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Substituent effects in bis(arene)chromium compounds containing a CN group in the aromatic ring

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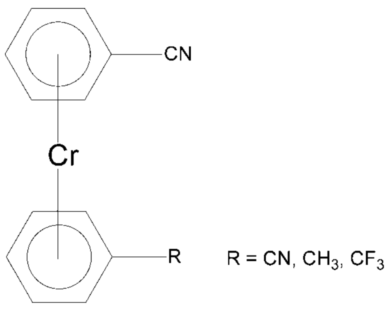
The crystal structures of $Cr(PhCN)_2$ (2), $(PhCN)Cr(PhCH_3)$ (3) and $(PhCN)Cr(PhCF_3)$ (4) prepared by means of the Metal Vapor Synthesis (MVS) technique have been determined. Compounds (2), (3) and (4) crystallize as discrete sandwich complexes having intrinsic $C_{2v}(mm2)$, $C_s(m)$ and $C_1(1)$ symmetries, respectively. The X-ray diffraction study has revealed a synperiplanar conformation for (2) and (3), and a synclinal conformation for (4) with a torsion angle ($C_{ipso}1$–Centroid1–Centroid2–$C_{ipso}2$) of $\varphi = 63.5°$. The angles between the ligand planes are 2.2, 3.9 and 1.8°, respectively. The Cr atom is slightly (by 0.04–0.06 Å) displaced towards the substituents from the line connecting the centers of the opposite aromatic rings. The $Cr-C_{ipso}$ distances are 2.115 (2)–2.137 (2), 2.112 (2) and 2.185 (3) Å for CN, CF_3 and CH_3 groups, respectively. The CN groups as well as the H atoms lie out of the C_6 ring planes and are bent towards the Cr atom, but the C atom of the CH_3 group also lying out of the C_6 ring plane is bent away from the Cr atom. The C atom of the CF_3 group is essentially coplanar to the C_6 ring plane. There are no unusual intermolecular contacts in the structures of (2)–(4).

1. Introduction

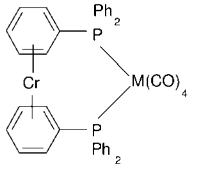
The direct reaction of a metal with a ligand is conceptually the most straightforward synthetic route to homoleptic organometallic complexes with the metal in a zero oxidation state. Strong metal–metal bonds in the bulk metal: the presence of oxide films on the metal and unfavorable thermodynamics often render this route impossible. A solution to this problem is offered by MVS, whereby the metal vapor consisting of transition metal atoms is generated and condensed in the presence of excess ligand before agglomeration to the bulk metal can take place (Timms, 1969). For arene sandwich complexes of group 6 metals, this is the most versatile method affording the sandwich complexes in yields up to 65% relative to the amount of metal evaporated (Kündig & Pache, 2003). This method also allows the syntheses of mixed bis-arene chromium π-complexes.

The literature lists a large number of bis-arene chromium complexes but shows that a relatively small number of neutral and cationic substituted di(benzene)chromium (1) complexes have been structurally characterized by X-ray diffraction. X-ray structures of mixed sandwich complexes are of special significance since their structural characteristics will reflect the bonding properties of the arenes.



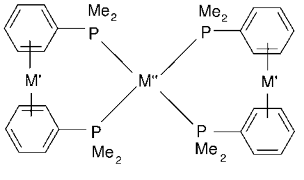
We have previously described the synthesis of a series of non-symmetric complexes $(C_6H_5CN)Cr(C_6H_5R)$, where R = CN (2), H, CH_3 (3), OCH_3, $COCH_3$, Cl, F and CF_3 (4) (Nesmeyanov *et al.*, 1981; Vasil'kov *et al.*, 1982; Sergeev *et al.*, 1984). Their ionization potentials and behavior in redox processes were studied (Yur'eva *et al.*, 1987). The use of electrochemical methods allows one to quantitatively estimate the influence of substituents on the redox parameters of the compounds. It was established that a variation of the nature of a substituent in one of the ligands of the non-symmetric bis-arene complexes changes the potential of the oxidation half-wave $E_{\frac{1}{2}}(0/+)$. Di(benzene)chromium has $E_{\frac{1}{2}}(1^{0/+}) = -0.8$ V as it is one of the most easily oxidizable transition metal π-complexes. The introduction of two σ-electron-withdrawing nitrile groups into (1) shifts the oxidation potential towards the anodic region to $E_{\frac{1}{2}}(2^{0/+}) = -0.175$ V. The electrochemical oxidation of non-symmetric complexes (3) and (4) occurs at $E_{\frac{1}{2}}(3^{0/+}) = -0.53$ V and $E_{\frac{1}{2}}(4^{0/+}) = -0.22$ V, which correlates with the σ-electron-donating (for CH_3) and σ-electron-withdrawing (for CF_3) character of the substituents.

The studies showed that nitrile as well as phosphorus-containing derivatives of (1), which possess a combination of interesting physicochemical properties, can be used to synthesize polynuclear bridged compounds of types *A* and *B* (Elschenbroich *et al.*, 1995, and references therein). The latter are convenient models for understanding the process of intramolecular electron transfer from a metal atom to a ligand or between two metal nuclei.



A

M = Cr, Mo, W



B

M' = Cr, V
M'' = Ni, Pd, CoH

It is to be expected that the electronic effects of the CH_3, CF_3 and CN substituents detected for the redox processes of (2)–(4) could influence the geometry of these compounds. To reveal the influence of the substituents on the stereochemistry of (2)–(4), we performed X-ray diffraction analyses of these compounds. Complexes (2)–(4) with CH_3, CF_3 and CN substituents were chosen for this study, because we intended to use the substituents with different electronic properties but which are similar in structure and volume. By choosing these substituents we also aimed to reduce the influence of steric effects. All three substituents contain a C atom, through which they are linked with the *ipso*-C atom of the aromatic ring, and they are structurally similar.

To the best of our knowledge, no crystallographic studies of bis-arene transition metal complexes containing a CN substituent in the aromatic ring have been reported so far.

2. Experimental

2.1. General synthetic procedure

Non-symmetric nitriles of (1) were synthesized in one step using the MVS technique, *i.e.* the reaction of atomic chromium with a mixture of benzonitrile and another monosubstituted arene. Compounds (2)–(4) were synthesized with some modifications from the procedures developed by us earlier (Sergeev *et al.*, 1986). These changes made it possible to increase the yield of the complexes due to a decrease in the fraction of side processes.

The reactions of organic compounds with Cr vapor were performed in a reactor at $P = 10^{-4}$ Torr and T = 77 K. A W-resistive evaporator was used for the vaporization of chromium. The organic compounds were continuously injected into the reactor, while the flow rate was controlled by a fine-adjustable valve. All the procedures to isolate the products were performed in an atmosphere of purified argon.

The reaction was accompanied by the cyclotrimerization of benzonitrile to form 1,3,5-triphenyltriazine. If unreacted chromium was not removed from the reaction mixture, by-products formed which decreased the yield of (2)–(4).

Owing to the destabilizing role of ultradisperse metal particles, which are almost always present in the reaction mixture, an approach that helps to avoid or substantially reduce their involvement is recommended: it is desirable to remove the unreacted metal as soon as possible. For example, a black Cr-containing precipitate is formed when a nonpolar solvent is added, *e.g.* pentane. Using this procedure, the yield of (2)–(4) can be increased.

2.1.1. $(PhCN)_2Cr$ (2). Chromium (0.81 g, 15 mmol) was co-condensed with PhCN (80 ml) and the co-condensate was allowed to melt. This mixture was then siphoned from the reactor to a Schlenk flask in an argon atmosphere. Pentane (30 ml) was added and the mixture obtained was filtered through a column (d = 40 mm, h = 20 mm, 10% H_2O, C_6H_6). After the removal of the solvents a dense oily substance remained, which was repeatedly chromatographed on a column [d = 25 mm, h = 200 mm, 10% H_2O, C_6H_6/petroleum ether (1:1) as the eluent; dark yellow band]. Evaporation of the solvents gave a viscous brown liquid.

Table 1
Crystallographic data for (2)–(4).

	(2)	(3)	(4)
Crystal data			
Chemical formula	$C_{14}H_{10}CrN_2$	$C_{14}H_{13}CrN$	$C_{14}H_{10}CrF_3N$
M_r	258.24	247.25	301.23
Cell setting, space group	Monoclinic, $P2_1/n$	Orthorhombic, *Pbca*	Monoclinic, $P2_1/c$
a, b, c (Å)	7.7300 (5), 12.0887 (8), 11.1762 (8)	12.9628 (19), 12.0803 (18), 13.610 (2)	9.7145 (13), 7.8227 (11), 15.740 (2)
β (°)	91.6830 (10)	90.00	98.276 (4)
V (Å^3)	1043.92 (12)	2131.3 (5)	1183.7 (3)
Z	4	8	4
D_x (Mg m^{-3})	1.643	1.541	1.690
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	4186	2085	5825
θ range (°)	2.5–30.0	3.0–28.8	2.3–30.0
μ (mm^{-1})	1.07	1.04	0.99
Temperature (K)	120 (2)	120 (2)	120 (2)
Crystal form, colour	Prism, brown	Prism, brown	Prism, dark brown
Crystal size (mm)	0.36 × 0.28 × 0.24	0.24 × 0.21 × 0.12	0.40 × 0.30 × 0.30
Data collection			
Diffractometer	Bruker SMART 1000 CCD area detector	Bruker SMART 1000 CCD area detector	Bruker SMART 1000 CCD area detector
Data collection method	φ and ω scans	φ and ω scans	φ and ω scans
Absorption correction	Multi-scan (based on symmetry-related measurements)	Multi-scan (based on symmetry-related measurements)	Multi-scan (based on symmetry-related measurements)
$T_{\min}$	0.700	0.788	0.693
$T_{\max}$	0.784	0.885	0.756
No. of measured, independent and observed reflections	7835, 2984, 2343	15 653, 2318, 1353	9037, 3386, 2915
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
$R_{\rm int}$	0.022	0.057	0.024
$\theta_{\max}$ (°)	30.0	27.0	30.0
Range of h, k, l	$-10 \Rightarrow h \Rightarrow 10$ $-14 \Rightarrow k \Rightarrow 17$ $-13 \Rightarrow l \Rightarrow 15$	$-15 \Rightarrow h \Rightarrow 16$ $-15 \Rightarrow k \Rightarrow 15$ $-17 \Rightarrow l \Rightarrow 17$	$-13 \Rightarrow h \Rightarrow 13$ $-10 \Rightarrow k \Rightarrow 10$ $-22 \Rightarrow l \Rightarrow 18$
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.037, 0.086, 1.02	0.059, 0.143, 1.05	0.042, 0.106, 1.00
No. of reflections	2984	2318	3386
No. of parameters	194	197	213
H-atom treatment	Refined independently	Refined independently	Refined independently
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.030P)^2 + 1.5P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.070P)^2 + 1.5P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.060P)^2 + 1.2P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	< 0.0001	0.001	< 0.0001
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.83, −0.51	1.78, −0.77	0.77, −0.80
Extinction method	None	None	*SHELXL*
Extinction coefficient			0.034 (2)

Computer programs used: *SMART* (Bruker AXS, 1998*b*), *SAINTPlus* (Bruker AXS, 1998*a*), *SHELXTL* (Sheldrick, 1998*a*).

After re-crystallization from toluene/hexane at ambient temperature, (2) (0.34 g, 9%) was isolated as brown crystals with m.p. = 478 K; lit. m.p. = 478–479 K, see Nesmeyanov *et al.* (1981). Found (%): C 65.31, H 3.85, Cr 20.69; $C_{14}H_{10}N_2Cr$ calculated (%): C 65.12, H 3.88, Cr 20.16.

2.1.2. (PhCN)Cr(PhCH$_3$) (3). The introduction of pentane into the reaction mixture immediately after the synthesis decreased the yield of 1,3,5-triphenyltriazine. Conditions for the isolation and analysis of the reaction products are presented elsewhere (Sergeev *et al.*, 1984). Product (3) was eluted with C_6H_6/petroleum ether, as a yellow band, and re-crystallized from a C_6H_6/pentane mixture at 261 K.

2.1.3. (PhCN)Cr(PhCF$_3$) (4). The synthesis of the non-symmetrical complex (4) has been described elsewhere (Sergeev *et al.*, 1986). The dark brown crystalline material suitable for X-ray diffraction was obtained by layering a solution of (4) in toluene with pentane at 261 K.

2.2. X-ray structure determination.

Data were collected on a Bruker three-circle diffractometer equipped with a SMART 1000 CCD detector and corrected for absorption using the *SADABS* program (Sheldrick, 1998*b*). Data reduction was performed using *SMART* (Bruker AXS, 1998*b*) and *SAINTPlus* (Bruker AXS, 1998*a*) programs. For details, see Table 1. The structures were solved by direct methods and refined by full-matrix least-squares refinement with anisotropic displacement parameters for all the non-H atoms. The H atoms were localized in a difference-Fourier map and were refined isotropically. All calculations were carried using the *SHELXTL* (PC Version 5.10) program (Sheldrick, 1998*a*).[1]

3. Results and discussion

The structures of (2)–(4) are shown in Figs. 1–3 and the corresponding geometric parameters are presented in Table 2. The intrinsic symmetries of (2)–(4) are very close to $C_{2v}(mm2)$, $C_s(m)$, and $C_1(1)$, respectively. Unlike (2) and (3), whose conformations in the crystals are synperiplanar, (4) has a synclinal conformation with $\tau = 63.5°$ as the torsion angle of the substituents relative to each other. The *syn* conformations found for the crystals of (2) and (3) have previously been observed for the monosubstituted bis-arene complexes of other transition metals, *viz.* $(\eta^6\text{-C}_6\text{H}_5\text{Me})_2M$ [M = Ti (Tairova *et al.*, 1982), Mo (Miao, 1982), W (Prout *et al.*, 1982), Nb (Clark *et al.*, 1996)] and $(\eta^6\text{-C}_6\text{H}_5\text{COOH})_2\text{Cr}$ (Braga *et al.*, 2001), while compounds $(\eta^6\text{-C}_6\text{H}_5R)_2\text{Cr}$ [R = CF_3 (Larson *et al.*, 1987) or NMe_2 (Lynch *et al.*, 1990)] have an antiperiplanar conformation in the crystals. The C atoms of the aromatic rings in (2)–(4) are close to being eclipsed. A slight rotation of the cycles in (4) by an angle of $\varphi = 3.5°$ from the eclipsed orientation is probably caused by steric interaction between the CN and CF_3 groups. The presence of the CN and CF_3 substituents decreases the Cr—C_R distance to the *ipso*-C atom compared with the other Cr—C_H distances in (4). While the Cr atom is formally neutral, there is some partial charge on the *ipso*-C atoms and apparently there is an electrostatic contribution into the interaction between the metal and the *ipso*-carbon atoms. The shortened Cr—C_{ipso} bonds are observed for all the mono- and di-CF_3-substituted derivatives of (1) studied by X-ray diffraction analysis: $(\text{CF}_3\text{C}_6\text{H}_5)_2\text{Cr}$, $(\text{CF}_3\text{C}_6\text{H}_5)\text{Cr}[p\text{-(CH}_3)_2\text{C}_6\text{H}_4]$ (Larson *et al.*, 1987), $[p\text{-(CF}_3)\text{C}_6\text{H}_4]_2\text{Cr}$, $[m\text{-(CF}_3)_2\text{C}_6\text{H}_4]_2\text{Cr}$ and $[m\text{-(CF}_3)\text{ClC}_6\text{H}_4]_2\text{Cr}$ (Eyring *et al.*, 1981). This effect is independent of the conformations of the molecules in crystals and, most likely, is inherent to all neutral bis(arene)chromium complexes bearing σ-electron-withdrawing substituents. The geometry of the sandwich complexes changes in a different way when a σ-electron-donating substituent is introduced. In (3) the Cr—C_R distance to the toluene ligand is 2.185 (3) Å (the maximum), and the distance to benzonitrile is 2.120 (3) Å (the minimum) compared with other Cr—C_H distances. An analysis of the published structural data for methyl-substituted complexes of the $(\text{arene})_2\text{Cr}$ type [arene = $\text{CH}_3\text{C}_6\text{H}_5$ (Starovskii & Struchkov, 1961; Shibaeva *et al.*, 1969; Braga *et al.*, 1997; Hönnerscheid *et al.*, 2002), 1,3,5-$(\text{Me})_3\text{C}_6\text{H}_3$ (Miller *et al.*, 1989; O'Hare *et al.*, 1990; Del Sesto *et al.*, 2001) and 1,2,4,5-$(\text{Me})_4\text{C}_6\text{H}_2$ (Ketkov *et al.*, 2002)] showed that the Cr—C_{ipso} bonds are somewhat elongated compared with Cr—C_H, regardless of the form of the complexes (neutral or cationic), their conformations and the number of CH_3 substituents introduced. A similar effect has also been observed for non-symmetric $(\text{CF}_3\text{C}_6\text{H}_5)\text{Cr}[p\text{-(CH}_3)_2\text{C}_6\text{H}_4]$. Earlier, the sandwich chromium π-complexes with polycyclic aromatic hydrocarbons (PAH), such as naphthalene (Kündig *et al.*, 1985; Bush *et al.*, 1987), triphenylene and fluoranthene (Elschenbroich *et al.*, 1998), also exhibited an increase in Cr—C_R distances compared with Cr—C_H, where C_R are the C atoms of the η^6-coordinated ring forming the C—C bonds with the non-coordinated part of the PAH ligand.

The shift of the C atoms from the plane of the aromatic ring was found for the C atoms of the substituent groups. While the

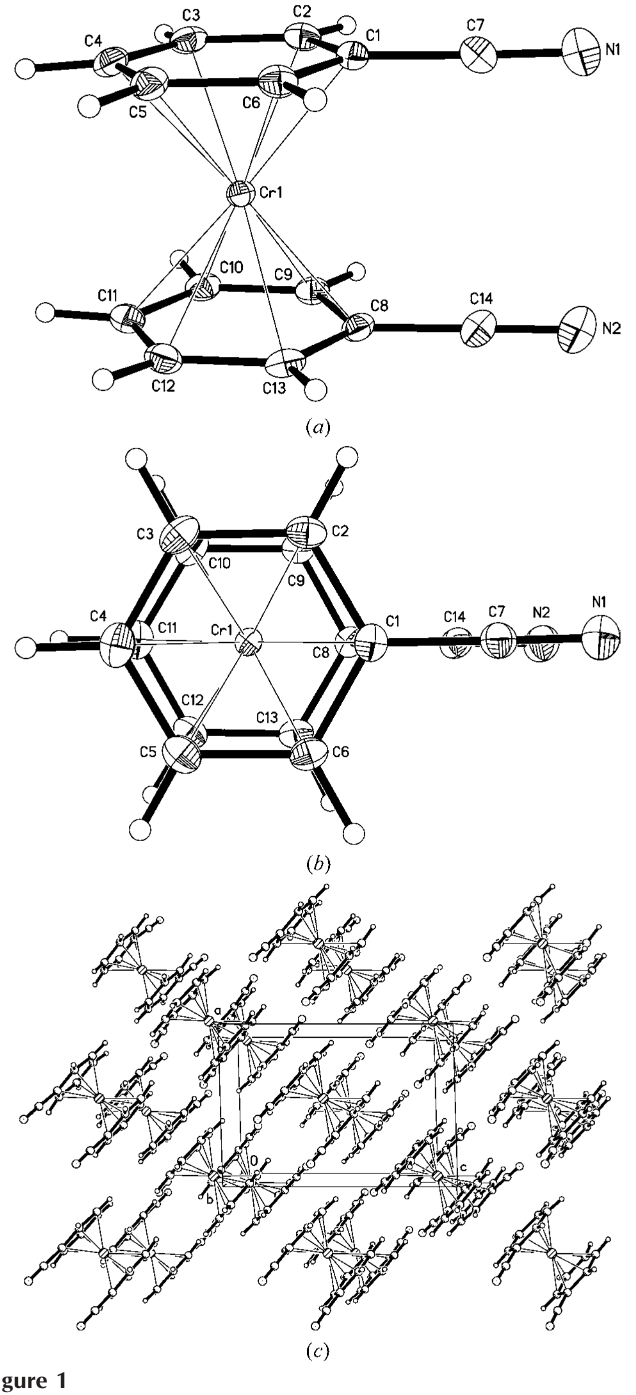


Figure 1
Molecular structure of (2); two projections and a packing diagram are shown (ellipsoids are drawn at the 50% probability level).

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV5032). Services for accessing these data are described at the back of the journal.

C atoms of the CN and CF_3 substituents are displaced towards the Cr center from the planes of the aromatic ring, the C atom of the CH_3 group is moved away from the Cr center in each complex. In (2)–(4) the Cr atom is shifted by 0.04–0.06 Å from the axis connecting the geometric centers of the aromatic rings towards the substituents. The longest $\mathrm{Cr-C}_H$ bonds are those to the C_H atoms, which are the most remote from the CN and CF_3 groups or the closest to the CH_3 substituent (Table 2, Fig. 4).

Compounds (2) and (3) exist in the synperiplanar conformations with eclipsed CN and CH_3 groups. This makes it possible to monitor changes in geometry with a change in the

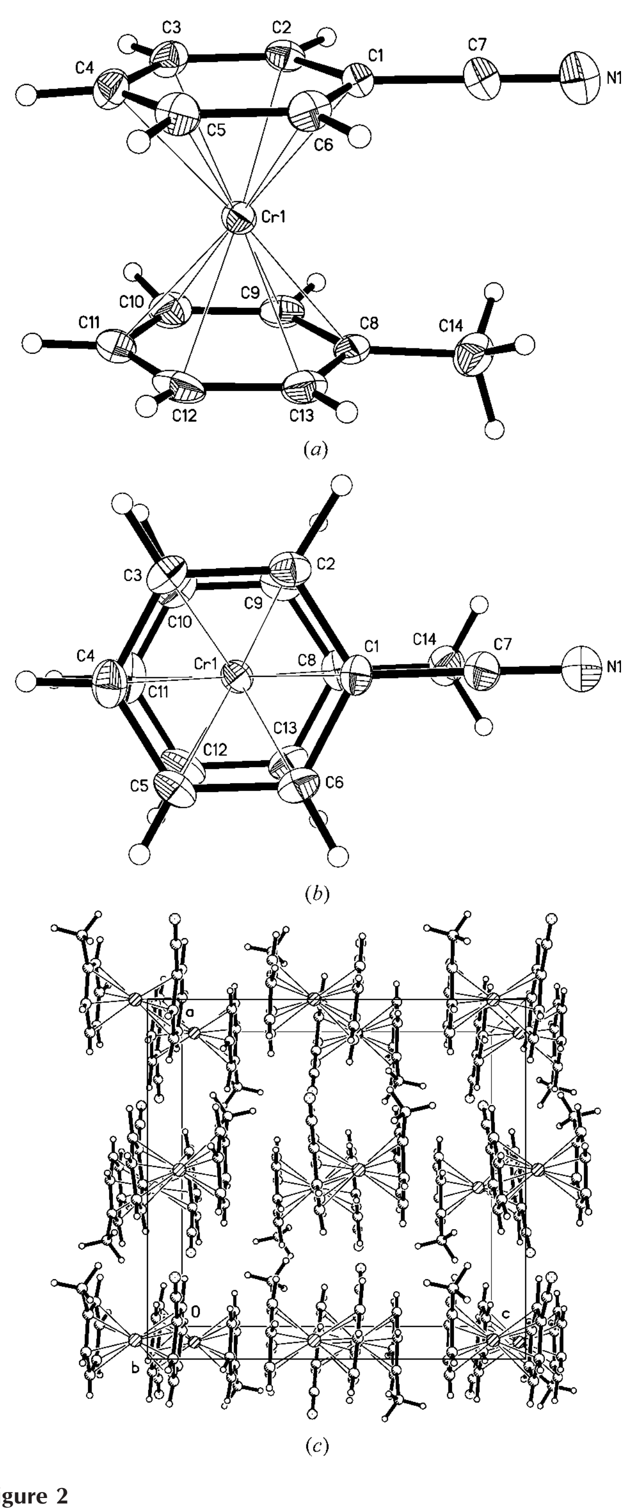

Figure 2
Molecular structure of (3); two projections and a packing diagram are shown (ellipsoids are drawn at the 50% probability level).

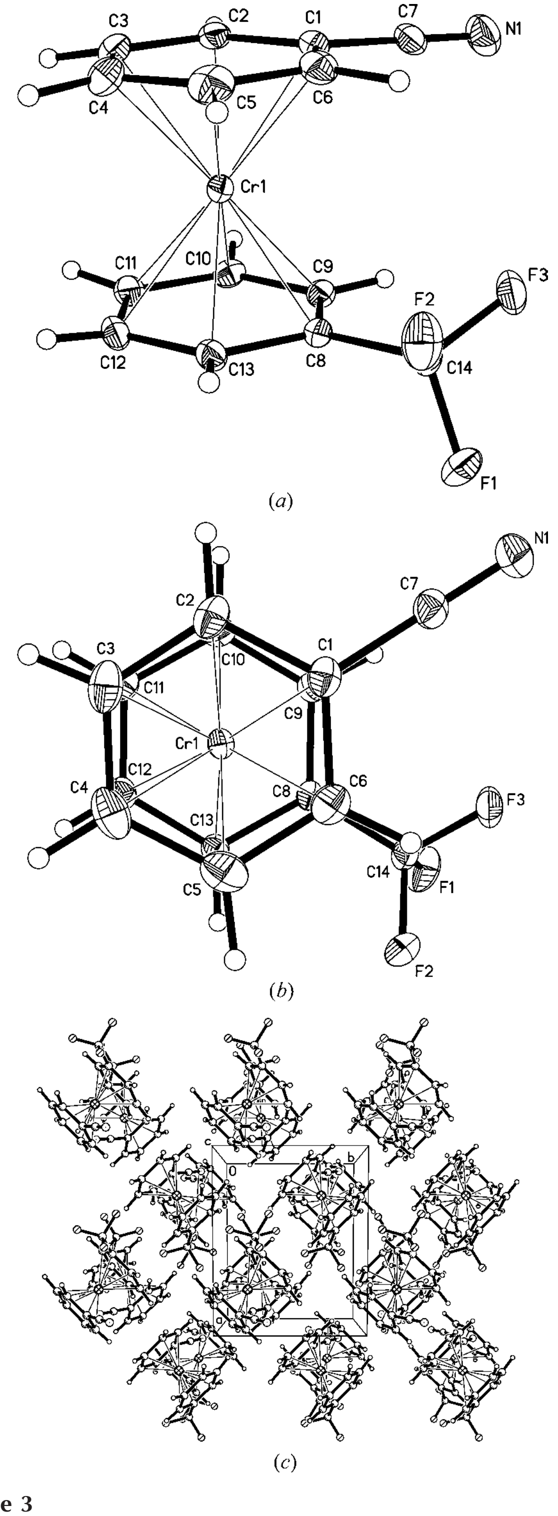

Figure 3
Molecular structure of (4); two projections and a packing diagram are shown (ellipsoids are drawn at the 50% probability level).

Table 2
Comparative selected structural data (Å and °) for (2)–(4).

Parameters		(2), R = CN	(3), R = CH_3	(4), R = CF_3
$Cr-C_{ring}$†	PhCN	1.621	1.607	1.604
	PhR	1.625	1.630	1.606
$Cr-C_H$	PhCN	2.146 (2)–2.164 (2)	2.133 (4)–2.149 (4)	2.141 (2)–2.157 (2)
	PhR	2.148 (2)–2.165 (2)	2.133 (4)–2.160 (4)	2.138 (2)–2.158 (2)
$Cr-C_R$	PhCN	2.137 (2)	2.120 (3)	2.115 (2)
	PhR	2.138 (2)	2.185 (3)	2.112 (2)
C_H-C_H	PhCN	1.405 (3)–1.414 (3)	1.396 (5)–1.407 (5)	1.408 (3)–1.421 (2)
	PhR	1.409 (3)–1.414 (3)	1.378 (6)–1.418 (6)	1.409 (2)–1.424 (3)
C_H-C_R	PhCN	1.425 (2), 1.427 (2)	1.416 (5), 1.419 (5)	1.426 (3), 1.429 (3)
	PhR	1.421 (3), 1.424 (2)	1.403 (6), 1.416 (5)	1.421 (2), 1.423 (2)
C_R-R	PhCN	1.433 (2)	1.440 (5)	1.441 (3)
	PhR	1.434 (2)	1.503 (5)	1.488 (2)
$C\cdots C$‡	$C_H\cdots C_H$	3.189 (2)–3.275 (2)	3.140 (5)–3.304 (5)	3.170 (3)–3.251 (3)
	$C_R\cdots C_R$	3.305 (2)	3.333 (5)	
δ§		0.06	0.06	0.04
α ($C_H-C_R-C_H$)	PhCN	120.3 (2)	120.3 (3)	120.6 (2)
	PhR	120.8 (2)	118.3 (3)	120.6 (2)
d_H(av.)¶	PhCN	0.04	0.04	0.09
	PhR	0.05	0.08	0.10
d_R††	PhCN	*0.039* (C), *0.069* (N)	*0.034* (C), *0.056* (N)	*0.130* (C), *0.224* (N)
	PhR	*0.028* (C), *0.028* (N)	$\underline{0.066\ (C)}$	*0.019* (C)
θ‡‡		2.2	3.9	1.8
φ§§		0.8	0.3	3.5

† C_{ring} is the center of the ring of the arene ligands. ‡ $C\cdots C$ is the distance between C atoms of opposite rings. § δ is the displacement of the Cr atom from the line connecting the centers of the opposite aromatic rings. ¶ d_H(av.) is the average displacement of H atoms from the C_6 ring plane. †† d_R is the displacement of the substituent atoms from the C_6 ring plane; values in *italic* represent the displacement towards the Cr atom; the value which is underlined represents a displacement away from the Cr atom. ‡‡ θ is the dihedral angle between the planes of the two arene ligands. §§ φ is the angle of rotation between C atoms in opposite rings.

substituent nature (see Fig. 4). The non-parallel orientation of the aromatic rings, which is characterized by the dihedral angle θ, is the maximum for (3) with θ = 3.9°. Similar deviations from the parallel arrangement of the planar PAH ligands with θ = 3.5–3.7° are observed for the bis-arene chromium complexes with triphenylene and fluoranthene, which have synperiplanar conformations in the crystal. However, the slope of ligands in non-symmetric complexes of the (PAH)(benzene)Cr type in the case of naphthalene (Kündig *et al.*, 1985) and pyrene (Vasil'kov *et al.*, 2003*a*) is rather small (θ = 0.5–0.9°), which can indicate weak repulsive interactions between the benzene and PAH ligands.

The significant changes in bond lengths and angles for both the mutual arrangement of the ligands relative to each other and parameters of the ligands themselves can be due to non-bonding interactions, caused by both the steric and electronic effects of the substituents in (2)–(4), and repulsive interactions of the non-coordinated parts of the PAH ligands.

The geometry of aromatic molecules is known to be sensitive to the electronic effects of substituents. Based on the crystallographic analysis of monosubstituted arenes, it was concluded (Domenicano *et al.*, 1975, Domenicano & Vaciago, 1979) that the internal angle of the ring at the *ipso*-C atom is > 120° for a σ-electron-withdrawing substituent and < 120° for a σ-electron-donating substituent.

The effects of coordination to a transition metal can be estimated by a comparison of the geometries of free and coordinated arenes.

Internal angles of the ring at the CN- and CF_3-substituted C atoms in (2)–(4) ($C_H-C_R-C_H$, Table 2) are slightly larger than 120° and equal to 120.6 (2)° for $(CF_3C_6H_5)_2Cr$, whereas the angle at the CH_3 substituent is 118.3 (3)°. These data are similar to the respective parameters of free arenes: 121.8 and 120.3° for C_6H_5CN (Fauvet *et al.*, 1978), 121.6° for $C_6H_5CF_3$ (Rahman *et al.*, 2003) and 117.8° for $C_6H_5CH_3$ (Anderson *et al.*, 1977).

The average C—C distance within the aromatic rings is 1.415, 1.406 and 1.417 Å for (2), (3) and (4), respectively. It is somewhat longer than the mean C—C distance of 1.39 Å determined for free C_6H_5CN, $C_6H_5CF_3$ and $C_6H_5CH_3$, but close to 1.415 Å in (1) (Jellinek, 1963). The X-ray diffraction analysis showed that the geometry of the aromatic rings of the ligand of both (1) and (2)–(4) are very similar, regardless of the substituent nature. It is noteworthy that the H atoms of the phenyl rings in (2)–(4) are shifted towards Cr from the arene plane by 0.04–0.10 Å, which has previously been reported for sandwich metal complexes (Rees & Coppens, 1973; Muetterties *et al.*, 1982). The C atom

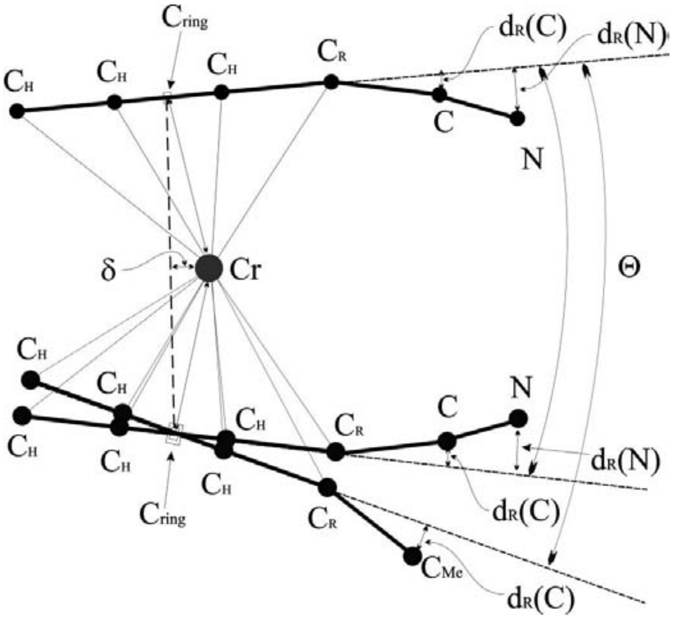

Figure 4
The geometry distortions of (2) and (3) caused by the CN or Me substituents inserted in the benzene rings; the geometric parameters are given in Table 2.

of the CH_3 group in (3) is shifted by 0.066 Å from the C_6-ring plane away from the Cr atom. A similar structural feature was observed for other bis-arene complexes of transition metals containing σ-electron-donating substituents [CH_3 (Braga & Sabatino, 1990; Calderazzo *et al.*, 1992), NMe_2 (Elschenbroich *et al.*, 2003)] in the phenyl rings.

Unexpectedly, unlike the previously studied neutral bis-arene complexes containing σ-electron-withdrawing groups (Cl, COOH, CF_3) in aromatic ligands, in which these substituents are virtually coplanar with the phenyl rings, the CN groups in (2)–(4) are shifted towards Cr from the plane of the rings. The magnitude of this shift, d_R, varies from 0.028–0.130 Å for the C atom to 0.028–0.224 Å for the N atom and is maximized in (4). Such a significant deviation of the CN substituent in (2)–(4) can be caused by the donor–acceptor interaction of the $C_{ipso}-C(N)$ and $C\equiv N$ bonds with orbitals localized on both the Cr atom and the $Cr-C$ bonds. A more detailed study of this effect by the density functional theory (DFT) method will be reported elsewhere.

The shift parameters of the CN group from the plane of the phenyl ring, d_R, for (4) are more than three times those in (2). This can be because of the absence of considerable repulsive interactions between the CN and CF_3 substituents (twisted by 63.5°) in (4). This is indirectly supported by the degree of non-parallelism in the ligands, $\theta = 1.8^\circ$ for (4), which is smaller than that in (2) and (3), which have eclipsed substituents. In (2) the CN substituents are perfectly eclipsed and one can expect significant repulsive interactions between the atoms bearing similar charges, which decreases the d_R parameters for (2).

Two out of three H or F atoms of the methyl or trifluoromethyl group in (3) or (4) are localized between the planes defined by the arene rings. A replacement of the H atoms with a van der Waals radius (WR) of 1.16 Å in the CH_3 group by the F atoms with a WR of 1.40 Å (Bondi, 1964) increases the substituent volume and, most likely, strengthens the repulsive interactions such that the crystallization of (4) with eclipsed CN and CF_3 groups becomes unfavorable.

Compound (3) can be crystallized in the synperiplanar conformation because of a decrease in the volume of the CH_3 substituent and also an increase in the non-parallelism of the phenyl rings to $\theta = 3.9^\circ$, which reduces steric hindrance.

The effect of the non-parallel arrangement of the aromatic rings in $(C_6H_5CH_3)_2Cr(0)$ with $\theta = 3.4^\circ$ was found in the theoretical study of the complex for a conformer with eclipsed CH_3 groups using DFT (Vasil'kov *et al.*, 2003*b*). The calculations showed that the relative energy of this conformer is only 0.4 kJ mol^{-1} higher than that of the conformer with the methyl groups rotated by 180°, which corresponds, according to the DFT calculations, to the global minimum. Such a low energy can be compensated for by crystal packing forces and, therefore, it can be expected that X-ray diffraction analysis of the neutral form of $(C_6H_5CH_3)_2Cr(0)$, which has not been described to-date, will exhibit a synperiplanar conformation as in (3). In the crystals, molecules of (2)–(4) are arranged at the van der Waals distances and have parallel [for (2) and (3)] or orthogonal [for (4)] orientations, which are characteristic of sandwich complexes of transition metals.

4. Conclusion

This paper presents X-ray diffraction data on the neutral di(benzene)chromium derivatives $(C_6H_5CN)Cr(C_6H_5R)$, where R = CN (2), CH_3 (3) and CF_3 (4) for the first time. A comparative analysis of the geometric parameters for substituents of different nature was performed.

It is shown that the $Cr-C_{ipso}$ distances are longer for σ-electron-donating (CH_3) and shorter for σ-electron-withdrawing (CN and CF_3) groups as compared to the $Cr–C_H$ distances, regardless of the type of complex [symmetric (2) or non-symmetric (3) and (4)] and the mutual arrangement of the substituents.

In all compounds, the CN group is shifted towards the Cr atom from the plane of the phenyl ring regardless of the electronic and steric factors of the substituents in the compound. Thus, the geometry of the bis(benzonitrile)chromium is very suitable for the synthesis of polynuclear chelate bridged complexes, which will be prepared and investigated by us in the future.

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References

Anderson, M., Bosio, L., Bruneaux-Poulle, J. & Fourme, R. (1977). *J. Chim. Phys. Phys. Chim. Biol.* **74**, 68–73.

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.

Braga, D., Costa, A. L., Grepioni, F., Scaccianoce, L. & Tagliaini, E. (1997). *Organometallics*, **16**, 2070–2079.

Braga, D., Maini, L., Grepioni, F., Elschenbroich, C., Paganelli, F. & Schiemann, O. (2001). *Organometallics*, **20**, 1875–1881.

Braga, D. & Sabatino, P. (1990). *Acta Cryst.* C**46**, 2308–2312.

Bruker AXS (1998*a*). *SAINTPlus*, Version 6.01. Bruker AXS, Madison, Wisconsin, USA.

Bruker AXS (1998*b*). *SMART*, Version 5.059. Bruker AXS, Madison, Wisconsin, USA.

Bush, B. F., Lynch, V. M. & Lagowski, J. J. (1987). *Organometallics*, **6**, 1267–1275.

Calderazzo, F., Gingl, F., Pampaloni, G., Rocchi, L. & Strahle, J. (1992). *Chem. Ber.* **125**, 1005–1010.

Clark, D. L., Gordon, J. C., McFarian, J. T., Vincent-Hollis, R. L., Watkin, J. G. & Zwick, B. D. (1996). *Inorg. Chim. Acta*, **244**, 269–272.

Domenicano, A. & Vaciago, A. (1979). *Acta Cryst.* B**35**, 1382–1388.

Domenicano, A., Vaciago, A. & Coulson, C. A. (1975). *Acta Cryst.* B**31**, 221–234.

Del Sesto, E., Arif, A. M. & Miller, J. S. (2001). *Chem. Commun.* pp. 2730–2731.

Elschenbroich, Ch., Isenburg, T., Behrendt, A., Frenzen, G. & Harms, K. (1995). *J. Organomet. Chem.* **501**, 129–144.

Elschenbroich, Ch., Möckel, R., Vasil'kov, A., Metz, B. & Harms, K. (1998). *Eur. J. Inorg. Chem.* pp. 1391–1401.

Elschenbroich, Ch., Pietras, M. & Harms, K. (2003). *J. Organomet. Chem.* **684**, 359–367.

Eyring, M. W., Zuerner, E. C. & Radonovich, L. J. (1981). *Inorg. Chem.* **20**, 3405–3410.

Fauvet, G., Massaux, M. & Chevalier, R. (1978). *Acta Cryst.* B**34**, 1376–1378.

Hönnerscheid, A., Dinnebier, R. E. & Jansen. M. (2002). *Acta Cryst.* B**58**, 482–488.

Jellinek, F. (1963). *J. Organomet. Chem.* **1**, 43–50.

Ketkov, S. Yu., Fukin, G. K., Zakharov, L. N., Green, J. C. & Clancy, G. (2002). *J. Organomet. Chem.* **649**, 100–107.

Kündig, E. P. & Pache, S. H. (2003). *Sci. Synth.* **2**, 153–228.

Kündig, E. P., Perret, C., Spichiger, S. & Bernardinelli, G. (1985). *J. Organomet. Chem.* **286**, 183–200.

Larson, S. B., Seymour, C. M. & Lagowsky, J. J. (1987). *Acta Cryst.* C**43**, 1624–1626.

Lynch, V. M., Yoon, M. O., Lagowski, J. J. & Davis, B. E. (1990). *Acta Cryst.* C**46**, 1094–1096.

Miao, F. M. (1982). *Cryst. Struct. Commun.* **11**, 153–156.

Miller, S., O'Hare, D. M., Chakraborty, A. & Epstein, A. J. (1989). *J. Am. Chem. Soc.* **111**, 7853–7856.

Muetterties, E. L., Bleeke, J., Wucherer, E. J. & Albright, T. A. (1982). *Chem. Rev.* **82**, 499–525.

Nesmeyanov, A. N., Sergeev, V. A., Zakurin, N. V., Vasil'kov, A. Yu., Kogan, A. S., Yur'eva, L. P., Zaitseva, N. N. & Uralets, I. A. (1981). *J. Organomet. Chem.* **217**, 195–198.

O'Hare, D., Ward, M. D. & Miller, J. S. (1990). *Chem. Mater.* **2**, 758–763.

Prout, K., Gourdon, A., Couldwell, C., Meunier, B., Miao, F. M. & Woolcock, J. (1982). *Acta Cryst.* B**38**, 456–462.

Rahman, A. N. M. M., Bishop, R., Craig, D. C. & Scudder, M. L. (2003). *Eur. J. Org. Chem.* pp. 72–81.

Rees, B. & Coppens, P. (1973). *Acta Cryst.* B**29**, 2516–2528.

Sergeev, V. A., Kogan, A. S., Uralets, I. A., Vasil'kov, A. Yu., Zakurin, N. V. & Yur'eva, L. P. (1984). *Izv. Akad. Nauk SSSR Ser. Khim.* pp. 420–422.

Sergeev, V. A., Kogan, A. S., Vasil'kov, A. Yu., Uralets, I. A., Zaitseva, N. N., Yur'eva, L. P. & Kravtsov, D. N. (1986). *Izv. Akad. Nauk SSSR Ser. Khim.* pp. 237–239.

Sheldrick, G. M. (1998*a*). *SHELXTL*, Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1998*b*). *SADABS*, Version 2.01. Bruker AXS Inc., Madison, Wisconsin, USA.

Shibaeva, P. R., Atovmyan, L. O. & Rozenberg, L. P. (1969). *Chem. Commun.* pp. 649–650.

Starovskii, O. V. & Struchkov, Yu. T. (1961). *Zh. Strukt. Khim.* **2**, 162–172 (in Russian).

Tairova, G. G., Krasochka, O. N., Ponomarev, V. I., Kvashina, E. F., Shvetsov, Yu. A., Lisetsky, E. M., Kiryukhin, D. P., Atovmyan, L. O. & Borod'ko, Yu. G. (1982). *Trans. Met. Chem.* **7**, 189–190.

Timms, P. L. (1969). *Chem. Commun.* p. 1033.

Vasil'kov, A., Elschenbroich, C. & Harms, K. (2003*a*). Abstr. of the XVth FECHEM Conference on Organometallic Chemistry. PO 274, Zürich, Switzerland.

Vasil'kov, A., Gloriozov, I. & Ustynyuk, Yu. (2003*b*). Abstr. of the Mark Vol'pin Memorial International Symposium. P49, Moscow, Russian Federation.

Vasil'kov, A. Yu., Zakurin, N. V., Uralets, I. A., Zaitseva, N. N., Vasyukova, N. I., Makarovskaya, A. G. & Yur'eva, L. P. (1982). *Izv. Akad. Nauk SSSR Ser. Khim.* pp. 2144–2146.

Yur'eva, L. P., Peregudova, S. M., Kravtsov, D. N., Vasil'kov, A. Yu., Nekrasov, L. N., Asfandiarov, N. L., Timoshenko, M. M. & Chizhov, Yu. V. (1987). *J. Organomet. Chem.* **336**, 371–376.