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Heterocyclophane Complexes of Transition Metals. 1. Synthesis and Crystal Structure of Both the (η^5-[2,2](2,5)Pyrroloparacyclophane)tricarbonylchromium and the (η^6-[2.2](2,5)Pyrroloparacyclophane)tricarbonylchromium

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Reaction of [2.2](2,5)pyrroloparacyclophane with $(MeCN)_3Cr(CO)_3$ in a dioxane/hexane mixture gives both (η^5-[2.2](2,5)pyrroloparacyclophane)tricarbonylchromium, 1, and (η^6-[2.2](2,5)pyrroloparacyclophane)tricarbonylchromium, 2, after appropriate workup. The mode of linkage of the $Cr(CO)_3$ unit to the heterocyclophane has been determined in each instance by X-ray diffraction techniques. 1 crystallizes in the orthorhombic space group *Pnma* with a = 13.782 (6) Å, b = 12.442 (6) Å, c = 8.617 (4) Å, and ρ_{calcd} = 1.50 g cm^{-3} for Z = 4. The structure was refined to R = 0.035 with 484 observed reflections. 2 belongs to the rhombohedral space group $R\bar{3}$ with a = 13.312 (6) Å, α = 98.59 (3)°, and ρ_{calcd} = 1.46 g cm^{-3} for Z = 6. The structure was refined to R = 0.024 for 769 observed reflections. 1 exhibits a crystallographic mirror plane which contains the chromium and nitrogen atoms and one carbonyl and bisects C–C bonds of the C_6 unit. The nitrogen atom of the heterocyclic ring is closest to the chromium atom at Cr–N = 2.102 (7) Å. The electron-rich nitrogen atom is positioned exactly anti to an electron-withdrawing carbonyl group. 2 contains no crystallographically imposed symmetry and the Cr–C(π) bond lengths range from 2.188 (5) to 2.423 (6) Å.

Introduction

Cyclophanes have been subjected to extensive and general investigation.[1] Initially, studies were concerned primarily with the presence of transannular electronic effects and high molecular strain, but, more recently, the use of cyclophanes as intermediates in the preparation of polynuclear aromatic hydrocarbons[2] and as models in the study of enzyme–substrate specificity[3] has attracted interest. [2.2]Cyclophanes are the most strained class of cyclophane, and, although metal complexes have been prepared of solely benzenoid [2.2]cyclophanes, none have been characterized where one or both of the aromatic rings present are heteroaromatic. We have therefore undertaken, and herein report, the syntheses, ^{1}H NMR spectra, and crystal structures of the first examples of transition-metal heterocyclophane complexation, (η^5-[2.2](2,5)-pyrroloparacyclophane)- and (η^6-[2.2](2,5)pyrroloparacyclophane)tricarbonylchromium. The former represent also the first example of any η^5-transition metal cyclophane complex.

Experimental Section

Synthetic Procedures. All reactions, filtrations, extractions, and recrystallizations were conducted under nitrogen. Solvents were dried and deoxygenated prior to use. ^{1}H NMR spectra were recorded on a Varian EM360A spectrometer using $SiMe_4$ as a reference standard. Elemental analysis was conducted at the Analytical Services Laboratory of the University of Alabama Chemistry Department.

Preparation of (η^5-[2.2](2,5)Pyrroloparacyclophane)tricarbonylchromium (1) and (η^6-[2,2](2,5)Pyrroloparacyclophane)tricarbonylchromium (2). A 0.508-g (2.58-mmol) sample of [2.2](2,5]pyrroloparacyclophane[4] in 30 mL of dioxane was added to a hexane solution of $(CH_3CN)_3Cr(CO)_3$ prepared from 0.670 g (3.04 mmol) of $Cr(CO)_6$.[5] The mixture was stirred at 70–80 °C for 2 h and 45 min and allowed to cool, and solvent

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[1] (a) Newkome, G. R.; Sauer, J. D.; Roper, J. M.; Hager, D. C. *Chem. Rev.* **1977**, *77*, 513. (b) Boekelheide, V. *Acc. Chem. Res.* **1980**, *13*, 65.

[2] Misumi, S.; Otsubo, T. *Acc. Chem. Res.* **1978**, *11*, 251.

[3] Tabushi, I. Koen Yoshi—Shinpojumu "Kagaku no Mirai" 1979, 18–23; *Chem. Abstr.* **1980**, *92*, 89673.

[4] Cram, D. J.; Montgomery, C. S.; Know, G. R. *J. Am. Chem. Soc.* **1966**, *88*, 515.

[5] Tate, D. P.; Knipple, W. R.; Augl, J. M. *Inorg. Chem.* **1962**, *1*, 443.

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Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement for (η^5-Pyrroloparacyclophane)Cr(CO)$_3$ (1) and (η^6-Pyrroloparacyclophane)Cr(CO)$_3$ (2)

	1	2
mol wt	333.3	333.3
space group	*Pnma*	$R\bar{3}$
cell const		
a, Å	13.782 (6)	13.312 (6)
b, Å	12.442 (6)	
c, Å	8.617 (4)	
α, deg		98.59 (3)
cell vol, Å^3	1477.6	2270.6
Z	4	6
ρ(calcd), g cm^{-3}	1.50	1.46
μ(calcd), cm^{-1}	8.2	8.0
radiatn	Mo Kα	Mo Kα
max cryst dimens, mm	0.05 × 0.07 × 0.20	0.45 × 0.50 × 0.65
scan, width, deg	0.90 + 0.20 tan θ	0.80 + 0.20 tan θ
std reflctns	400, 040, 004	400, 040, 004
variatn of std	±2%	±2%
reflctns measd	914	1811
2θ range, deg	2–44	2–36
reflctns, $I > 3\sigma(I)$	484	769
no. of parameters varied	106	199
largest parameter shift/est	0.01	0.01
GOF	1.62	1.63
R	0.035	0.024
R_w	0.038	0.025

Table II. Final Fractional Coordinates for (η^5-Pyrroloparacyclophane)Cr(CO)$_3$ (1)

atom	x/a	y/b	z/c
Cr	0.5048 (1)	0.7500	0.6393 (2)
O(1)	0.5293 (5)	0.9223 (7)	0.8764 (8)
O(2)	0.2931 (5)	0.7500	0.7130 (9)
N	0.6403 (5)	0.7500	0.5276 (8)
C(1)	0.5198 (5)	0.8540 (8)	0.786 (1)
C(2)	0.3755 (7)	0.7500	0.679 (1)
C(3)	0.5953 (5)	0.8432 (6)	0.4720 (7)
C(4)	0.5138 (5)	0.8079 (5)	0.3905 (7)
C(5)	0.6446 (5)	0.9521 (6)	0.4841 (9)
C(6)	0.7199 (6)	0.9688 (6)	0.350 (1)
C(7)	0.7604 (5)	0.8627 (6)	0.2961 (8)
C(8)	0.8291 (5)	0.8074 (6)	0.3832 (8)
C(9)	0.7100 (5)	0.8061 (6)	0.1826 (8)

Table III. Bond Lengths (Å) and Angles (deg) for 1

	Bond Distances		
Cr–N	2.102 (7)	Cr–C(1)	1.822 (9)
Cr–C(2)	1.81 (1)	Cr–C(3)	2.232 (6)
Cr–C(4)	2.265 (6)	Cr–Cent	1.866
O(1)–C(1)	1.158 (9)	O(2)–C(2)	1.17 (1)
N–C(3)	1.399 (7)	C(3)–C(4)	1.395 (8)
C(3)–C(5)	1.520 (9)	C(4)–C(4)	1.44 (1)
C(5)–C(6)	1.568 (9)	C(6)–C(7)	1.51 (1)
C(7)–C(8)	1.39 (1)	C(7)–C(9)	1.391 (9)
C(8)–C(8)	1.43 (1)	C(9)–C(9)	1.40 (1)
	Bond Angles		
Cr–C(1)–O(1)	178.0 (9)	Cr–C(2)–O(2)	176.3 (9)
N–C(3)–C(4)	105.6 (6)	C(3)–N–C(3)	111.9 (6)
C(4)–C(4)–C(3)	108.3 (6)	N–C(3)–C(5)	121.2 (6)
C(4)–C(3)–C(5)	132.4 (7)	C(3)–C(5)–C(6)	111.2 (6)
C(5)–C(6)–C(7)	110.9 (6)	C(6)–C(7)–C(8)	121.3 (7)
C(8)–C(8)–C(7)	119.7 (7)	C(9)–C(9)–C(7)	120.4 (7)
C(6)–C(7)–C(9)	118.3 (7)	C(8)–C(7)–C(9)	118.0 (7)

Table IV. Final Fractional Coordinates for (η^6-Pyrroloparacyclophane)Cr(CO)$_3$, 2

atom	x/a	y/b	z/c
Cr	0.24665 (7)	0.61474 (7)	−0.00826 (7)
O(1)	0.0855 (4)	0.7468 (4)	0.0132 (4)
O(2)	0.1918 (4)	0.6138 (4)	−0.2337 (4)
O(3)	0.3971 (3)	0.8035 (3)	−0.0078 (3)
N	0.3087 (4)	0.3741 (4)	0.1826 (4)
C(1)	0.1465 (5)	0.6951 (5)	0.0059 (5)
C(2)	0.2114 (5)	0.6097 (4)	−0.1465 (5)
C(3)	0.3371 (5)	0.7298 (5)	−0.0078 (4)
C(4)	0.2147 (5)	0.4303 (5)	−0.0107 (4)
C(5)	0.3166 (5)	0.4722 (5)	−0.0189 (4)
C(6)	0.3761 (4)	0.5482 (5)	0.0590 (5)
C(7)	0.3348 (5)	0.5853 (4)	0.1467 (4)
C(8)	0.2276 (5)	0.5633 (4)	0.1404 (4)
C(9)	0.1670 (4)	0.4856 (5)	0.0603 (5)
C(10)	0.1727 (4)	0.3197 (5)	−0.0566 (4)
C(11)	0.2053 (5)	0.2541 (4)	0.0284 (5)
C(12)	0.3056 (5)	0.2996 (5)	0.0989 (5)
C(13)	0.4068 (6)	0.2980 (5)	0.0870 (5)
C(14)	0.4705 (4)	0.3765 (6)	0.1637 (6)
C(15)	0.4081 (5)	0.4249 (5)	0.2205 (4)
C(16)	0.4265 (4)	0.5246 (5)	0.2968 (4)
C(17)	0.4066 (4)	0.6221 (4)	0.2478 (5)

was removed under reduced pressure. The orange solid was washed with hexane (3 × 20 mL), and unreacted ligand was removed by sublimation. The final residue was extracted repeatedly with chloroform to yield an orange solution and an orange yellow powder. The orange-yellow powder was extracted with tetrahydrofuran which was then removed at reduced pressure. The resulting solid was washed with chloroform and crystallized from tetrahydrofuran to yield light orange air-sensitive crystals of 1 (estimated yield 25%): NMR (acetone-d_6) δ 7.07 (4 H, AA′XX′), 4.75 (2 H, s), 2.81 (8 H, m). Anal. Calcd: C, 61.26; H, 4.54; N, 4.20. Found: C, 61.17; H, 4.31; N, 4.11. The proton on the nitrogen atom could not be resolved. The chloroform extract from above yielded orange crystals of 2 in 32% yield after crystallization from hexane: NMR (CDCl$_3$) δ 5.77 (2 H, s), 4.93 (4 H, AA′XX′), 4.27 (1 H, m), 2.75 (8 H, m). Anal. Calcd: C, 61.26; H, 4.54; N, 4.20. Found, C, 61.15; H, 4.40;, N, 4.15.

X-ray Structural Characterizations. Crystallographic parameters for 1 and 2, as determined on an Enraf-Nonius CAD-4 diffractometer, are presented in Table I. Data were collected and corrected as previously described (no absorption corrections were applied).[6]

The structure of 1 was solved through utilization of the direct methods program MULTAN[7] and refined by using the SHELX[8] program package. The chromium atom was found to lie on a mirror plane in the space group *Pnma* (successful refinement in the centric space group ruled out the noncentrosymmetric choice). All non-hydrogen atoms were refined with anisotropic thermal parameters, and final R values after location of all hydrogen atoms were $R = \sum||F_o| - |F_c||/\sum|F_o|) = 0.035$ and $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum F_o^2\}^{1/2} = 0.038$. No unaccountable electron density was evident after the final cycle of full-matrix least-squares refinement. Final fractional atomic coordinates are given in Tables II, and Table III contains bond lengths and angles.

The structure of 2 was solved through application of a Patterson synthesis, which revealed the chromium atom position. The remaining non-hydrogen atoms were found on a subsequent difference Fourier, and refinement converged at values of $R = 0.032$ and $R_w = 0.034$ after inclusion of hydrogen atoms in calculated positions. No unaccountable electron density was noted on the final difference Fourier, and final fractional atomic coordinates and bond distances and anbles are given in Tables IV and V, respectively. Neutral atom scattering factors for C, N, O, and Cr were taken from the compilations of Cromer and Mann[9] whereas those for H were taken from ref 10. Corrections for the

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(6) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45.

(7) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogra., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1971**, *A27*, 368.

(8) SHELX, a system of computer programs for X-ray structure determination by G. M. Sheldrick, 1976. Other crystallographic programs used on a UNIVAC 1100 computer included BPL (best least-squares planes by W. E. Hunter) and ORTEP (therml ellipsoid plots by C. K. Johnson).

(9) Cromer, D. T.; Mann, B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 321.

Table V. Bond Lengths (Å) and Angles (deg) for 2

Bond Distances			
Cr–C(1)	1.843 (7)	Cr–C(2)	1.819 (7)
Cr–C(3)	1.800 (7)	Cr–C(4)	2.423 (6)
Cr–C(5)	2.230 (5)	Cr–C(6)	2.188 (5)
Cr–C(7)	2.333 (6)	Cr–C(8)	2.225 (5)
Cr–C(9)	2.263 (5)	O(1)–C(1)	1.146 (6)
O(2)–C(2)	1.162 (6)	O(3)–C(3)	1.169 (6)
N–C(12)	1.368 (6)	N–C(15)	1.377 (6)
C(4)–C(5)	1.413 (7)	C(4)–C(9)	1.396 (7)
C(4)–C(10)	1.496 (7)	C(5)–C(6)	1.389 (7)
C(6)–C(7)	1.417 (7)	C(7)–C(8)	1.401 (7)
C(7)–C(17)	1.498 (7)	C(8)–C(9)	1.422 (7)
C(10)–C(11)	1.579 (7)	C(11)–C(12)	1.498 (7)
C(12)–C(13)	1.383 (7)	C(13)–C(14)	1.418 (7)
C(14)–C(15)	1.370 (7)	C(15)–C(16)	1.510 (8)
C(16)–C(17)	1.577 (8)		

Bond Angles			
C(1)–Cr–C(2)	86.4 (3)	C(1)–Cr–C(3)	88.8 (3)
C(2)–Cr–C(3)	86.6 (2)	C(12)–N–C(15)	111.0 (4)
Cr–C(1)–O(1)	178.2 (5)	Cr–C(2)–O(2)	175.2 (6)
Cr–C(3)–O(3)	178.9 (5)	C(5)–C(4)–C(9)	117.7 (5)
C(5)–C(4)–C(10)	119.1 (6)	C(9)–C(4)–C(10)	121.4 (6)
C(4)–C(5)–C(6)	120.2 (5)	C(5)–C(6)–C(7)	120.3 (5)
C(6)–C(7)–C(8)	117.7 (5)	C(6)–C(7)–C(17)	118.6 (6)
C(8)–C(7)–C(17)	122.0 (5)	C(7)–C(8)–C(9)	119.8 (5)
C(4)–C(9)–C(8)	120.0 (5)	C(4)–C(10)–C(11)	106.7 (4)
C(10)–C(11)–C(12)	114.5 (5)	N–C(12)–C(11)	120.3 (6)
N–C(12)–C(13)	106.5 (5)	C(11)–C(12)–C(13)	131.7 (7)
C(12)–C(13)–C(14)	107.6 (5)	C(13)–C(14)–C(15)	108.1 (5)
N–C(15)–C(14)	106.6 (5)	N–C(15)–C(16)	119.5 (6)
C(14)–C(15)–C(16)	133.0 (6)	C(15)–C(16)–C(17)	114.7 (4)
C(7)–C(17)–C(16)	107.9 (4)		

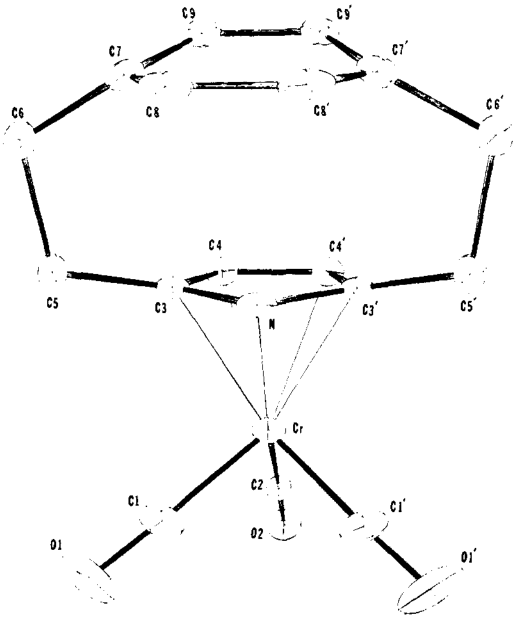

Figure 1. Molecular structure of (η^5-pyrroloparacyclophane)-$Cr(CO)_3$, 1.

real and imaginary components of anomalous dispersion were taken from the compilations of Cromer and Liberman[11] and were applied to all atoms.

Discussion

Views of 1 and 2 are presented in Figures 1 and 2. Both complexes have adopted conformations such that the $Cr(CO)_3$ tripod is staggered with respect to the π-bonded aromatic ring (in the case of 1 one carbonyl is anti to the nitrogen atom of the pyrrole moiety). The conformations are illustrated schematically in Figure 3. The geometry that may be adopted by (η^6-arene)$Cr(CO)_3$ complexes has recently been discussed and rationalized in detail by Muetterties, Albright, and co-workers.[12] Para-substituted arenes can adopt one of two conformations, eclipsed or staggered. The latter is favored sterically and also electronically when the substituents are identical and have electron-donating characteristics. 2 is symmetrically substituted, and therefore it is not surprising that the observed conformation has been adopted. The staggered arrangement is also preferred in the closely related complex ([2.2]paracyclophane)$Cr(CO)_3$, 3.[13] The only system so far studied that has markedly different substituents is [p-$C_6H_4(CMe_3)(COOH)$]$Cr(CO)_3$, and this complex is only slightly distorted from the idealized staggering seen for 2 and 3.[14]

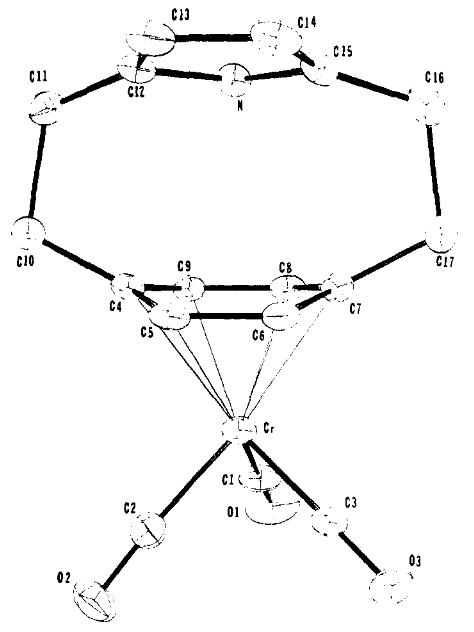

Figure 2. Structure of (η^6-pyrroloparacyclophane)$Cr(CO)_3$, 2. The molecule resides on a crystallographic mirror plane.

1 2

Figure 3. Schematic representations of the conformations of 1 and 2.

The conformation of 1 also follows precedent in that η^6-heterocyclic arene $Cr(CO)_3$ complexes have hitherto always adopted a geometry such that an electron-rich X atom of the heterocyclic ring places itself anti to the electron-withdrawing carbonyl.[15]

Table VI compares structural features of the ligands in 1 and 2 with 3 and uncomplexed [2.2]paracyclophane.[16]

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(10) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1962; Vol. III.

(11) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(12) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499.

(13) Kai, Y.; Yasuoka, N.; Kasai, N. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 2840.

(14) van Meurs, F.; van Koningsveld, H. *J. Organomet. Chem.* **1974**, *78*, 229.

(15) The most closely related example is (2,4,6-trimethylpyridine)Cr-$(CO)_3$: Onnuch, A.; Reynolds, S.; Albright, T. A.; Shakir, R.; Atwood, J. L., unpublished results.

Table VI. Comparison of the Structural Parameters of Several Cyclophane Compounds

compound	θ,[a] deg	D[b]	C–C(bridge),[c] Å (av)	Cr–C, Å (range)	C–C–C– deg (bridge av)
[2.2]paracyclophane	0	0.17	1.558		
[2.2](2,5)furano(2,5)pyridinophane[d]	23	0.17	1.574		111.3
([2.2]paracyclophane)Cr(CO)$_3$			1.595	2.191 (4)–2.344 (4)	111.8
1	13	0.17	1.568	2.232 (6)–2.265 (6)	111.1
2	11	0.19	1.572	2.189 (7)–2.430 (8)	110.6

[a] θ is the dihedral angle formed by two aromatic ring planes. [b] Maximum deviation of substituted carbon atoms from plane formed by other four benzenoid carbon atoms. [c] Between sp^3 carbons. [d] Reference 22.

It is evident that the heterophanes of the present study show similarity to the [2.2]paracyclophane analogues in terms of the strain present within the ligand. This manifests itself most noticeably in the deviation of planarity seen for the aromatic rings.

In 1 least-squares planes calculations show that the substituted carbon atoms of the benzenoid ring lie 0.17 Å out of the plane formed by the other four-ring carbon atoms, resulting in a boat conformation similar to that seen in [2.2]paracyclophane. The Cr–ring bond distances in 1 show that the nitrogen atom is closest to the chromium atom, with the Cr–N distance being 2.102 (7) Å. This is more a result of displacement of the Cr(CO)$_3$ moiety away from the center of the ring rather than deviation from planarity within the ring (ring atoms are planar to 0.03 Å). A similar phenomenon is observed in (*N*-methylpyrrole)-Cr(CO)$_3$.[17] The Cr–C distances are typical of Cr–C(π) distances (2.232 (6) and 2.265 (6) Å), comparing closely to those observed for (C$_6$Me$_6$)Cr(CO)$_3$[18] and (C$_6$H$_6$)Cr(CO)$_3$,[19] which averaged 2.23 (1) and 2.233 (7) Å, respectively.

The benzenoid ring in 2 also shows substantial deviation from planarity, the substituted carbons being 0.19 Å out of the plane formed by the other four-ring atoms. The Cr–C(π) bond distances reflect this effect by exhibiting a wide range of 2.188 (5)–2.423 (6) Å, similar to the range seen for 3.

One significant difference between the geometry of the heterophanes and their [2.2]paracyclophane analogues is seen in the dihedral angle θ that is formed between the two ring planes. In 1 and 2 tilting of the rings is evident, with θ being 13.0 and 11.0°, respectively, but no such effect is seen for 3 ($\theta = 2.2°$) or its uncomplexed analogue ($\theta = 0.0°$). The origin of the ring tilting in heterophanes has been discussed.[22]

The Cr–C(carbonyl) bond distances in 1 and 2, averaging 1.82 Å in both instances, are close to the 1.8-Å average seen for 3 and also to the 1.84- and 1.81-Å averages seen for (C$_6$H$_6$)Cr(CO)$_3$ and [C$_6$(CH$_3$)$_6$]Cr(CO)$_3$, respectively. All other intramolecular bond distances of 1 and 2 are typical, and no abnormally close intermolecular approaches are evident.

Upon coordination to electron-withdrawing transition-metal moieties such as Cr(CO)$_3$[20] or Mn(CO)$_3^+$[21] arene ring protons have consistently exhibited significant (1–2 ppm) upfield shifts. The title compounds do not deviate from this behavior. In the case of 1 the 3- and 4-protons of the pyrrole ring are shifted 0.6 ppm upfield compared to the uncomplexed ligand. 2 demonstrates a similar pattern, with the aromatic ring protons being shifted 1.8 ppm upfield. The protons of the uncomplexed ring are moved 0.3–0.6 ppm downfield relative to the uncomplexed ligand.

Acknowledgment. We are grateful to the National Science Foundation for support of this work.

Registry No. 1, 96928-56-2; 2, 96898-08-7; (CH$_3$CN)$_3$Cr(CO)$_3$, 16800-46-7; [2.2](2,5)pyrroloparacyclophane, 51053-69-1.

Supplementary Material Available: Tables of hydrogen atom coordinates, anisotropic thermal parameters, best planes results, and observed and calculated structure factors for 1 and 2 (19 pages). Ordering information is given on any current masthead page.

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(16) Hope, H.; Bernstein, J.; Trueblood, K. N. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, **1972**, *B28*, 1733.

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(18) Bailey, M. F.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 1298.

(19) Rees, B.; Coppens, P. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1973**, *B29*, 2516.

(20) Polycyclic aromatics complexed to the Cr(CO)$_3$ moiety have been studied in detail, e.g.: (a) Brown, D. A.; Raju, J. R. *J. Chem. Soc. A* **1966**, 1617. (b) Reinke, H.; Oehme, Cr. *J. F. Prak. Chem.* **1978**, *320*, 967. The complexed rings show upfield shifts of up to 2 ppm compared to the uncomplexed rings.

(21) A wide range of [(monoarene)Mn(CO)$_3$]$^+$ cations have been characterized, with ring protons appearing in the range δ 5–6, compared to the δ 7–8 seen for the uncomplexed arenes, e.g.: Pauson, P. L.; Segal, J. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1677.

(22) Atwood, J. L.; Hunter, W. E.; Wong, C.; Paudler, W. W. *J. Heterocycl. Chem.* **1975**, *12*, 433.