Preparation and NMR Properties of Tricarbonylchromium(0) Derivatives of Dithiacyclophanes. An Estimate of the Reduction in Ring Current of an Aromatic Ring on Tricarbonylchromium Complexation

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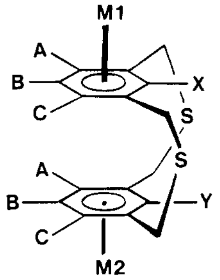
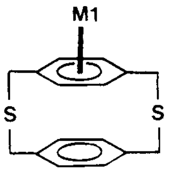
The tricarbonylchromium(0) complexes **9–16** of 2,11-dithia[3.3]metacyclophane (**1**) its 6,15-dimethyl (**2**), *syn*- and *anti*-9,18-dimethyl (**6, 7**), 5,7,14,16-tetramethyl (**3**), 9-fluoro (**4**), and 9,18-difluoro (**5**) derivatives, the complex **17** from 2,11-dithia[3.3]paracyclophane (**8**), and the bis complex **18** of **1** were prepared in 20–80% yields by reaction of the cyclophane with either 1.6 or 6 equiv of $Cr(CO)_6$ or $Cr(CO)_3(CH_3CN)_3$. The IR, UV, and ^1H, ^{19}F, and ^{13}C NMR spectra of the complexes are reported and discussed. Characteristically different spectra are obtained for the *syn*- and *anti*-cyclophanes, and some shifts are reversed in the thiacyclophanes from the cyclophanes themselves. Analysis of their NMR spectra indicates that the time-averaged conformation of the tricarbonylchromium umbrella is eclipsing the cyclophane bridges. The reduction of ring current of an arene on complexation with a tricarbonylchromium moiety is estimated at 40% by analysis of the shift data of these cyclophanes. The complexation shifts in these dithiacyclophanes for protons is 1.6–2.0 ppm and for carbons is 32–39 ppm (tertiary carbons) and 26–29 ppm (quaternary carbons).

Introduction

Cyclophanes have attracted much attention because of their unusual geometry and interesting NMR spectra.[1,2] More recently arene–metal complexes of the cyclophanes have been studied[3] because of interest in their crystal structures[4-7] and their NMR spectra with regard to the anisotropy effect of the metals[8-12] and because the complexes themselves have potential as organic conductors.[13-16] Surprisingly the analogous dithiacyclophanes, which commonly are the precursors to the cyclophanes themselves, have almost no metal complexes reported, even though they have been well studied by NMR spectroscopy[17] and have many crystal structures[18] determined and like the cyclophanes provide an opportunity to comment on anisotropy effects. Since the metal also strongly withdraws electrons from the arene, modification of the thiacyclophane chemistry can be expected.[19-22] This paper reports the synthesis and NMR properties of the tricarbonylchromium derivatives **9–19** of the dithiacyclophanes **1–8** (Chart I).

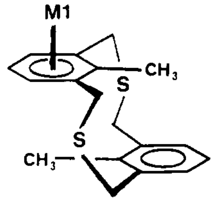
Chart I





8 M1: –

17 M1: $Cr(CO)_3$



7 M1: –

16 M1: $Cr(CO)_3$

	A	B	C	X	Y	M1	M2
1	H	H	H	H	H		
2	H	CH_3	H	H	H		
3	CH_3	H	CH_3	H	H		
4	H	H	H	F	H		
5	H	H	H	F	F		
6	H	H	H	CH_3	CH_3		
9	H	H	H	H	H	$Cr(CO)_3$	
10	H	CH_3	H	H	H	$Cr(CO)_3$	
11	CH_3	H	CH_3	H	H	$Cr(CO)_3$	
12	H	H	H	F	H		$Cr(CO)_3$
13	H	H	H	F	H	$Cr(CO)_3$	
14	H	H	H	F	F	$Cr(CO)_3$	
15	H	H	H	CH_3	CH_3	$Cr(CO)_3$	
18	H	H	H	H	H	$Cr(CO)_3$	$Cr(CO)_3$
19	H	H	H	F	F	$Cr(CO)_3$	$Cr(CO)_3$

Syntheses

The only reported[23] example of a tricarbonylchromium complex of a thiacyclophane is compound **20** (Chart II), derived from the tetrathia[7.7]paracyclophane **21**, in 30%

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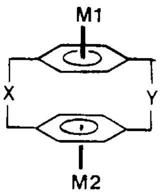
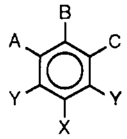
Chart II



	X	Y	M1	M2
20	$-S(CH_2)S-$	$-S(CH_2)S-$	$Cr(CO)_3$	
21	$-S(CH_2S-$	$-S(CH_2)S-$		
22		$-S(CH_2)S-$	$Cr(CO)_3$	
23			$Cr(CO)_3$	
24	$-S(CH_2)S-$	$-S(CH_2)S-$	$Cr(CO)_3$	$Cr(CO)_3$

Chart III

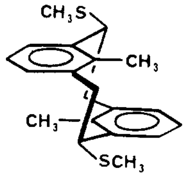


	A	B	C	X	Y
25	H	H	H	H	CH_2SH
26	H	CH_3	H	H	CH_2SH
27	CH_3	H	CH_3	H	CH_2SH
28	H	H	H	CH_3	CH_2SH
29	H	H	H	F	CH_2SH
31	H	H	H	H	CH_2Br
32	H	CH_3	H	H	CH_2Br
33	CH_3	H	CH_3	H	CH_2Cl
34	H	H	H	CH_3	CH_2Br
35	H	H	H	F	CH_2Br

Chart IV

30 Y: SH

36 Y: Br



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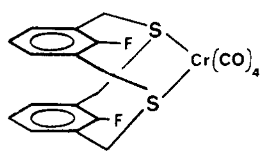

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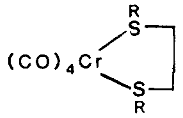

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yield by heating **21** with $Cr(CO)_6$. Products were also obtained arising by extrusion of the 1,3-propanedithiol units, i.e., **22** and **23**, and a very small (0.2%) amount of the bis complex **24**.

The reaction of an arene and $Cr(CO)_6$ to form an (η^6-arene)$Cr(CO)_3$ complex was first reported in 1958, independently by three groups,[24-26] and because of its simplicity is the most widely used to prepare such complexes. In many cases the yield of complex is low, probably because of decomposition of the complex at the relatively high (100–160 °C) temperatures involved. The yields can however be improved by addition of donor solvents.[27,28] While such complexes can also be prepared by photochemical replacement of CO from $Cr(CO)_6$,[29] and replacement of a more labile ligand L (=pyridine, acetonitrile, ammonia) from a complex of the type $[Cr(CO)_3L_3]$,[30] the simplicity of the thermal replacement method using $Cr(CO)_6$ led us to try this first.

The required dithiacyclophanes **1–8** were all prepared in over 70% yield by using our standard procedure[31,32] in which a dilute equimolar mixture of the corresponding dithiol **25–30** (Chart III) and dihalide **31–36** (Chart IV) in benzene was added dropwise to a solution of KOH in approximately 3 times the volume of ethanol:water (9:1). The dithiols were prepared from the dihalides through the isothiouronium salts[33] (the thiourea method), and the dihalides were either commercial or prepared by NBS bromination of the corresponding methyl compound or by chloromethylation of the appropriately substituted aromatic as indicated in the Experimental Section.

When the dithiacyclophanes **1–8** were heated with 1.1–1.4 equiv of $Cr(CO)_6$ in n-Bu_2O for 3–4 h at reflux, good yields (50–80%, Table I) of the complexed phanes were obtained, except for the difluorocyclophane **5**, which gave only 28% of **14**, and the *anti*-cyclophane **7**, which did not yield any of **16**. When only one fluorine was present as in **4**, then complexation occurred mostly on the more electron-rich H ring (46% yield) to form **13** with only about 2% complexation on the F ring to give **12**. The reduced electron density in the fluorine-containing arene rings presumably weakens the metal–arene bond and makes dissociation of the complex easier at the temperatures involved. Use of the more reactive complexing agent $Cr(CO)_3(CH_3CN)_3$[34] gave a poorer yield of **14** (12%) but did enable the anti complex **16** to be obtained, albeit in poor yield (20%). It is not obvious to us why **7** is so resistant to complex, since *anti*-[2.2]metacyclophanes complex readily with $Cr(CO)_6$[35] and so do the bridge–SMe-substituted derivatives, e.g., **37**.[36] The sulfur atoms appear to be involved, since in most complexations, a small amount of a compound that is faster moving than the products on chromatography is also obtained. In each reaction, this faster moving product has similar TLC properties and thus are probably similar to each other. In the reaction of **5** with $Cr(CO)_3(CH_3CN)_3$, this other compound can actually be isolated as a flaky yellow solid, which decomposes at 193 °C. This we believe to have structure **38**, since the compound shows a mass spectrum molecular ion at m/e 472, which is consistent with **5** plus one Cr and four carbonyls, with the next peak at m/e 308 being formation of the uncomplexed phane **5**. Moreover the ^1H NMR spectrum shows both aryl rings uncomplexed at δ 7.1–6.7 and

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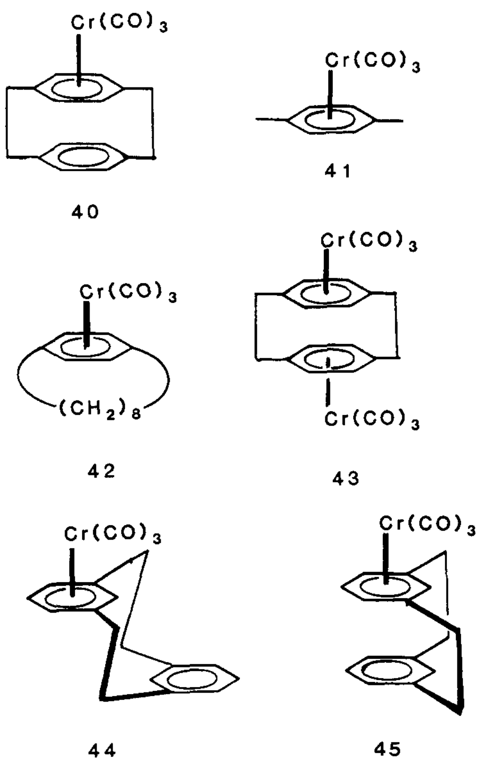
Chart V



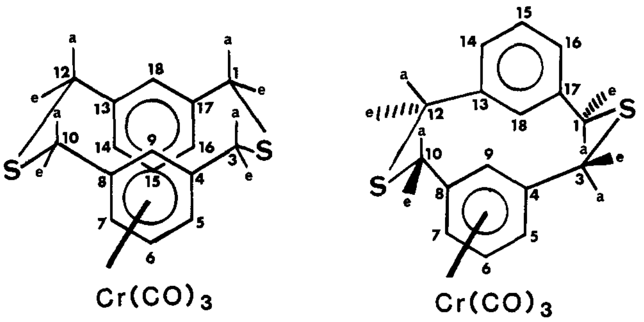
AB methylene bridges at δ 4.46 and 3.53. Ziegler et al.[23,37] have reported that cyclophane **21** forms mono- and bis-$M(CO)_4$ (where M = W, Mo) complexes between the two sulfur atoms in each bridge. It is also known[38-40] that both $Cr(CO)_6$ and $Cr(CO)_3(CH_3CN)_3$ react with sulfides such as 2,5-dithiahexane to yield complexes of the type **39**; when R in **39** is a substituted arene ring that is electron rich, the normal η^6-arene complex is formed instead of **39**.[40] In the case of the difluorocyclophane **5**, reaction with the electron-poor aryl rings is presumably sufficiently slow that significant quantities of the sulfur adduct **38** can be isolated. Reaction of dithiacyclophane **1** with 6 equiv of $Cr(CO)_6$ in di-*n*-butyl ether at reflux yielded 65% of the bis-complexed cyclophane **18**. Since traces of the other bis-complexed cyclophanes from **2–6** could also be detected in the appropriate reactions, presumably **2–6** on reflux with excess $Cr(CO)_6$ would also yield their analogous bis-complexed cyclophanes. No tris-complexed species could be detected.

Properties of the Complexed Dithiacyclophanes

The complexes **9–19** were all yellow solids, whose mp, IR, UV, and analytical data are given in Table I.

IR and UV Spectra. A characteristic feature of $[(\eta^6\text{-arene})Cr(CO)_3]$ complexes in their IR spectra are the two intense bands in the 2000–1950- and 1950–1850-cm^{-1} regions.[41,42] For the complexed dithiacyclophanes **9–18**, these bands occur close to 1960 and close to 1870 cm^{-1} (Table I) and are easily recognizable. $[(\eta^6\text{-arene})Cr(CO)_3]$ complexes also show a characteristic charge-transfer band in their UV spectra at about 320 nm.[43] The band for **9–11**, **15**, and **17** does occur at 321–324 nm, and that for the anti compound **16** appears at 330 nm (Table I). The 320-nm band is believed to arise from charge transfer from the Cr → arene, since the position of the maximum does not depend on the nature of substituents on the arene ring, though the extinction coefficient does.[43] Charge transfer across the rings in cyclophanes however does have an effect. The paracyclophane **40** (Chart V) absorbs at 341 nm, while the *p*-xylene complex **41** absorbs at 318 nm, and the complex **42**, which has about the same degree of ring deformation as **40**, also absorbs at 324 nm,[44] indicating that it is not the bending of the arene ring that results in the bathochromic shift. Clearly except for **16** and **18**, in the thiacyclophane complexes above, little interaction is occurring across the rings. In the bis-complex **18**, however, the $Cr(CO)_3$ group on the opposite benzene ring substantially reduces the electron density in this ring and allows easier donation from Cr → arene in the first ring. This also occurs for the bis-complexed paracyclophane **43**, which absorbs at 358 nm.[44] Increased methyl substitution on the arene ring of **40** marginally increases the λ_{max} by 1–2 nm[45] as it also does for **9** → **10** → **11**. Comparison of the anti complex **16** (330 nm) with its syn isomer **15** (321 nm) suggests that there is more interaction across the rings in **16** than in **15**, despite the fact that other authors[46] suggest that no π–π interaction occurs across the rings in the [2.2]cyclophane **44**.

Scheme I. Numbering System for the Complexed Dithiacyclophanes



NMR Features of the Dithiacyclophane Complexes

Conformations of the Cyclophanes (Scheme I). The syn structure assigned to **9**, **10**, **11**, and **18** follows by comparison of the chemical shifts of H-5,7 with the shifts for those protons in the syn isomer **15** relative to the anti isomer **16** (see Table II). The syn isomer **6** is not thermally convertible to the anti isomer **7**, and hence the structures of **15** and **16** are known unambiguously. The structures of **15** and **16** are further verified by the highly shielded internal methyl protons of the anti isomer **16**. If any of **9**, **10**, **11**, or **18** were anti isomers, H-9 would be shielded as is the internal methyl of **16**. The fluorocyclophanes **4** and **5** are both syn.[47] The chemical shifts of all the arene protons in **13** and **14** also indicate that they are syn, if

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Table I

compd	yield, %	mp, °C	mol formula[a]	IR (KBr) C=O, cm^{-1}	UV (CH_3CN) Cr → arene λ, nm ($10^{-3}\epsilon$)
9	80	157–158	$C_{19}H_{16}CrO_3S_2$	1950, 1868	322 (10.6)
10	70	210–212	$C_{21}H_{20}CrO_3S_2$	1950, 1870	323 (10.0)
11	70	229–231	$C_{23}H_{24}CrO_3S_2$	1960, 1885	324 (10.0)
12	2	(by nmr, not isolated)			
13	46	169–170	$C_{19}H_{15}CrFO_3S_2$	*b*	*b*
14	28	185 (dec)	$C_{19}H_{14}CrF_2O_3S_2$	*b*	*b*
15	68	202–203	$C_{21}H_{20}CrO_3S_2$	1970, 1875	321 (9.7)
16	20	212–214	$C_{21}H_{20}CrO_3S_2$	1950, 1860	330 (8.2)
17	52	170–171	$C_{19}H_{16}CrO_3S_2$	1950, 1860	323 (9.2)
18	65	202–204	$C_{22}H_{16}Cr_2O_6S_2$	1960, 1870	330 (22.3)

[a] Satisfactory C, H, analyses obtained. [b] Data not available.

Table II. ^1H NMR Chemical Shifts (δ), Complexation Shifts (Δ), Substituent Shifts (Δδ), and Conformation Shifts (ΔΔδ) for the Dithiacyclophanes 1–8 and Their Chromium Tricarbonyl Complexes 9–18

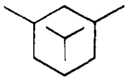
	H-5,7				H-6				H-9				H-14,16		H-15		H-18		H-3,10-ax		H-3,10-eq		H-1,12-ax		H-1,12-eq	
	δ	Δ[a]	Δδ[b]	ΔΔδ[c]	δ	Δ[a]	Δδ[b]	ΔΔδ[c]	δ	Δ[a]	Δδ[b]	ΔΔδ[c]	δ	Δ	δ	Δ	δ	Δ	δ	Δ	δ	Δ	δ	Δ	δ	Δ
1	6.91		−0.37		6.91		−0.37		6.82		−0.46		6.91		6.91		6.82		3.72		3.72		3.72		3.72	
		1.97		−0.06		1.73		+0.18		1.99		−0.08		−0.13		−0.13		−0.42		+0.21		+0.27		−0.13		−0.13
9	4.94		−0.43		5.18		−0.19		4.83		−0.54		7.04		7.04		7.24		3.51		3.45		3.85		3.85	
2	6.66		−0.62		2.13[d]				6.58		−0.70		6.66		2.13[d]		6.58		3.65		3.65		3.65		3.65	
		1.84		+0.07		0.05				1.89		+0.02		−0.22		−0.12		−0.45		+0.16		+0.17		−0.17		−0.17
10	4.82		−0.55		2.08[d]				4.69		−0.68		6.88		2.25[d]		7.03		3.49		3.48		3.82		3.82	
3	2.21[d]				6.80		−0.48		6.70		−0.58		2.21[d]		6.80		6.70		3.77		3.77		3.77		3.77	
		0.14				1.65		+0.26		1.80		+0.11		−0.02		+0.01		−0.33		+0.13		+0.37		−0.10		−0.03
11	2.07[d]				5.15		−0.22		4.90		−0.47		2.23[d]		6.79		7.03		3.64		3.40		3.87		3.80	
4	6.94		−0.34		6.94		−0.34		7.11		−0.17		6.94		6.69		124.0[e]		3.79		3.79		4.20		3.50	
		1.97		−0.06		1.77		+0.14		1.91		0.00		−0.12		−0.14		−1.0		+0.31		+0.31		−0.01		−0.01
13	4.97		−0.40		5.17		−0.20		5.20		−0.17		7.06		6.83		125.0[e]		3.48		3.48		4.21		3.51	
5	6.98		−0.30		6.70		−0.58		−126.7[e]				6.98		6.70		126.7[e]		4.34		3.43		4.34		3.43	
		1.74		+0.17		2.02		−0.11		−18				−0.17		−0.15		0		+0.27		+0.18		+0.03		−0.04
14	5.24		−0.13		4.68		−0.69		−144.7[e]				7.15		6.85		126.7[e]		4.07		3.25		4.31		3.47	
6	6.59		−0.69		6.59		−0.69		2.51[d]				6.59		6.59		2.51[d]		4.00		3.80		4.00		3.80	
		1.68		+0.23		1.68		+0.23		0.07				−0.35		−0.28		−0.06		+0.18		+0.22		−0.09		−0.13
15	4.91		−0.46		4.91		−0.46		2.44[d]				6.94		6.87		2.57[d]		3.82		3.58		4.09		3.93	
7	7.27		−0.01		7.27		−0.01		1.30[d]				7.27		7.06		1.30[d]		3.68		3.68		3.68		3.68	
		1.77		−0.12		1.77		−0.12		0.18				−0.09		−0.08		−0.48		+0.16		+0.27		−0.15		−0.15
16	5.50		−0.13		5.50		−0.13		1.12[d]				7.36		7.14		1.78		3.52		3.41		3.83		3.83	
8	6.86[f]		−0.42										6.86[f]						3.82		3.82		3.82		3.82	
		1.85		+0.06										−0.26						+0.39		+0.39		−0.07		−0.07
17	5.01		−0.36										7.12						3.43		3.43		3.89		3.89	
1	6.91		−0.37		6.91		−0.37		6.82		−0.46								3.72		3.72					
		1.81		+0.10		1.58		+0.33		1.59		+0.32								+0.10		+0.18				
18	5.10		−0.27		5.33		−0.04		5.23		−0.14								3.62		3.54					

[a] $\Delta = (\delta_{arene} - \delta_{complex})$. [b] $\Delta\delta = (\delta_{arene} - \delta_{benzene})$ or $(\delta_{complex} - \delta_{benzene\ complex})$. [c] $\Delta\Delta\delta = \Delta\delta_{complex} - \Delta\delta_{arene}$. [d] Methyl protons. [e] ^{19}F NMR shift. [f] H-5,6,8,9.

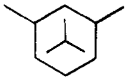
comparison to **15** (syn) and **16** (anti) is made, and as well the fluorine shifts in the uncomplexed ring (F-18, Table II) remain unchanged.

Complexation Shift. A characteristic feature in both ^{1}H and ^{13}C NMR spectra of [(η^6-arene)Cr(CO)$_3$] complexes is the shift to higher fields of the coordinated arene protons (~2 ppm) and carbons (~20–40 ppm) relative to the free arene.[8,10,12,48-51] This feature is particularly helpful in characterizing complexation reaction products from the dithiacyclophanes, since if the mono-complexed product is formed, only one of the two arene rings appears upfield, whereas if the bis complex has formed, both arene rings appear upfield. The upfield shifts have been interpreted in terms of a combination of effects including quenching of the ring current, withdrawal of electron density from the ring by the Cr(CO)$_3$ moiety, the magnetic anisotropy of the chromium–ligand bond, and partial rehybridization of the ring carbon atoms. In fact study of several cyclophane–metal complexes has allowed at least some separation of these effects.[8-12,50] Since in the dithiametacyclophanes both syn and anti isomers are known and the spacing between the arene rings is different from the [2.2]metacyclophanes, additional information is provided by analysis of the spectra of the complexes **9**–**18**. The chemical shifts for the protons in complexes **9**–**18** are given in Table II, together with their shifts in the free arenes, the complexation shift Δ, and for the complexed arene ring protons substituent shifts $\Delta\delta$ and $\Delta\Delta\delta$ (see table for calculation).

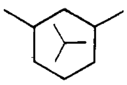
Conformation of the Tricarbonyl Umbrella Relative to the Arene Ring. The complexation shifts, Δ, for the arene ring protons of the complexed dithiacyclophanes fall in the range 1.6–2.0 ppm. The actual shift depends on the other substituents and the time-averaged conformation adopted by the Cr(CO)$_3$ moiety. This can be assessed by examination of $\Delta\Delta\delta$: In Table II are given the substituent shifts $\Delta\delta$, calculated by subtracting δ(benzene) = 7.28 or δ(benzene chromium tricarbonyl) = 5.37 from the respective chemical shift of each proton. These indicate the effect of the arene substituents on the remaining protons. The difference between $\Delta\delta$ for the complexed and the uncomplexed arene ($\Delta\Delta\delta$) then indicates a difference in the shielding of that proton on complexation relative to that in the parent (benzene), caused by that pattern of substituents. For example, consider **1** and **9**: H-6 in **9** is more deshielded by 0.18 ppm than would be expected on the basis of substituent shifts,[52] and H-5,7 and H-9 are marginally shielded by ~0.06 ppm. This suggests that **9** adopts a somewhat different time-averaged conformation from benzene chromium tricarbonyl. Deshielding of protons meta to methyl substituents in arene chromium tricarbonyl complexes has been observed previously and interpreted as indicating a preference for the eclipsed conformer A, rather than B or a staggered conformer such as C.[49,52-54] Clearly a similar conformation is also preferred in the complexed dithiacyclophane **9**, in which the carbonyl groups eclipse the cyclophane bridge carbons and H-6. An estimate of the relative amounts of A and B present at room temperature can be made using the method of Brocard.[55] The maximum difference between H-5$_A$ and H-6$_B$ of the two conformers A and B of m-xylene has been estimated at 0.84 ppm. If x_a is the proportion of A, then



A



B



C

$$\delta_5 - \delta_6 = 0.84(2x_a - 1) \qquad \text{(ref 55)}$$

For m-xylene chromium tricarbonyl, x_a is about 0.75, while for **9** it is about 0.65. It is also about 0.65 for both **44** and **45**. All three cyclophanes (**9**, **44**, and **45**) thus show the same conformational preference for A. This effect would be expected to be enhanced for **10**, where the three carbonyls can eclipse the three substituents in A and would be expected to be decreased for **11**, in which in both A and B two substituents are eclipsed. Unfortunately, the methyl substituents preclude the above analysis; however, the chemical shift of H-9 gives an indication that this is correct, in that we would expect for H-9 $\delta_{10} < \delta_9 < \delta_{11}$, which is what is observed (eclipsing by the carbonyls increases chemical shift (deshields)).[53] For the bis-complexed example **18**, the difference in chemical shift between H-5 and H-6 is 0.23 ppm, almost identical with that in **9**, indicating a similar conformational preference for A. The absolute chemical shifts are however both deshielded by about 0.15 ppm, which reflects the effect of the electron-withdrawing nature of the Cr(CO)$_3$ group on the opposite ring, i.e., this ring is less shielding than an uncomplexed ring. In the case of the compounds with an internal methyl substituent, **15** and **16**, $\delta_{\text{H-5}} - \delta_{\text{H-6}} = 0$, which on the basis of the above analysis would indicate no preference for either the A or B conformer. However in these two cases, molecular mechanics calculations indicate that the internal methyl group is bent out of the plain of the arene ring as it is in the dithiacyclophanes themselves, and this may affect the conformer populations.

The two fluorophanes **13** and **14** appear to adopt conformations A and B, respectively. For **13**, $\Delta\Delta\delta$ of H-6 and H-5 are of the same sign and magnitude as for those of **9** (as are $\Delta\delta$), and hence the same conformation may be assumed. For **14** however, $\Delta\Delta\delta$ of H-5 and H-6 are of opposite sign, leaving H-5 more deshielded than H-6 by 0.56 ppm (in **5**, only 0.28 ppm). This thus indicates conformation B for **14**. The complexation shift for the fluorine nucleus is very large at 18 ppm and has been reported[56] to be 20 ppm for fluorobenzene chromium tricarbonyl. No good explanation for such a large shift has been advanced, though it appears to involve charge development at the carbons involved in the complexation.[56] In contrast, the complexation shifts of both the protons and carbons in methyl substituents are rather small (<0.2 and <0.8 ppm, respectively). In the m-xylene complex, for protons, it is 0.04 ppm.[52] The complexation shifts for the bridge protons H-3,10 are also small, 0.10–0.39 ppm, but in all examples are positive, i.e., are shielded in the complex. The more deshielded proton of each bridge methylene pair is assigned as pseudoaxial[57], i.e., parallel to the C-9 substituent, fluorine having the largest effect in **5**.

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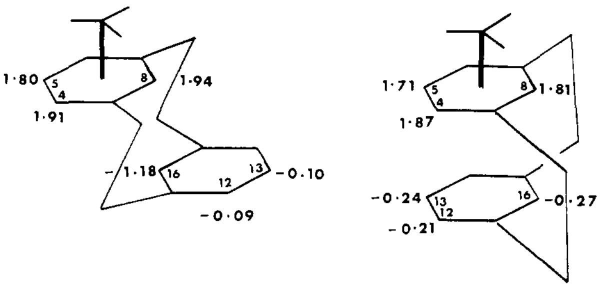
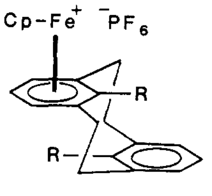


44 45

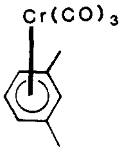
Figure 1. Proton NMR complexation shifts for compounds 44 and 45.

Change in Ring Current on Complexation of an Arene Ring. The complexation shifts for the uncomplexed arene protons (H-14,15,16,18) are all small, <0.45 ppm, and negative, i.e., the protons are deshielded. This can be interpreted as a reduction of the ring-current shielding caused by the opposite complexed ring in the syn complexes. The complexation shifts for the *anti*-[2.2]-cyclophane 44[50] and *syn*-cyclophane 45[19,58] are shown in Figure 1. The large reduction of shielding of H-16 of 44 by 1.18 ppm must reflect the reduction in ring current in the complexed ring, whereas the small changes in H-12,13, which are not affected by the ring current of the opposite deck, must reflect a change in electron density in that ring. Clearly on comparing H-12,13 of 44 with 45, the shifts are larger in the latter. This could be either because of greater interaction between the syn rings, (though the earlier UV results make this less likely) or because of the change in ring current of the complexed ring is now felt by all hydrogens. Of significance is exactly the same results are obtained for the pair 16 (*anti*) and 15 (*syn*). The reduction of the shielding of the methyl group on C-18 is 0.48 ppm. Thus the ring-current shielding of H-16 is reduced from 3.0 ppm in [2.2]metacyclophane to 1.82 ppm in 44 (i.e., 61%), and for the methyl group on C-18, it is reduced from 1.21 ppm in 7 to 0.73 ppm in 16 (i.e., 61%). The fact that these two independent measurements are both 61% may be coincidence but clearly indicates that the "reduction of ring-current effect" on complexation of the benzene ring by a chromium tricarbonyl is of the order of 100 − 61%, or about ~40%. The analogous values for the iron complexes 46 and 47 prepared by Boekelheide[11] are 81% and 75%, respectively, indicating a reduction of ring current of about 20–25%.



46 R: H

47 R: CH_3



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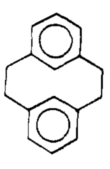
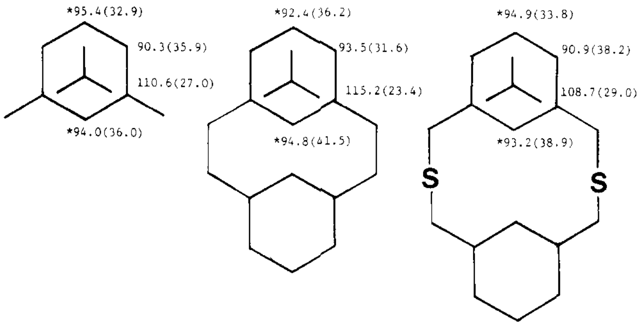


49

^{13}C NMR Data. The carbon chemical shifts for the complexes 9–18 are given in Table III, together with their shifts in the free arenes, and for the complexed arene carbons the complexation shifts, Δ.

Both complexed [2.2]metacyclophanes[8,9,12,59] and methylarenes[51,60–63] have been reasonably well studied by ^{13}C NMR analysis, and the relevant shift data are given in Figure 2 for complexed *m*-xylene, 48, and [2.2]metacyclophane, 44, together with our data for dithia[3.3]-metacyclophane, 1. The assignment of shifts to the latter presents a problem because of the change in order of the chemical shifts at the carbons marked with an asterisk in 44 and 48 (Figure 2). The shifts of C-2 (94.0 ppm) and C-5 (95.4 ppm) in 48 have been unambiguously assigned on the basis of deuterio-substituted compounds.[60] The shifts of C-8 (94.8 ppm) and C-5 (92.4 ppm) in 44 have been assigned on the basis of study of a number of substituted compounds[9,59] and as well on the basis that in *anti*-[2.2]-metacyclophane itself, 49, C-8 is strongly deshielded (136.3 ppm) relative to C-5 (128.6 ppm), attributed to a decrease in electron density at that site due to p-orbital compression[64] across the rings. In *m*-xylene, the difference in chemical shift between C-2 (130.0 ppm) and C-5 (128.3 ppm) is only 1.7 ppm. In the complex 48, this difference is −1.4 ppm. The overall change of 1.7 + 1.4 = 3.1 ppm is believed[60] to be due primarily to the overlap of the carbonyl groups over C-1,3,5, which results in these carbons being deshielded relative to C-2,4,6, which is in agreement with the proton results above. If this 3.1 ppm expected difference is applied to 49, then Δδ(C-8 − C-5) = 136.3 − 128.6 = 7.7 ppm in 49, which would be expected to be reduced by the 3.1 ppm in 44. This should still leave, in 44, C-8 more deshielded than C-5 by 4.6 ppm. In fact however Δδ is only found to be 2.4 ppm, and thus the reduction in deshielding by about 2.2 ppm is probably due to the difference in geometry between *m*-xylene and the metacyclophanes.[8,9,59] This procedure can now be applied to 9, since the thiacyclophanes have geometries in between those of *m*-xylene and the metacyclophanes. Thus in 1, Δδ(C-9 − C-6) = 132.1 − 128.7 = 3.4 ppm. On reduction by the 3.1 ppm, this would leave Δδ in 9 to be about 0.3 ppm. From this however, 2.2 ppm needs to be subtracted, leaving −1.9 ppm as the expected difference in shift for Δδ (C-9 − C-6). The assignments of C-9 and C-6 in 9 have thus been made to make this value (−1.7 ppm) approximately fit that expected. This assignment then leaves the complexation shifts, Δ in Table III, consistent.



48 44 9

Figure 2. Carbon NMR chemical shifts (and complexation shifts) for the tricarbonylchromnium derivatives of *m*-xylene, [2.2]-metacyclophane, and 2,11-dithia[3.3]metacyclophane.

The complexation shifts found in the thiacyclophanes, 32–39 ppm for tertiary carbons and 26–29 ppm (except C-9 of 16) for quaternary carbons, then agree very well with

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Table III. ^{13}C NMR Chemical Shifts (δ) and Complexation Shifts (Δ) for the Dithiacyclophanes 1–8 and Their Chromium Tricarbonyl Complexes 9–18

	C-5,7	Δ	C-6	Δ	C-9	Δ	C-4,8	Δ	other C
1	127.3		128.7		132.1		137.7		
		38.2		33.8		38.9		29.0	
9	90.9		94.9		93.2		108.7		
2	127.8		137.9		129.1		136.9		21.1 [C-6 Me]
		36.0		28.8		36.3		27.5	
10	91.8		109.1		92.8		109.4		20.4 [C-6 Me]
3	134.9		132.3		133.7		132.0		18.6 [C-5,7 Me]
		27.2		32.6		36.9		28.1	
11	107.7		99.7		96.8		103.9		18.2 [C-5,7 Me]
4	127.4		130.1		130.1		138.3		
		36.6		36.2		37.0		27.2	
13	90.8		93.9		93.1		109.1		
5	130.4		124.7		159.2		125.7		
		37.6		37.3		18.2		29.1	
14	92.8		87.4		141.0		96.6		
6	129.8		126.1		135.5		135.7		17.1 [C-9 Me]
		35.1		36.3		25.4		25.6	
15	94.7		89.8		110.1		110.1		17.1 [C-9 Me]
7	130.1		125.4		138.8		135.5		14.7 [C-9 Me]
		34.9		35.6		32.9		26.5	
16	95.2		89.8		105.9		109.0		15.3 [C-9 Me]
8	135.5[a]		129.5[b]						
		27.7		37.3					
17	107.8[a]		92.2[b]						
1	127.3		128.7		132.1		137.7		
		36.5		33.8		38.8		29.3	
18	90.8		94.9		93.3		108.4		

	carbon no.							
	14,16	15	18	13,17	3,10	1,12	CO	other
1	127.3	128.7	132.1	137.7	38.3	38.3		
9	127.9	129.3	132.2	137.6	37.1	38.3	233.1	
2	127.8	137.9	129.1	136.9	37.7	37.7		21.1 [C-15 Me]
10	128.6	138.8	129.6	137.5	37.1	38.2	233.7	21.1 [C-15 Me]
3	134.9	132.3	133.7	132.0	36.9	36.9		18.6 [C-14,16 Me]
11	135.7	133.5	133.4	132.5	36.6	37.3	233.8	18.7 [C-14,16 Me]
4	129.2	124.5	158.6	126.1	38.4	30.2		
13	130.2	124.8	158.5	126.1	37.5	29.7	216.0	
5	130.4	124.7	159.2	125.7	29.7	29.7		
14	130.4	124.7	159.0	125.8	28.9	29.5	*c*	
6	129.8	126.1	135.5	137.7	36.8	36.8		17.1 [C-18 Me]
15	129.9	126.1	137.1	136.2	35.6	36.8	233.9	17.2 [C-18 Me]
7	130.1	125.4	138.8	135.5	31.5	31.5		
16	130.7	126.2	138.2	135.8	30.2	32.2	233.2	16.6 [C-18 Me]
8	135.5[d]	129.5[e]			38.3	38.3		
17	136.9[d]	130.3[e]			36.2	37.4	233.8	
1					38.3	38.3		
18					37.8	37.8	232.3	

[a] C-4,7. [b] C-5,6,8,9. [c] Not available. [d] C-13,16. [e] C-14,15,18,19.

other systems.[59,60] Further more detailed analysis, however, must await a confirmation of the shift assignment in **9**. The substantially reduced complexation shift of C-9 in the fluoro complex **14** is of note however, and, together with the larger value found for Δ for C-6, may confirm conformer B for **14**, as indicated by the proton data above. The complexation shift of C-9 of the *anti*-isomer **16** is also of note since it is some 4–6 ppm greater than that for other quaternary carbons. This probably reflects the considerable increase in deformation out of the plane of the ring toward the chromium of this carbon when it is substituted.

Concluding Remarks

Eleven tricarbonylchromium complexes of eight dithia[3.3]cyclophanes have been prepared in 20–80% yields from $Cr(CO)_6$, and their ^1H and ^{13}C NMR, UV, and IR spectral properties reported in detail. Characteristically different spectra are obtained for the *syn*- and *anti*-cyclophanes, and some shifts in the thiacyclophanes are reversed from those in the cyclophanes themselves. The complexation shifts in these dithiacyclophanes is 1.6–2.0 ppm for protons, 32–39 ppm for tertiary carbons, and 26–29 ppm for quaternary carbons. An analysis of the ^1H data indicates that the time-averaged conformation of the tricarbonylchromium umbrella eclipses the cyclophane bridges. The reduction in ring current in the arene rings is estimated at 40% on $Cr(CO)_3$ complexation. The chemistry[19] of the complexes will be reported in detail in the subsequent paper.

Experimental Section

Melting points were determined on a Kofler hot-stage or Buchi SMP-20 melting-point apparatus and are uncorrected. The ^1H NMR spectra were determined in $CDCl_3$ (unless otherwise stated) on a Perkin-Elmer R32 (90 MHz) or Bruker WM-250 (250 MHz) spectrometer. ^{13}C NMR spectra were recorded on a Bruker WM-250 (62.9 MHz) spectrometer. All chemical shifts are reported in ppm downfield from tetramethylsilane as internal standard. Mass spectra were determined on a Finnigan 3300 mass spectrometer at 70 eV (EI) or by using methane chemical ionization (CI). IR spectra were recorded on a Perkin-Elmer 283 infrared spectrometer. Microanalyses were carried out by this department or by Canadian Microanalytical Services Ltd. (Vancouver, BC). All evaporations were carried out under reduced pressure on a rotary evaporator at about 40 °C, and all organic layers were washed with water (unless otherwise stated) and dried with anhydrous $MgSO_4$.

Materials were obtained as follows: bromides **31** and **36** (Aldrich), **32**,[65] **34**,[33] **35**;[66] chloride **33**;[67] thiols **25**,[33] **26**,[65] **28**,[33] **30**;[69] thiacyclophanes **1**,[31,33] **2**,[65] **6**,[31,33] **7**,[31,33] **8**.[31,70]

1,5-Bis(mercaptomethyl)-2,4-dimethylbenzene (27). A solution of chloride **33**[67] (12.5 g, 62 mmol) and thiourea (11.3 g, 149 mmol) in 95% ethanol (150 mL) was stirred under reflux for 5 h. The reaction was cooled, most of the solvent was removed, and then the precipitated bis(isothiouronium) salt was collected and heated under reflux with a deoxygenated solution of KOH (13.9 g, 250 mmol) in water (250 mL) under N_2 for 5 h. Then 50% H_2SO_4 was added with ice cooling under N_2. The smelly dithiol was extracted into ether. The organic layers were dried and evaporated to yield dithiol **27** (10.5 g, 95%) as a white solid which on recrystallization from benzene:hexane (1:1) gave mp 44–46 °C: ^{1}H NMR (90 MHz) δ 7.10 (s, 1 H, Ar H), 6.95 (s, 1 H, Ar H), 3.64 (d, J = 7.5 Hz, 4 H, $ArCH_2SH$), 2.28 (s, 6 H, CH_3), 1.58 (t, J = 7.5 Hz, 2 H, CH_2SH). Anal. Calcd for $C_{10}H_{14}S_2$: C, 60.56, H, 7.11. Found: C, 60.29, H, 7.08.

2-Fluoro-1,3-bis(mercaptomethyl)benzene (29). This was prepared as described for **27** above. From bromide **35**[66] (33.1 g, 117 mmol) and thiourea (18.7 g, 246 mmol) in 95% ethanol (600 mL), there was obtained thiol **29** (19.6 g, 89%) as a liquid, bp >250 °C; ^{1}H NMR (250 MHz) δ 7.21 (t, J = 7.3 Hz, 2 H, 4,6-Ar H), 7.04 (t, J = 7.1 Hz, 1 H, 5-Ar H), 3.74 (d, J = 7.8 Hz, 4 H, $ArCH_2SH$), 1.87 (t, J = 7.9 Hz, 2 H, $ArCH_2SH$); ^{13}C NMR δ 158.1 (d, J = 248.8 Hz, C-2), 129.0 (d, J = 4.4 Hz, C-4,6), 128.7 (d, J = 15.3 Hz), C-1,3), 124.4 (d, J = 4.5 Hz, C-5), 22.1 (d, J = 4.7 Hz, $ArCH_2SH$). Anal. Calcd for $C_8H_9FS_2$: C, 51.04, H, 4.82. Found: C, 50.88, H, 4.80.

***syn*-5,7,14,16-Tetramethyl-2,11-dithia[3.3]metacyclophane (3).** A solution of chloride **33**[67] (4.80 g, 24.2 mmol) and thiol **27** (4.70 g, 24.2 mmol) in deoxygenated benzene (600 mL) was added dropwise over 60–70 h to a vigorously stirred solution of KOH (4.1 g, 72 mmol) in 95% ethanol (600 mL, deoxygenated) at 20 °C under N_2. After a further 2 h, the solvent was evaporated and the residue extracted with aqueous HCl and dichloromethane. The organic layers were combined, washed with water, dried, and evaporated. The residue was preadsorbed on silica gel and then was chromatographed over silica gel by using pentane:dichloromethane (3:1) as eluant. Recrystallization from hexane gave **3** (5.60 g, 71%) as white needles, mp 230–231 °C (lit.[57] mp 231–232 °C); ^{1}H NMR, see Table II; ^{13}C NMR, see Table III, MS, *m/e* 328 (M^+, 25), 133 (100), 132 (56).

***syn*-9-Fluoro-2,11-dithia[3.3]metacyclophane (4).** The reaction was carried out as described for **3** above using thiol **25**[33] (4.19 g, 24.6 mmol) and bromide **35**[66] (6.94 g, 24.6 mmol) in benzene (500 mL), which were added to KOH (6.9 g, 123 mmol) in water (150 mL) and 95% ethanol (600 mL). This gave **4** (4.87 g, 68%) as white crystals, mp 146–148 °C (lit.[68] mp 149–150 °C); ^{1}H and ^{19}F NMR, see Table II [the following peaks showed couplings: δ 7.11 (d, J = 3.4 Hz), 6.69 (t, J = 7.6 Hz), 4.20 (d, J = 14.6 Hz), 3.50 (d, J = 14.6 Hz)]; ^{13}C NMR, see Table III [the following peaks were doublets: δ 158.6 (J = 242.5 Hz), 130.1 (J = 4.8 Hz), 126.1 (J = 15.2 Hz), 124.5 (J = 3.2 Hz), 30.2 (J = 3.7 Hz)]; MS, *m/e* 290 (M^+, 42), 184 (54), 143 (100), 141 (55), 123 (37), 112 (32).

***syn*-9,18-Difluoro-2,11-dithia[3.3]metacyclophane (5).** The reaction was carried out as described for **3** above using thiol **29** (15.74 g, 83.6 mmol) and bromide **35**[66] (23.57 g, 83.6 mmol) in benzene (1250 mL), which were added to KOH (23.45 g, 0.418 mol) in water (300 mL) and 95% ethanol (1200 mL) over 98 h, and gave **5** (20.68 g, 80%) as white crystals, mp 198–200 °C (lit.[66] mp 199–200 °C); ^{1}H NMR, see Table II [the following peaks showed couplings: δ 6.70 (t, J = 7.6 Hz), 4.34 (d, J = 15.2 Hz), 3.43 (d, J = 15.2 Hz)]; ^{13}C NMR, see Table III [the following peaks showed couplings: δ 159.2 (dd, J = 251.5 Hz, 7.8 Hz), 125.7 (d, J = 15.7 Hz)]; MS, *m/e* 308 (M^+, 35), 185 (21), 155 (29), 154 (23), 153 (23), 123 (100), 109 (26).

(η^6-*syn*-2,11-Dithia[3.3]metacyclophane)tricarbonylchromium(0) (9). General Procedure for Preparation of the Chromium Tricarbonyl Complexes. A mixture of dithiacyclophane **1** (1.00 g, 3.67 mmol) and chromium hexacarbonyl (0.88 g, 4.04 mmol) was heated under reflux in *n*-butyl ether (50 mL) under N_2 for 3–4 h. The mixture was cooled, diluted with pentane (20 mL), and cooled in the freezer for 15 h. The resulting brown precipitate was collected, washed with pentane, and Soxhlet extracted by using dichloromethane until the extract was colorless. The solvent was evaporated, and the residue was preabsorbed and chromatographed on silica gel by using dichloromethane:pentane (1:3) as eluant. Eluted first was any unchanged starting material, followed by the product **9**, (1.20 g, 80%), which on recrystallization from dichloromethane–pentane gave golden yellow crystals, mp 157–158 °C; ^{1}H NMR, see Table II [the following peaks showed couplings: δ 5.18 (t, J = 6.4 Hz), 4.94 (d, J = 6.4 Hz), 3.51 and 3.45 (ABq, J = 15.0 Hz)]; ^{13}C NMR, see Table III; IR and UV, analysis see Table I; MS, *m/e* 408 (M^+, 10), 324 (100). A crystal structure of **9** was attempted but could not be refined below R = 0.124 because of a disordering of the sulfur atoms.

Complexes 9–15 and **17** were prepared as above.

(η^6-*syn*-6,15-Dimethyl-2,11-dithia[3.3]metacyclophane)tricarbonylchromium(0) (10). Compound **2** (0.50 g, 1.67 mmol) and $Cr(CO)_6$ (0.41 g, 1.84 mmol) gave **10** as yellow crystals in 70% yield, mp 210–212 °C: ^{1}H NMR, see Table II; ^{13}C NMR, see Table III; IR and UV analysis, see Table I; MS (CI), *m/e* 437 (M + 1, 80), 301 (100).

(η^6-*syn*-5,7,14,16-Tetramethyl-2,11-dithia[3.3]metacyclophane)tricarbonylchromium(0) (11). Compound **3** (0.70 g, 2.1 mmol) and $Cr(CO)_6$ (0.52 g, 2.3 mmol) gave **11** as yellow crystals in 70% yield, mp 229–231 °C: ^{1}H NMR, see Table II [the following peaks showed couplings: δ 3.87 and 3.80 (ABq, J = 14.3 Hz), 3.64 and 3.40 (ABq, J = 15.0 Hz)]; IR and UV analysis, see Table I; MS (CI), *m/e* 465 (M + 1, 100).

(η^6-*syn*-18-Fluoro-2,11-dithia[3.3]metacyclophane)tricarbonylchromium(0) (13). Compound **4** (2.00 g, 6.89 mmol), $Cr(CO)_6$ (2.12 g, 9.64 mmol), and *n*-Bu_2O (50 mL), after 5–6 h of reflux and direct chromatography of precipitate, gave unchanged starting material (30–40%) and then **13** (1.36 g, 46%) as yellow crystals, mp 169–170 °C; ^{1}H NMR, see Table II [the following peaks showed couplings: δ 7.06 (t, J = 7.5 Hz), 6.83 (t, J = 7.6 Hz), 5.17 (t, J = 6.4 Hz), 4.97 (d, J = 6.4 Hz), 4.21 (d, J = 14.9 Hz), 3.51 (d, J = 11.6 Hz)]; ^{13}C NMR, see Table III [the following peaks showed couplings: δ 158.5 (d, J = 242.5 Hz), 130.2 (d, J = 3.6 Hz), 126.1 (d, J = 14.8 Hz), 124.8 (d, J = 3.5 Hz), 93.1 (d, J = 6.8 Hz)]; ^{19}F NMR δ −125.0 (br s); MS, *m/e* 426 (M^+, 36), 370 (21), 342 (100), 290 (79), 143 (70); IR and UV analysis, see Table I.

The mother liquors from which **13** was crystallized contained a second complex, assigned structure **12**, but this could not be obtained free of **13**.

(η^6-*syn*-9,18-Difluoro-2,11-dithia[3.3]metacyclophane)tricarbonylchromium(0) (14). Compound **5** (2.00 g, 6.49 mmol), $Cr(CO)_6$ (1.99 g, 9.05 mmol), and *n*-Bu_2O (55 mL), after 5–6 h of reflux, gave after direct chromatography of the precipitate first unchanged starting material (50–60%) and then the product **14** (0.81 g, 28%) as yellow crystals, mp (dec) 185 °C; ^{1}H NMR, see Table II [the following peaks showed couplings: δ 7.15 (t, J = 6.6 Hz), 6.85 (t, J = 7.6 Hz), 4.31 (d, J = 15.1 Hz), 4.07 (d, J = 15.2 Hz), 3.47 (d, J = 15.2 Hz), 3.25 (d, J = 15.0 Hz)]; ^{13}C NMR, see Table III [the following peaks were doublets: δ 159.0 (J = 245.6 Hz), 141.0 (J = 259.4 Hz), 130.4 (J = 3.3 Hz), 125.8 (J = 15.2 Hz), 96.6 (J = 15.2 Hz), 92.8 (J = 4.1 Hz), 28.9 (J = 4.1 Hz)]; ^{19}F NMR δ −126.7 (dt, J = 43 Hz, 6.0 Hz, F-18), −144.7 (d, J = 43 Hz, F-9); MS, *m/e* 444 (M^+, 36), 360 (71), 308 (52), 223 (22), 203 (29), 191 (73), 181 (53), 155 (23), 153 (24), 135 (71), 123 (100); IR and UV analysis, see Table I.

Eluted next was the bis-complex **19**, which after recrystallization from dichloromethane gave yellow needles (60 mg, 2%), mp (dec) 203 °C: ^{1}H NMR δ 5.41 (d, J = 4.9 Hz, 4 H, H-5,7,14,16), 4.83 (t, J = 6.0 Hz, 2 H, H-6,15), 4.09 (d, J = 15.2 Hz) 4 H, H-1,3,10,12), 3.35 (d, J = 15.3 Hz, 4 H, H-1,3,10,12); ^{13}C NMR δ 96.7 (s, C-4,8,13,17), 92.7 (s, C-5,7,14,16), 87.0 (s, C-5,16), 29.4 (s, C-1,3,10,12);

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^{19}F NMR δ −145.0 (br s).

(η^6-*syn*-9,18-Dimethyl-2,11-dithia[3.3]metacyclophane)tricarbonylchromium(0) (15). Compound **6** (100 mg, 0.33 mmol) and $Cr(CO)_6$ (81 mg, 0.36 mmol) gave 68% of **15**, as yellow crystals mp 202–203 °C: ^{1}H NMR, see Table II [the following peaks showed couplings: δ 6.94 (d, J = 7.2 Hz), 6.87 (t, J = 7.2 Hz), 4.09 and 3.93 (ABq, J = 15.1 Hz), 3.82 and 3.58 (ABq, J = 15.0 Hz)]; ^{13}C NMR, see Table III; MS (CI), *m/e* 437 (M + 1, 80), 301 (100); IR and UV analysis, see Table I.

(η^6-2,11-Dithia[3.3]paracyclophane)tricarbonylchromium(0) (17). Compound **8** (300 mg, 1.1 mmol) and $Cr(CO)_6$ (270 mg, 1.2 mmol) gave 52% of **17** as yellow crystals, mp 170–171 °C; ^{1}H NMR, see Table II; ^{13}C NMR see Table III; IR and UV analysis, see Table I; MS, *m/e* 408 (M^+, 6), 325 (20), 221 (20), 104 (100).

(η^6-*anti*-9,18-Dimethyl-2,11-dithia[3.3]metacyclophane)tricarbonylchromium(0) (16). $Cr(CO)_6$ (806 mg, 3.66 mmol) was heated under reflux in dry acetonitrile (50 mL) under N_2 for 48 h. The solvent was then evaporated by using a stream of N_2, while the flask was gently warmed. To the resulting dry $(CH_3CN)_3Cr(CO)_3$ complex was added a solution of cyclophane **7** (1.00 g, 3.3 mmol) in dry THF (60 mL). The mixture was heated under reflux under N_2 for 10 h. The solution was then cooled, the solvent was evaporated, and the residue was chromatographed over silica gel by using dichloromethane:pentane (1:1) as eluant to yield **16** (290 mg, 20%) as yellow needles from dichloromethane–pentane (1:1), mp 212–214 °C; ^{1}H NMR see Table II [the following peaks showed couplings: δ 7.36 (d, J = 7.5 Hz), 7.14 (t, J = 7.5 Hz), 3.52 and 3.41 (ABq, J = 14.2 Hz)]; ^{13}C NMR, see Table III; IR and UV analysis, see Table I; MS (CI), *m/e* 409 (M + 1, 20), 380 (22), 352 (100).

Reaction of Difluorocyclophane 5 with Tris(acetonitrile)tricarbonylchromium(0) To Yield 14 and 38. This was carried out as described for **16** above by using $Cr(CO)_6$ (1.00 g, 4.52 mmol) and **5** (1.00 g, 3.25 mmol). Pentane was used to elute the first yellow band, which gave a flaky yellow solid (404 mg, 36%), mp (dec) 193 °C, assigned structure **38**: ^{1}H NMR (90 MHz) δ 7.10–6.70 (m, Ar H), 4.46 (d, J = 15.0 Hz, bridge CH), 3.53 (d, J = 15.0 Hz, bridge CH); MS, *m/e* 472 (M^+, 3), 308 (84), 181 (15), 135 (40), 123 (100).

Eluted next was unchanged starting material **5** (500 mg, 50%).

Eluted third was the complex **14** (160 mg, 11%), identical with the previously obtained sample.

(η^6,η^6-*syn*-2,11-Dithia[3.3]metacyclophane)bis[tricarbonylchromium(0)] (18). A mixture of cyclophane **1** (1.00 g, 3.67 mmol) and $Cr(CO)_6$ (4.10 g, 18.4 mmol) in n-Bu_2O (80 mL) was refluxed for 6 h under N_2. The mixture was cooled, diluted with pentane (20 mL), and further cooled in a freezer for 15 h. The resulting brown precipitate was washed with pentane and Soxhlet extracted with acetone until the extract was colorless. The solvent was evaporated to yield **18** (1.29 g, 65%), which on recrystallization from ethyl acetate gave yellow crystals, mp 202–204 °C: ^{1}H NMR, see Table II [the following peaks showed couplings: δ 5.33 (t, J = 6.4 Hz), 5.10 (d, J = 6.4 Hz), 3.62 and 3.54 (ABq, J = 15.2 Hz)]; ^{13}C NMR, see Table III; IR and UV analysis, see Table I; MS, *m/e* 545 (M + 1, 18), 326 (100).

Attempted Crystal Structure of 9. Approximate cell dimensions from Weissenberg and precession photographs were obtained by using Cu Kα radiation. The crystal system was monoclinic, space group $P2_1/n$. The crystals parameters at 23 °C are a = 12.267 (2), b = 14.450 (2), and c = 11.584 (3) Å, β = 102.85 (2)°, molecular formula $C_{19}H_{16}CrO_3S_2$, mol wt = 408.45, cell volume 2001.9 (6) Å^3, density 1.355 g·cm^{-3} calculated, 1.487 g·cm^{-3} measured (flotation). The crystal was mounted along the a axis, and Zr filtered Mo Kα radiation (λ = 0.71069 Å) was used for measuring 1389 reflections and 84 standards. However, direct-methods least-squares refinement gave only R = 0.124. This compound will be reinvestigated at low temperatures.

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Registry No. **1**, 72150-45-9; **2**, 72150-46-0; **3**, 72150-47-1; **4**, 123050-35-1; **5**, 106972-81-0; **6**, 26787-71-3; **7**, 26787-70-2; **8**, 28667-63-2; **9**, 96212-60-1; **10**, 123002-98-2; **11**, 123002-99-3; **12**, 123003-00-9; **13**, 123003-01-0; **14**, 119700-76-4; **15**, 96212-64-5; **16**, 96290-44-7; **17**, 123003-02-1; **18**, 96212-62-3; **19**, 123026-05-1; **25**, 41563-69-3; **27**, 58074-29-6; **29**, 113391-65-4; **33**, 1585-15-5; **35**, 25006-86-4; **38**, 123003-03-2; **44**, 96290-43-6; **45**, 96290-41-4; **48**, 12129-28-1; **49**, 2319-97-3; $(CH_3CN)_3Cr(CO)_3$, 16800-46-7; chromium hexacarbonyl, 13007-92-6; carbamidothioic acid (4,6-dimethyl-1,3-phenylene)bis(methylene) ester dihydrochloride, 63498-27-1.