature 100 K. Direct methods[13] were used to solve the structure, with all atoms except H from E-map, and H atoms from Fourier synthesis, R = 0.037 (R_w = 0.050). For atomic coordinates of **3**, see Table 5.

Crystal structure analysis of (μ-3-8-η-[2.2]paracyclophane-1,9-diene)bis(tricarbonyl)chromium(0) (**4**). A crystal of **4**, grown from a solution in benzene/hexane/ethanol (1:1:1), was sealed in a thin-walled quartz capillary in an inert atmosphere. The monoclinic crystal had space group *C*2/*c* with

Table 5. Positional parameters and isotropic temperature factors ($\times 10^4$) of tricarbonyl(3-8-η-[2.2]paracyclophane-1,9-diene)chromium(0) (**3**).

Atom	*x*	*y*	*z*	U_{eq}[a]
Cr	1.2532(1)	0.3877(1)	0.9884(1)	188 (3)
O1	1.2228(3)	0.1756(3)	1.1318(3)	330(17)
O2	1.2064(3)	0.2245(3)	0.8036(3)	338(17)
O3	0.9758(3)	0.4303(3)	1.0033(3)	329(17)
C1	1.2347(4)	0.2566(4)	1.0769(4)	263(22)
C2	1.2248(4)	0.2883(4)	0.8744(4)	262(21)
C3	1.0816(4)	0.4248(4)	0.9974(3)	233(21)
C4	1.3885(4)	0.4813(4)	1.1095(3)	217(20)
C5	1.2981(4)	0.5601(4)	1.0707(3)	226(20)
C6	1.2897(4)	0.5829(4)	0.9611(3)	225(20)
C7	1.3731(4)	0.5273(4)	0.8916(3)	242(21)
C8	1.4416(4)	0.4266(4)	0.9287(3)	242(21)
C9	1.4496(4)	0.4033(4)	1.0375(3)	234(21)
C10	1.4441(4)	0.4982(4)	1.2173(3)	272(23)
C11	1.5400(4)	0.5760(5)	1.2238(3)	322(24)
C12	1.5807(4)	0.6411(4)	1.1253(3)	268(22)
C13	1.6673(4)	0.5875(4)	1.0568(4)	258(22)
C14	1.6609(4)	0.6115(4)	0.9483(3)	273(22)
C15	1.5670(4)	0.6867(4)	0.9073(4)	276(23)
C16	1.5032(4)	0.7601(4)	0.9799(4)	301(26)
C17	1.5098(4)	0.7374(4)	1.0869(4)	290(24)
C18	1.5114(4)	0.6644(5)	0.8004(3)	315(24)
C19	1.4150(4)	0.5872(5)	0.7921(3)	327(25)
H5	1.2397	0.6008	1.1215	
H6	1.2238	0.6383	0.9317	
H8	1.4844	0.3711	0.8767	
H9	1.4990	0.3315	1.0660	
H10	1.4100	0.4524	1.2822	
H11	1.5847	0.5905	1.2943	
H13	1.7336	0.5317	1.0872	
H14	1.7249	0.5754	0.8979	
H16	1.4515	0.8301	0.9551	
H17	1.4633	0.7916	1.1367	
H18	1.5453	0.7078	0.7353	
H19	1.3737	0.5685	0.7209	

[a] $U_{eq} = 1/3(U_{11}+U_{22}+U_{33})$.

$a = 1690.1(7)$, $b = 784.1(2)$, $c = 2010.2(6)$ pm, $\beta = 115.97(5)°$, $D = 1.32$ g·cm^{-3}, $\mu = 8.80$ cm^{-1}, $V = 2394.9 \cdot 10^6$ pm^3, $Z = 4$. 2108 reflections with $2\theta < 50°$ [1594 with $I > 3\sigma(I)$] were recorded on a four-circle automated Syntex $P2_1$ diffractometer, Mo$K\bar{\alpha}$ radiation (71.07 pm) room temp. Direct methods[13] were used to solve the structure, with all atoms except H from E-map, and H atoms from Fourier synthesis, $R = 0.044$ ($R_w = 0.035$). For atomic coordinates of **4**, see Table 6.

Crystal structure analysis of tricarbonyl(4,7-dimethoxy-11-16-η-[2.2]paracyclophane-1,9-diene)-chromium(0) (**5**). A crystal of **5**, grown from a solution in dichloromethane/hexane (1:1), was sealed in a thin-walled quartz capiallary in an inert atmosphere. The monoclinic crystal had spce group $P2_1/c$ with $a = 1475.2(2)$, $b = 970.1(1)$, $c = 1360.5(1)$ pm, $\beta = 113.08(1)°$, $D = 1.48$ g·cm^{-3}, $\mu = 55.83$ cm^{-1}, $V = 1791 \cdot 10^6$ pm^3, $Z = 4$. 2637 reflections with $2\theta < 120°$ [2134 with $I >$

Table 6. Positional parameters and isotropic temperature factors ($\times 10^4$) of (η-3-8-μ:11-16-η-[2.2]paracyclophane-1,9-diene)bis(tricarbonylchromium(0) (**4**).

Atom	*x*	*y*	*z*	*K*	U_{eq}[a]
Cr1	0.8354	0.2434	0.4135	1.0000	382 (3)
	0.0000	0.0001	0.0000	0.0000	
C10	0.0114	0.0568	0.4574	1.0000	472(26)
	0.0003	0.0006	0.0002	0.0000	
O10	0.7965	−0.0658	0.4821	1.0000	756(24)
	0.0002	0.0004	0.0002	0.0000	
C20	0.8116	0.1208	0.3325	1.0000	478(26)
	0.0003	0.0006	0.0002	0.0000	
(20	0.7947	0.0418	0.2801	1.0000	694(23)
	0.0002	0.0004	0.0002	0.0000	
C30	0.7179	0.3024	0.3752	1.0000	511028)
	0.0003	0.0005	0.0002	0.0000	
O30	0.3438	0.3344	0.3489	1.0000	702(23)
	0.0002	0.0004	0.0002	0.0000	
C1	0.9674	0.2831	0.5262	1.0000	372(23)
	0.0002	0.0005	0.0002	0.0000	
C2	0.8999	0.3961	0.5196	1.0000	441(26)
	0.0003	0.0006	0.0002	0.0000	
C3	0.8638	0.5059	0.4590	1.0000	400(24)
	0.0003	0.0005	0.0002	0.0000	
C4	0.8953	0.5072	0.4044	1.0000	364(22)
	0.0002	0.0005	0.0002	0.0000	
C5	0.9452	0.3667	0.4032	1.0000	415(25)
	0.0003	0.0005	0.0002	0.0000	
C6	0.9827	0.2551	0.4649	1.0000	396(20)
	0.0002	0.0006	0.0002	0.0000	
C11	1.0353	0.2288	0.6017	1.0000	492(27)
	0.0003	0.0006	0.0002	0.0000	
C41	0.8968	0.6662	0.3648	1.0000	458(26)
	0.0003	0.0006	0.0002	0.0000	
C50	0.5000	0.3492	0.7500	0.5000	756(60)
	0.0000	0.0011	0.0000	0.0000	
C51	0.4238	0.2608	0.7091	1.0000	692(35)
	0.0003	0.0009	0.0003	0.0000	
C52	0.4238	0.0861	0.7092	1.0000	660(37)
	0.0003	0.0008	0.0003	0.0000	
C53	0.5000	−0.0015	0.7500	0.5000	666(49)
	0.0000	0.0010	0.0000	0.0000	
H2	0.0073	0.4082	−0.5573	1.0000	
	0.0020	0.0044	0.0017	0.0000	
H3	0.8292	0.5889	0.4588	1.0000	
	0.0020	0.0038	0.0017	0.0000	
H5	0.9589	0.3593	0.3632	1.0000	
	0.0020	0.0040	0.0017	0.0000	
H6	1.0223	0.1611	0.4646	1.0000	
	0.0021	0.0042	0.0018	0.0000	
H11	1.0298	0.1221	0.6171	1.0000	
	0.0027	0.0052	0.0022	0.0000	
H41	0.8508	0.6917	0.3175	1.0000	
	0.0023	0.0042	0.0019	0.0000	
H50	0.5000	0.4703	0.7500	0.5000	
	0.0000	0.0097	0.0000	0.0000	
H51	0.3756	0.3192	0.3792	1.0000	
	0.0027	0.0054	0.0022	0.0000	
H51	0.3746	0.0232	0.6767	1.0000	
	0.0027	0.0055	0.0023	0.0000	
H53	0.5000	−0.1425	0.7500	0.5000	
	0.0000	0.0086	0.0000	0.0000	

[a] $U_{eq} = 1/3\ (U_{11}+U_{22}+U_{33})$.

Table 7. Positional parameters and isotropic temperature factors ($\times 10^4$) of tricarbonyl(4,7-dimethoxy-11-16-η-[2.2]paracyclophane-1,9-diene)chromium(0) (**5**).

Atom	*x*	*y*	*z*	U_{eq}[a]
Cr	0.71898(8)	0.1453(1)	0.86922(8)	485(5)
O1	0.9892(3)	−0.1472(6)	1.2020(4)	73(3)
O2	0.5973(4)	−0.3015(6)	1.0236(4)	81(3)
O3	0.8375(5)	0.4029(6)	0.9031(5)	94(4)
O4	0.5363(4)	0.3150(7)	0.7881(4)	89(3)
O5	0.7102(4)	0.1253(6)	0.6462(4)	97(4)
C1	0.8870(5)	−0.1566(8)	0.9217(5)	62(4)
C2	0.9123(5)	−0.2603(8)	0.9932(5)	62(4)
C3	0.8588(5)	−0.2635(7)	1.0686(5)	53(4)
C4	0.8913(5)	−0.1840(7)	1.1609(5)	55(4)
C5	0.8232(5)	−0.1332(8)	1.1976(5)	58(4)
C6	0.7230(5)	−0.1635(8)	1.1451(5)	64(4)
C7	0.6957(5)	−0.2670(8)	1.0691(5)	61(4)
C8	0.7641(5)	−0.3155(7)	1.0300(5)	56(4)
C9	0.6473(6)	−0.0599(9)	1.1470(5)	78(5)
C10	0.6247(5)	0.0504(9)	1.0795(5)	64(4)
C11	0.6796(5)	0.0508(7)	1.0068(5)	50(3)
C12	0.6441(5)	−0.0262(7)	0.9105(5)	51(4)
C13	0.7110(5)	−0.0791(7)	0.8703(5)	46(3)
C14	0.8126(5)	−0.0543(7)	0.9244(4)	48(3)
C15	0.8434(5)	0.0489(7)	1.0011(5)	49(3)
C16	0.7773(5)	0.1015(7)	1.0449(5)	49(3)
C17	1.0239(6)	−0.054(1)	1.2863(6)	87(6)
C18	0.5677(6)	−0.399(1)	0.9395(7)	83(5)
C19	0.7922(6)	0.3021(8)	0.8905(6)	69(4)
C20	0.6077(5)	0.2478(8)	0.8203(5)	59(4)
C21	0.7133(5)	0.1333(8)	0.7315(6)	68(4)
H1	0.906(4)	−0.143(6)	0.877(4)	
H2	0.991(7)	−0.31(1)	1.005(7)	
H5	0.845(4)	−0.063(6)	1.247(3)	
H8	0.737(5)	−0.369(7)	0.956(4)	
H9	0.604(8)	−0.08(1)	1.196(7)	
H10	0.550(7)	0.08(1)	1.039(6)	
H12	0.576(4)	−0.056(6)	0.866(4)	
H13	0.687(4)	−0.142(6)	0.822(3)	
H15	0.918(5)	0.080(7)	1.033(4)	
H16	0.811(4)	0.169(7)	1.113(4)	
H17	1.107(5)	−0.043(8)	1.318(5)	
H172	1.017(5)	−0.081(7)	1.333(4)	
H173	0.988(5)	0.045(8)	1.262(5)	
H181	0.482(5)	−0.408(7)	0.914(5)	
H182	0.572(8)	−0.37(1)	0.862(7)	
H183	0.586(5)	−0.481(7)	0.965(4)	

[a] $U_{eq} = 1/3\ (U_{11}+U_{22}+U_{33})$.

were recorded on a CAD 4-SDP (Enraf Nonius) diffractometer, Cu$K\bar{\alpha}$ radiation (154.18 pm) , room temp. Direct methods[14] were used to solve the structure, with all atoms except H from E-map, and H atoms from Fourier synthesis, $R = 0.061$ ($R_w = 0.070$). For atomic coordinates, see Table 7.

Table 8. positional parameters and isotropic temperature factors ($\times 10^4$) of tricarbonyl[1,10-bis(trimethylsilyl)-11-16-η-[2.2]paracyclophane-1,9-diene]chromium(0) (**6**).

Atom	*x*	*y*	*z*	U_{eq}
Cr	0.23013(5)	0.36029(2)	0.54644(2)	358(2)
Si1	0.28512(10)	0.54355(4)	0.72731(4)	496(4)
Si2	0.51201(11)	0.15914(4)	0.48656(4)	533(4)
O1	−0.03612(27)	0.26277(10)	0.47856(11)	776(14)
O2	0.27118(29)	0.41107(12)	0.38134(11)	878(15)
O3	−0.08251(23)	0.45210(9)	0.56654(10)	610(12)
C1	0.40378(31)	0.45899(11)	0.72505(12)	423(12)
C2	0.52061(36)	0.43906(13)	0.78185(14)	521(16)
C3	0.61445(33)	0.37213(12)	0.77719(13)	456(14)
C4	0.54028(36)	0.31224(14)	0.80492(14)	502(16)
C5	0.57421(37)	0.25045(14)	0.76829(14)	511(16)
C6	0.68397(32)	0.24748(12)	0.70357(13)	446(14)
C7	0.79066(33)	0.30394(14)	0.68998(14)	471015)
C8	0.75556(34)	0.36552(14)	0.72646(14)	486(15)
C9	0.65329(35)	0.19857(12)	0.63713(14)	486(15)
C10	0.54126(31)	0.21386(11)	0.57741(13)	421(13)
C11	0.44759(30)	0.28104(11)	0.58646(12)	362(12)
C12	0.52062(30)	0.34149(11)	0.55862(12)	367(12)
C13	0.48574(30)	0.40439(12)	0.59606(13)	371(13)
C14	0.37793(29)	0.40616(11)	0.66109(12)	357(12)
C15	0.26843(30)	0.34910(12)	0.67423(12)	386(12)
C16	0.30409(31)	0.28718(12)	0.63742(13)	388(12)
C17	0.07041(33)	0.29965(13)	0.50458(14)	489(15)
C18	0.25753(34)	0.39253(14)	0.44459(14)	548(16)
C19	0.04051(32)	0.41826(12)	0.55857(13)	420(14)
C20	0.25918(57)	0.57774(18)	0.62616(21)	689(23)
C21	0.42267(65)	0.60337(21)	0.78857(20)	862(28)
C22	0.06332(53)	0.53098(22)	0.77064(27)	806(27)
C23	0.69109(67)	0.09354(22)	0.48718(28)	936(31)
C24	0.29106(56)	0.11671(20)	0.48838(24)	770(25)
C25	0.52581(56)	0.21515(19)	0.39896(18)	680(22)
H2	0.54769(315)	0.47004(118)	0.82541(132)	
H4	0.44146(311)	0.31397(116)	0.84518(129)	
H5	0.50857(331)	0.21250(121)	0.78390(135)	
H7	0.87199(321)	0.30047(115)	0.64789(134)	
H8	0.81701(323)	0.40167(118)	0.70828(130)	
H9	0.71569(314)	0.16125(112)	0.63639(127)	
H12	0.60938(257)	0.33854(94)	0.52148(106)	
H13	0.55593(277)	0.44201(102)	0.58471(114)	
H5	0.18447(308)	0.35125(113)	0.71133(126)	
H16	0.24510(274)	0.24903(100)	0.64900(113)	
H201	0.18484(465)	0.55186(169)	0.59666(191)	
H202	0.36682(499)	0.58077(180)	0.60658(204)	
H203	0.18789(444)	0.61755(159)	0.62758(176)	
H211	0.36719(502)	0.64004(176)	0.79332(206)	
H212	0.53056(479)	0.60507(176)	0.77398(197)	
H213	0.42897(450)	0.58801(159)	0.84840(190)	
H221	0.01324(501)	0.56943(182)	0.77870(206)	
H222	0.07411(485)	0.52230(176)	0.82094(202)	
H223	−0.00900(477)	0.50619(174)	0.74108(193)	
H231	0.67204(456)	0.06177(172)	0.43626(195)	
H232	0.68931(479)	0.05907(170)	0.53636(193)	
H233	0.79439(506)	0.10841(191)	0.49330(223)	
H241	0.28202(457)	0.08497(166)	0.44136(184)	
H242	0.19578(439)	0.14181(159)	0.49449(188)	
H243	0.28524(437)	0.08656(159)	0.53338(186)	
H251	0.51821(463)	0.19048(169)	0.35811(188)	
H252	0.64778(422)	0.23754(145)	0.39377(165)	
H253	0.43318(411)	0.24651(145)	0.39355(166)	

[a] $U_{eq} = 1/3\ (U_{11}+U_{22}+U_{33})$.

Crystal structure analysis of tricarbonyl(1,10-bis-(trimethylsilyl)-11-16-η-[2.2]paracyclophane-1,9-diene)chromium(0) (**6**). A crystal, grown from a solution in hexane, was sealed in a thin-walled quartz capillary in an inert atmosphere. The monoclinic crystal had space group $P2_1/n$ with a = 750.8(2), b = 1963.6(5), c = 1699.6(4) pm, β = 91.48(3)°, D = 1.29 g·cm^{-3}, μ = 5.25 cm^{-1}, V = 2504.8·10^6 pm^3, Z = 4. 5784 reflections with 2 θ < 50° [4290 with $I > 3\sigma(I)$] were recorded on a four-circle automated Syntex $P2_1$ diffractometer, Mo$K\bar{\alpha}$ radiation (71.07 pm), room temp. Direct methods[13] were used to solve the structure, with all atoms except H from E-map, and H atoms from Fourier synthesis, R = 0.038 (R_w = 0.028). For atomic coordinates, see Table 8.

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