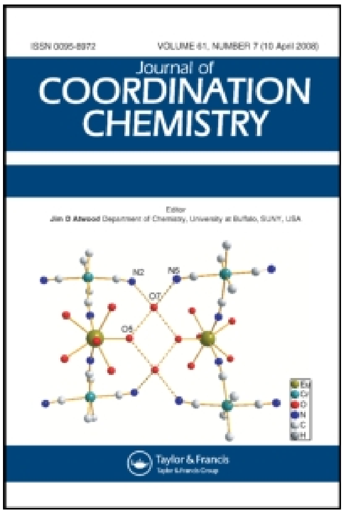

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Structure, Conformation and Reactivity of Organotransition Metal π-Complexes. part 2[1]. X-Ray Crystallographic Characterization of Two Neutral Half-Sandwich $Cr(CO)_3$ Complexes

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STRUCTURE, CONFORMATION AND REACTIVITY OF ORGANOTRANSITION METAL π-COMPLEXES. PART 2[1]. X-RAY CRYSTALLOGRAPHIC CHARACTERIZATION OF TWO NEUTRAL HALF-SANDWICH $Cr(CO)_3$ COMPLEXES

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The preferred solid state conformations adopted by two (η^6-ligand)$Cr(CO)_3$ (η^6-ligand: mesitylene, *1*; *N*-phenyl-2,5-dimethylpyrrole, *2*) complexes have been determined via single crystal X-ray crystallographic methods. *1* adopts a conformation such that the C_6 ring carbon atoms are eclipsed with respect to the carbonyl ligands. Such a conformation is predictable from both steric and electronic considerations. *2*, however, adopts a staggered conformation that must be attributed to the steric requirements of the bulky 2,5-dimethylpyrrole substituent.

Keywords: Chromium, carbonyl, arene, conformation, X-ray structure

INTRODUCTION

Complexation of π-ligands, particularly arenes, to transition metal moieties has been employed by a number of groups as a key method to facilitate stereospecific addition of nucleophiles to the π-ligand.[2] In such a context the nature and disposition of arene ring substituents play a significant role in determining the regioselectivity of the reaction.[3] However, another factor that is relevant in influencing the regioselectivity of the addition is the conformation that is adopted by the complex.[4] This is especially so for half-sandwich substrates such as the widely investigated (η^6-arene)$Cr(CO)_3$ series of complexes. In this contribution we report the results of an X-ray crystallographic study we have effected in order to ascertain the preferred solid-state conformations of two (η^6-ligand)$Cr(CO)_3$ (η^6-ligand: mesitylene, *1*; *N*-phenyl-2,5-dimethylpyrrole, *2*) half-sandwich complexes. The conformations adopted by *1* and *2* are discussed in the context of previous work.

EXPERIMENTAL

1 and *2* were prepared from $Cr(CO)_3(CH_3CN)_3$[5] using established procedures.[6]

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Crystals suitable for X-ray crystallographic analysis were sealed in thin-walled glass capillaries and placed on an Enraf-Nonius CAD-4 diffractometer. The lattice parameters were determined from least-squares refinement of the angular settings of fifteen high angle (theta >15°) reflections. Pertinent data collection parameters are given for *1* and *2* in Table I. The data were corrected for Lorentz, polarization and anomalous dispersion effects but not for absorption (μ was $9.2\,\mathrm{cm}^{-1}$ and $7.8\,\mathrm{cm}^{-1}$ for *1* and *2*, respectively). The positions of the chromium atoms were determined *via* direct (*1*) or heavy atom (*2*) methods. The structures were solved *via* subsequent difference Fourier map inspection and refined using full-matrix least-squares techniques with anisotropic thermal parameters for all non-hydrogen atoms. The programs used were MULTAN[7] (direct methods) and SHELX-76[8] (Patterson, difference Fourier, least-squares refinement). For both compounds, hydrogen atoms were located and placed from difference Fourier maps but they were not refined. Neutral atom scattering factors for C and O were taken from reference 9 whereas those for Cr were taken from reference 10 and those for H from reference 11. Corrections for the real and imaginary components of anomalous dispersion were taken from the compilations of Cromer and Liberman.[12] The final values of R and R_w are given along with other relevant structure refinement parameters in Table I. Final fractional coordinates are given in Tables II and III for *1* and *2*, respectively.

TABLE I

Crystallographic data collection and structure refinement parameters for *1* and *2*.

Compound	*1*	*2*
Formula	$CrO_3C_{12}H_{12}$	$CrO_3NC_{15}H_{13}$
Formula Wt.	256.2	307.3
Radiation	MoK_α	MoK_α
Crystal System	Triclinic	Triclinic
Space Group	$P\bar{1}$	$P\bar{1}$
a, Å	8.872(5)	7.914(5)
b, Å	10.506(6)	8.432(5)
c, Å	14.805(8)	11.653(7)
α, °	66.89(3)	80.21(3)
β, °	81.69(3)	77.41(3)
γ, °	80.41(3)	71.99(3)
V, Å^3	1186.1	717.3
Z	4	2
D_{calc}, gcm^{-3}	1.43	1.42
μ, cm^{-1}	9.2	7.8
Scan type	ω-2θ	ω-2θ
2θ range, °	4–36	4–36
Reflections observed*	1207	757
Parameters refined	289	181
Ratio data/parameter	5.1	4.2
R	0.049	0.029
R_w	0.060	0.033
GOF	2.2	0.84

* $I > 3\,\sigma(I)$.

TABLE II
Final fractional coordinates for (mesitylene)Cr(CO)$_3$.

Atom	*x/a*	*y/b*	*z/c*
(i) Molecule 1			
Cr(1)	0.3050(2)	0.2664(2)	0.0254(2)
O(1)	0.194(1)	0.419(1)	0.1663(8)
O(2)	0.094(1)	0.055(1)	0.154(1)
O(3)	0.546(1)	0.107(1)	0.1689(8)
C(1)	0.237(2)	0.361(2)	0.110(1)
C(2)	0.173(2)	0.134(2)	0.105(1)
C(3)	0.455(2)	0.165(1)	0.114(1)
C(4)	0.171(2)	0.389(2)	−0.114(1)
C(5)	0.270(2)	0.473(2)	−0.106(1)
C(6)	0.427(2)	0.428(2)	−0.103(1)
C(7)	0.486(2)	0.293(2)	−0.1041(9)
C(8)	0.385(2)	0.208(1)	−0.1109(9)
C(9)	0.226(2)	0.253(2)	−0.115(1)
C(10)	0.212(2)	0.615(1)	−0.106(1)
C(11)	0.656(2)	0.238(2)	−0.102(1)
C(12)	0.115(2)	0.167(2)	−0.128(1)
(ii) Molecule 2			
Cr(2)	0.6954(2)	0.2096(2)	0.5163(2)
O(4)	0.751(1)	−0.094(1)	0.6493(8)
O(5)	0.873(1)	0.273(1)	0.6529(8)
O(6)	0.411(1)	0.233(1)	0.6558(9)
C(13)	0.730(1)	0.021(2)	0.599(1)
C(14)	0.805(2)	0.248(1)	0.600(1)
C(15)	0.518(2)	0.224(1)	0.604(1)
C(16)	0.665(2)	0.414(1)	0.384(1)
C(17)	0.823(2)	0.360(2)	0.385(1)
C(18)	0.868(2)	0.224(2)	0.384(1)
C(19)	0.755(2)	0.143(2)	0.382(1)
C(20)	0.598(2)	0.201(2)	0.378(1)
C(21)	0.552(2)	0.333(2)	0.382(1)
C(22)	0.937(2)	0.450(2)	0.386(1)
C(23)	0.812(2)	0.001(2)	0.374(1)
C(24)	0.389(2)	0.389(2)	0.377(1)

RESULTS AND DISCUSSION

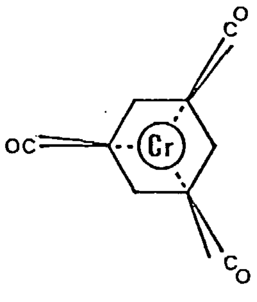
There are numerous examples of structurally characterized (arene)Cr(CO)$_3$ complexes and an extensive review was published in 1982.[13] *1* and *2* are discussed below in the context of the earlier studies.

1: There are two molecules in the asymmetric unit and, as revealed by the perspective SNOOPI[14] views presented in Figure 1 and the intramolecular bond distances and angles (Table IV), they are almost identical to one another. Both molecules adopt the same conformation, **I**, such that the mesitylene methyl groups eclipse the chromium tricarbonyl tripodal moiety. In molecule A the C(CO)-Cr-C(ring)-C(methyl) torsion angles average 3.6°; in molecule B they average 0.9°. Steric

TABLE III
Final fractional coordinates for (η^6-*N*-phenyl-2,5-dimethylpyrrole)Cr(CO)$_3$.

Atom	*x/a*	*y/b*	*z/c*
Cr	0.1824(1)	0.2353(1)	0.34822(9)
O(1)	0.1689(8)	−0.1037(7)	0.3137(5)
O(2)	−0.2184(8)	0.3292(7)	0.4353(5)
O(3)	0.2524(8)	0.0984(8)	0.5934(5)
N	0.2250(9)	0.2548(6)	0.0494(5)
C(1)	0.1738(9)	0.025(1)	0.3284(6)
C(2)	−0.065(1)	0.2924(9)	0.4041(6)
C(3)	0.225(1)	0.151(1)	0.4995(7)
C(4)	0.2541(9)	0.3055(8)	0.1520(6)
C(5)	0.1332(9)	0.4477(9)	0.2027(6)
C(6)	0.177(1)	0.5011(8)	0.2995(7)
C(7)	0.335(1)	0.417(1)	0.3430(6)
C(8)	0.454(1)	0.273(1)	0.2933(7)
C(9)	0.4123(9)	0.2142(8)	0.1998(6)
C(10)	0.067(1)	0.2274(8)	0.0326(8)
C(11)	0.097(1)	0.1868(8)	−0.0790(9)
C(12)	0.272(1)	0.1921(8)	−0.1348(7)
C(13)	0.351(1)	0.2339(8)	−0.0564(8)
C(14)	−0.1021(9)	0.2444(9)	0.1204(7)
C(15)	0.532(1)	0.2626(9)	−0.0693(6)

effects might be expected to favour staggering of the methyl substituents, *i.e.*, conformation **II**. However, a similar conformation was also observed for the molybdenum analogue of *1*, (mesitylene)Mo(CO)$_3$,[15] and has been rationalized[13] on the basis of a general tendency for regions of high electron density on the η^6 ligand to orient themselves towards empty hybrid orbitals of the tripod. Since the methyl groups cause the C–H ring carbon atoms to become electron-rich and the empty hybrid orbitals are staggered with respect to the carbonyl ligands the expected conformation in terms of electronic effects is indeed the one observed.



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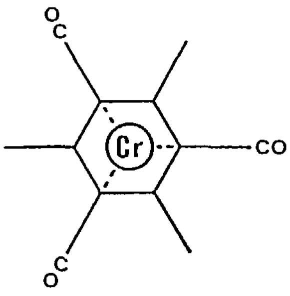

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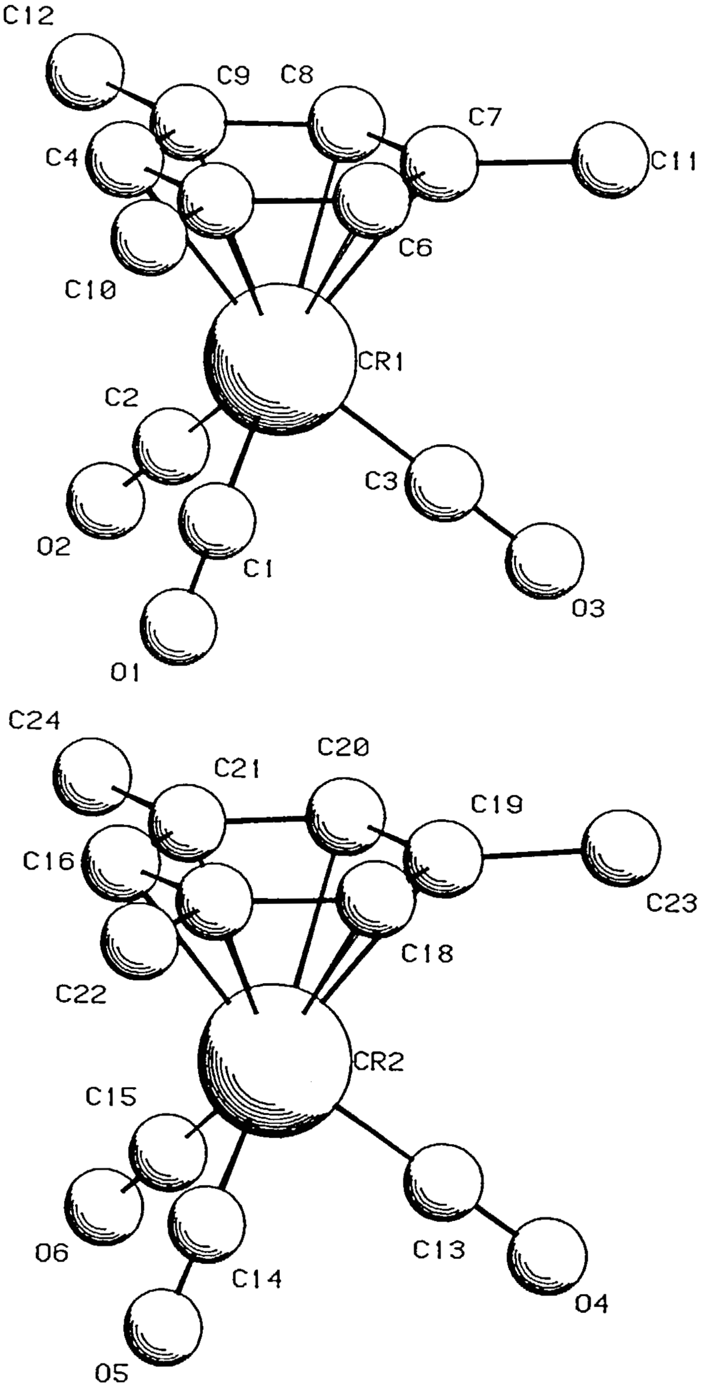


FIGURE 1 Perspective views of the two independent molecules of (mesitylene)Cr(CO)$_3$ present in the asymmetric unit.

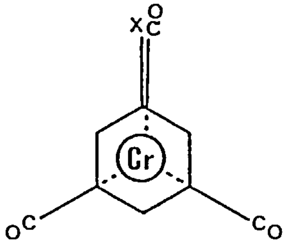
TABLE IV
Bond distances (Å) and angles (°) for (mesitylene)Cr(CO)$_3$.

Atoms	Distance	Atoms	Distance
Cr(1)-C(1)	1.82(2)	Cr(1)-C(2)	1.87(2)
Cr(1)-C(3)	1.85(2)	Cr(1)-C(4)	2.26(1)
Cr(1)-C(5)	2.24(1)	Cr(1)-C(6)	2.22(1)
Cr(1)-C(7)	2.21(1)	Cr(1)-C(8)	2.22(1)
Cr(1)-C(9)	2.26(1)	Cr(2)-C(13)	1.86(2)
Cr(2)-C(14)	1.82(2)	Cr(2)-C(15)	1.88(2)
Cr(2)-C(16)	2.23(1)	Cr(2)-C(17)	2.21(1)
Cr(2)-C(18)	2.21(1)	Cr(2)-C(19)	2.23(1)
Cr(2)-C(20)	2.27(1)	Cr(2)-C(21)	2.26(1)
O(1)-C(1)	1.16(1)	O(2)-C(2)	1.12(2)
O(3)-C(3)	1.13(1)	O(4)-C(13)	1.13(1)
O(5)-C(14)	1.15(1)	O(6)-C(15)	1.13(2)
C(4)-C(5)	1.39(2)	C(4)-C(9)	1.44(2)
C(5)-C(6)	1.39(2)	C(5)-C(10)	1.50(2)
C(6)-C(7)	1.43(2)	C(7)-C(8)	1.40(2)
C(7)-C(11)	1.52(2)	C(8)-C(9)	1.41(2)
C(9)-C(12)	1.51(2)	C(16)-C(17)	1.42(2)
C(16)-C(21)	1.42(2)	C(17-C(18)	1.42(2)
C(17)-C(22)	1.51(2)	C(18)-C(19)	1.43(2)
C(19)-C(20)	1.42(2)	C(19-C(23)	1.53(2)
C(20)-C(21)	1.40(2)	C(21)-C(24)	1.47(2)

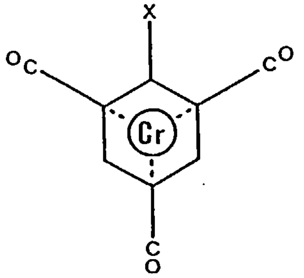
Atoms	Angle	Atoms	Angle
C(1)-Cr(1)-C(2)	88.6(6)	C(1)-Cr(1)-C(3)	88.8(6)
C(2)-Cr(1)-C(3)	88.8(6)	C(13)-Cr(2)-C(14)	89.0(6)
C(13)-Cr(2)-C(15)	88.6(6)	C(14)-Cr(2)-C(15)	88.9(6)
Cr(1)-C(1)-O(1)	179(1)	Cr(1)-C(2)-O(2)	178(1)
Cr(1)-C(3)-O(3)	178(1)	C(5)-C(4)-C(9)	121(1)
C(4)-C(5)-C(6)	120(1)	C(4)-C(5)-C(10)	121(2)
C(6)-C(5)-C(10)	119(2)	C(5)-C(6)-C(7)	120(1)
C(6)-C(7)-C(8)	119(1)	C(6)-C(7)-C(11)	123(2)
C(8)-C(7)-C(11)	118(2)	C(7)-C(8)-C(9)	121(1)
C(4)-C(9)-C(8)	118(1)	C(4)-C(9)-C(12)	120(2)
C(8)-C(9)-C(12)	122(2)	Cr(2)-C(13)-O(4)	180(1)
Cr(2)-C(14)-O(5)	179(1)	Cr(2)-C(15)-O(6)	179(1)
C(17)-C(16)-C(21)	121(1)	C(16)-C(17)-C(18)	120(1)
C(16)-C(17)-C(22)	118(2)	C(18-C(17)-C(22)	122(2)
C(17)-C(18)-C(19)	120(1)	C(18-C(19)-C(20)	119(1)
C(18)-C(19)-C(23)	117(2)	C(20)-C(19)-C(23)	123(2)
C(19)-C(20)-C(21)	121(1)	C(16)-C(21)-C(20)	119(1)
C(16)-C(21)-C(24)	122(2)	C(20)-C(21)-C(24)	119(2)

The ring carbon atoms are planar to 0.01 Å (average deviation 0.006 Å) and 0.02 Å (average deviation 0.005 Å) for molecules A and B, respectively. The methyl carbon atoms reside 0.017 to 0.073 Å (average deviation 0.043 Å) out of the C_6 plane with all carbon atoms pointing away from the Cr(CO)$_3$ moiety. Within experimental error, the Cr-mesitylene bond lengths are equivalent, with the average value of 2.24(2) Å being within the range previously observed for (arene)Cr(CO)$_3$ complexes.[13] The M–C(CO) bond lengths are also equivalent and within the expected range (average = 1.85(3) Å). All other bond distances and angles are within expected ranges.

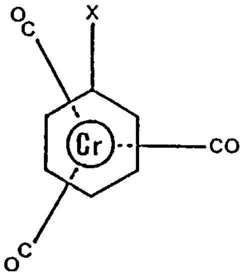
2: There are three idealized conformations possible for monosubstituted arene ligands in (arene(Cr(CO)$_3$ complexes. Electronic considerations would tend to favour eclipsing of the ring carbon atoms with respect to the carbonyl moieties. Conformations with the arene substituent either eclipsed with respect to a carbonyl group (electron donor substituent), EE, or staggered (electron acceptor substituent),[13] E, are therefore possible. However, neither of these is observed as *2* adopts a staggered conformation, S, as do a number of other monosubstituted arenes that possess a bulky substituent (*e.g.*, isopropylbenzene[16]).



EE



E



S

TABLE V

Bond distances (Å) and angles (°) for (η^6-*N*-phenyl-2,5-dimethylpyrrole)Cr(CO)$_3$.

Atoms	Distance	Atoms	Distance
Cr-C(1)	1.847(8)	Cr-C(2)	1.859(8)
Cr-C(3)	1.848(9)	Cr-C(4)	2.254(7)
Cr-C(5)	2.249(6)	Cr-C(6)	2.207(6)
Cr-C(7)	2.210(7)	Cr-C(8)	2.213(6)
Cr-C(9)	2.207(6)	O(1)-C(1)	1.143(7)
O(2)-C(2)	1.147(7)	O(3)-C(3)	1.147(8)
N-C(4)	1.422(8)	N-C(10)	1.400(8)
N-C(13)	1.404(8)	C(4)-C(5)	1.410(8)
C(4)-C(9)	1.426(8)	C(5)-C(6)	1.428(9)
C(6)-C(7)	1.388(9)	C(7)-C(8)	1.409(9)
C(8)-C(9)	1.411(8)	C(10)-C(11)	1.354(9)
C(10)-C(14)	1.479(9)	C(11)-C(12)	1.407(9)
C(12)-C(13)	1.356(9)	C(13)-C(15)	1.497(9)

Atoms	Angle	Atoms	Angle
C(1)-Cr-C(2)	88.9(3)	C(1)-Cr-C(3)	88.1(3)
C(2)-Cr-C(3)	90.3(3)	C(4)-N-C(10)	127.1(7)
C(4)-N-C(13)	124.5(7)	C(10)-N-C(13)	108.4(6)
Cr-C(1)-O(1)	178.7(6)	Cr-C(2)-O(2)	178.0(6)
Cr-C(3)-O(3)	179.8(2)	N-C(4)-C(5)	120.7(6)
N-C(4)-C(9)	118.7(6)	C(5)-C(4)-C(9)	120.5(6)
C(4)-C(5)-C(6)	118.3(6)	C(5)-C(6)-C(7)	121.4(6)
C(6)-C(7)-C(8)	120.1(7)	C(7)-C(8)-C(9)	119.9(6)
C(4)-C(9)-C(8)	119.6(6)	N-C(10)-C(11)	107.0(6)
N-C(10)-C(14)	125.9(8)	C(11)-C(10)-C(14)	127.1(9)
C(10)-C(11)-C(12)	109.0(7)	C(11)-C(12)-C(13)	108.3(7)
N-C(13)-C(12)	107.2(7)	N-C(13)-C(15)	121.6(8)
C(12)-C(13)-C(15)	131.1(9)		

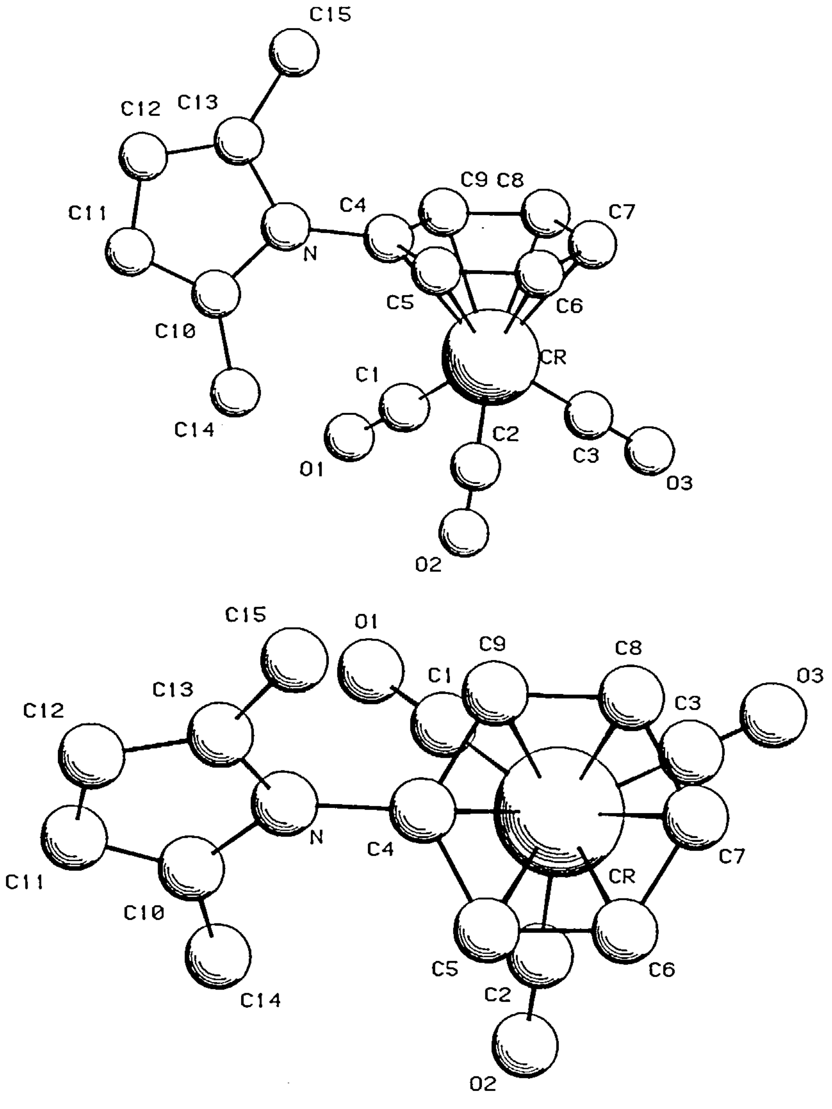


FIGURE 2 Perspective (a) and overhead (b) views of (η^6-N-phenyl-2,5-dimethylpyrrole)Cr(CO)$_3$.

It is clear from the perspective and overhead views of *2* presented in Figure 2 that this conformation is a result of the orientation of the bulky dimethylpyrrole moiety, which subtends an angle of 52.7° with the C_6 ring and therefore angles itself between two carbonyl groups.

Bond distances and angles are presented in Table V. They reveal that steric effects also appear to be manifested in the Cr–C(arene) distances, which range from 2.207(6) to 2.254(7) Å (average = 2.22(2) Å). Significantly, the longest bond length is observed for Cr–C(4) and C(4) is the substituted ring carbon atom. The Cr–C(CO) bond lengths are equivalent within experimental error, averaging 1.851(7) Å. The 2,5-dimethylpyrrole moiety is planar to within 0.01 Å (for the five-membered ring) and the C–N and C–C bond lengths are similar to those observed in uncomplexed pyrrole[17] and (*N*-methylpyrrole)Cr(CO)$_3$.[18] All other bond distances and angles are within expected ranges.

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SUPPLEMENTARY DATA

Full lists of hydrogen atomic positions, anisotropic thermal parameters and observed and calculated structure factors are available from the authors upon request.

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