The synthesis and X-ray study of (η^6-benzamide)- and (η^6-phenylacetamide)tricarbonyl chromium complexes. Structural effects of the substituent

M.M. Kubicki, P. Richard, B. Gautheron and M. Viotte

Université de Bourgogne, Laboratoire de Synthèse et d'Electrosynthèse Organométalliques, associé au CNRS (URA 1685), 6, bd. Gabriel, BP 138, 21004 Dijon Cedex (France)

Š. Toma, M. Hudecek and V. Gajda

Department of Organic Chemistry, Faculty of Science, Comenius University, 842 15 Bratislava (Slovak Republic)

(Received October 14, 1993)

Abstract

(η^6-Benzamide)tricarbonylchromium and tricarbonyl(η^6-phenylacetamide)chromium (1 and 2) have been synthesized from the corresponding amides and chromium hexacarbonyl. Decalin, a mixture of decalin and butyl acetate, and neat butyl acetate have been used as the reaction media. The first system gave best yields. Both amide complexes form adducts with non-complexed molecules of the type $[(CO_3)CrL] \cdot L$ through hydrogen bonds, suggested on the basis of ^{1}H and ^{13}C NMR spectroscopy. Similar associations by hydrogen bonds exist in the solid state structure of 3 and 4. The π-donor-acceptor abilities of the substituents on the rings are discussed on the basis of geometrical parameters and ^{13}C NMR data.

Key words: Chromium; X-ray structure; Amides; Carbonyl; Hydrogen bonding

1. Introduction

In a recent article [1] Hunter *et al.* reported on the structural effects of the substituents in substituted (hexahapto arene)tricarbonylchromium complexes. They found that the distortion of the arene planarity does not depend on the steric bulk of the substituent but is essentially due to electronic effects. They rationalized these effects in terms of the π-donor and/or π-acceptor character of the arene substituents. π-Donor substituents and the *ipso*-carbon atoms to which they are attached are found moved away from the $Cr(CO)_3$ tripod whereas π-acceptor substituents are very close to the arene plane or bent slightly towards the chromium atom. Numerous substituents have been studied but to our knowledge nothing is known of arylamide tricarbonyls in benchrotrene chemistry.

We report here the synthesis and structure of two new complexes (η^6-benzamide)tricarbonyl- and tricarbonyl(η^6-phenylacetamide)-chromium.

2. Results and discussion

We have chosen the two simplest representatives of the aromatic series to assess the scope of the method we described earlier [2]. We have found that the experimental conditions which gave consistently the best results for monocyclic aromatic hydrocarbons, ketones, esters, ethers and amines, failed almost completely in this case. These conditions were decalin solution of a pro-ligand with 4% of butyl acetate under reflux. The low yields (14% for benzamide) are probably due to the formation of unidentified coloured by-products with high R_f values. Neither in neat butyl acetate nor in neat decalin were such materials observed. However, as the reaction time required in the case of butyl

---

Correspondence to: Dr. B. Gautheron or Dr. Š. Toma.

0022-328X/94/$7.00
SSDI 0022-328X(93)24313-T

acetate is considerably longer and the rate of decomposition of the complex is not negligible, the yield obtained is even lower (6%). Neat decalin gave the best, although still not satisfactory, yield, 20% for both benzamide and phenylacetamide complexes.

Attempts to isolate the products met with certain difficulties. The usual workup of the reaction mixture after complexation (chromatography on a silica column with 2-methylpentane/ethyl acetate as eluent, and crystallization from the same mixture) yielded crystalline materials with microanalyses not consistent with that of simple complexes. Repeated chromatography did not change this. The elemental analyses and ^{1}H and ^{13}C NMR spectra suggested a molecular adduct of

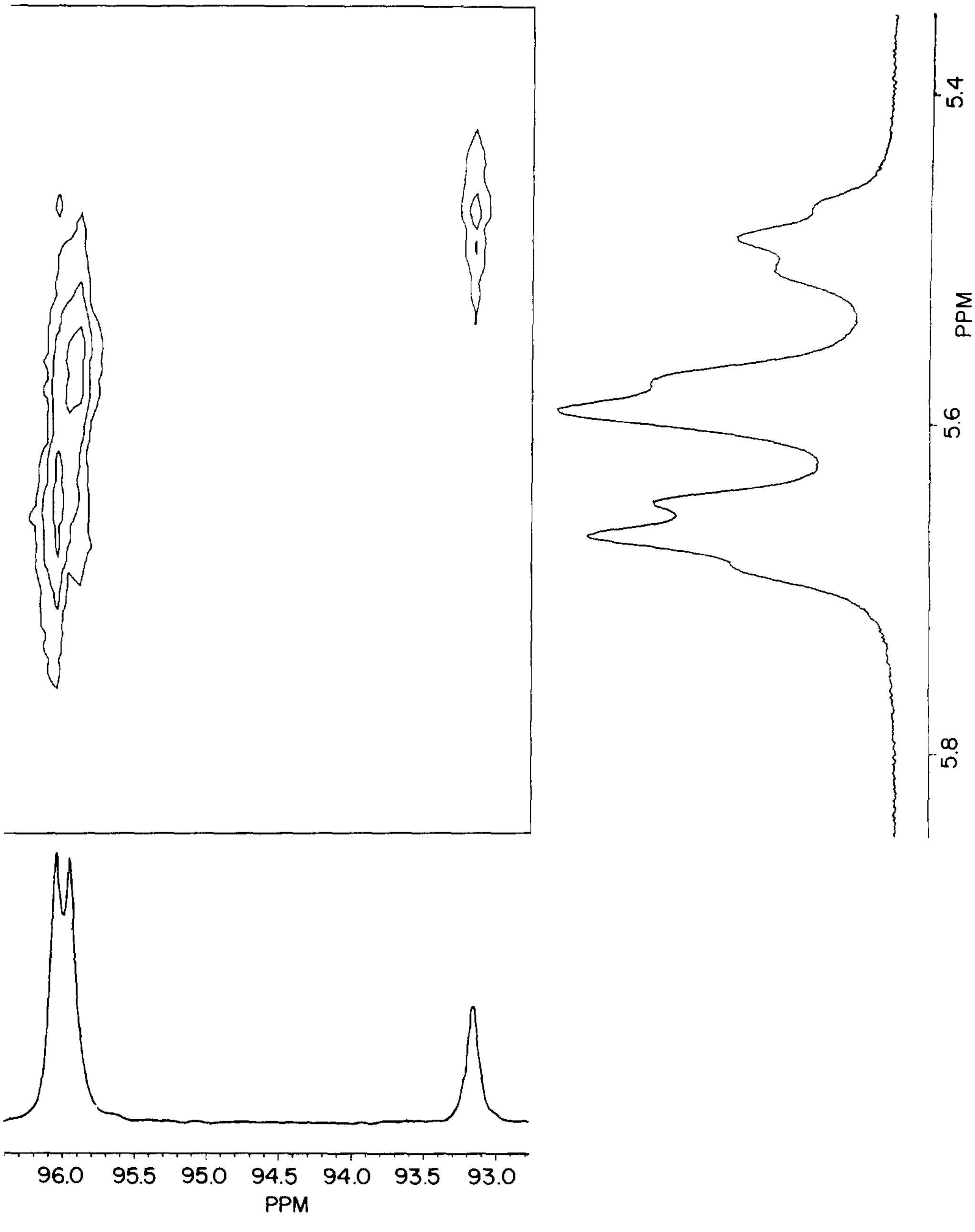
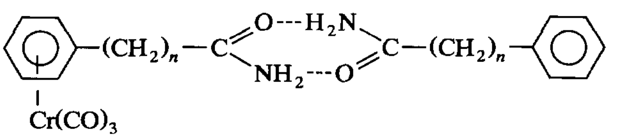


Fig. 1. ^{1}H-^{13}C NMR correlation for **2** (aromatic part).

TABLE 1. Spectroscopic values for adducts 1 and 2 (solvent: acetone-d_6)

	^{1}H (ppm)			^{13}C (ppm)					IR (cm^{-1})	
	CH_2	C_6H_5	NH_2	CH_2	C_6H_5		C=O	C≡O	C=O	C≡O
1 $PhCONH_2$		7.40–7.63m(H^3, H^4, H^5)	6.80br		128.05(C^3C^5)	129.23(C^2, C^6)	169.60		1660	
		7.95–8.01m(H^2, H^3)			132.28(C^4)	135.57(C^1)				
- non-complexed part		7.41–7.53m(H^3, H^4, H^5)	6.80br		128.43	129.18	169.15		1650	
		7.91–7.95m(H^2, H^3)			132.19	135.43				
		5.67pt(H^3, H^5, J(ortho) = 6.10 Hz)	6.90br		92.91(C^3C^5)	94.93(C^2, C^6)	166.55	233.30	1650	1982
- $PhCONH_2Cr(CO)_3$		5.82pt(H^4, J(orhto = 6.10 Hz)			96.52(C^4)	98.13(C^1)				1907
		6.29d(H^2, H^6, J(ortho) = 6.35 Hz)								1879
2 $PhCH_2CONH_2$	3.48s, 2H	7.20–7.34m, 5H	6.88br	43.47	127.35(C^4)	129.19(C^2, C^6)	173.55		1650	
					130.14(C^3C^5)	137.46(C^1)				
- non-complexed part	3.49s, 2H	7.29–7.35m, 5H	7.10br	43.47	127.32	129.20	173.30		1680(br)	
					130.17	137.43				
	3.30s, 2H	5.50pt(H^4, J(ortho) = 6.35 Hz)	7.10br	42.02	93.15(C^4)	95.93(C^2, C^6)	171.61	237.74	1697	1959
- $PhCH_2CONH_2Cr(CO)_3$		5.58d(H^2, H^6, J(ortho) = 5.86 Hz)			96.03(C^3C^5)	109.38(C^1)				1886
		5.69pt(H^2, H^5, J(ortho) = 6.35 Hz)								1863

the type $[(ArX)Cr(CO)_3]ArX$ [X = $C(O)NH_2$ (1); X = $CH_2C(O)NH_2$ (2)].



$n = 0$ (1)
$n = 1$ (2)

The proton chemical shifts (Table 1) of the amide in 1 and 2 are almost unaffected by the association, except that the NH_2 protons are to some degree deshielded by intermolecular electronic interactions. In contrast, strong shielding is observed for the protons of

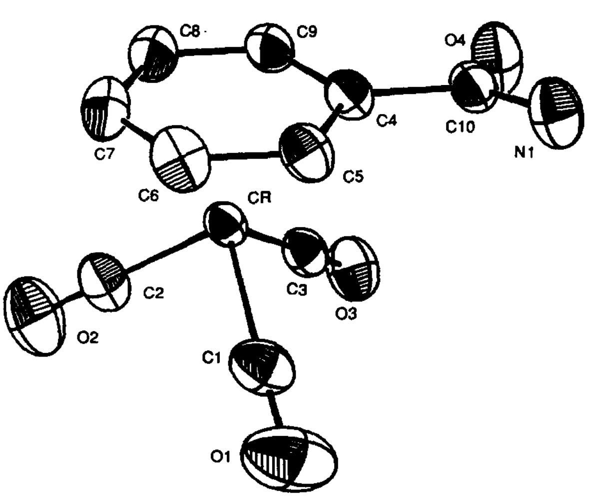


Fig. 2. ORTEP drawing and numbering scheme for $[Cr(CO)_3\{\eta^6\text{-}C_6H_5C(O)NH_2\}]$ (3).

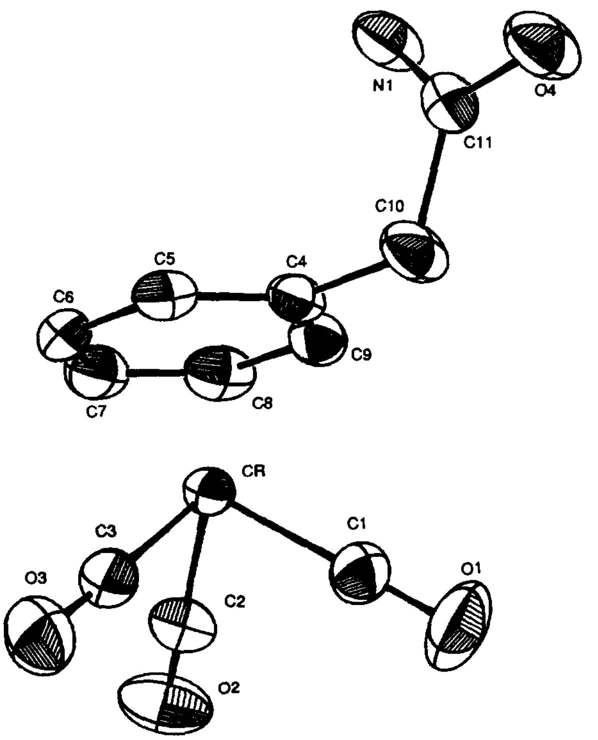


Fig. 3. ORTEP drawing and numbering scheme for $[Cr(CO)_3\{\eta^6\text{-}C_6H_5CH_2C(O)NH_2\}]$ (4).

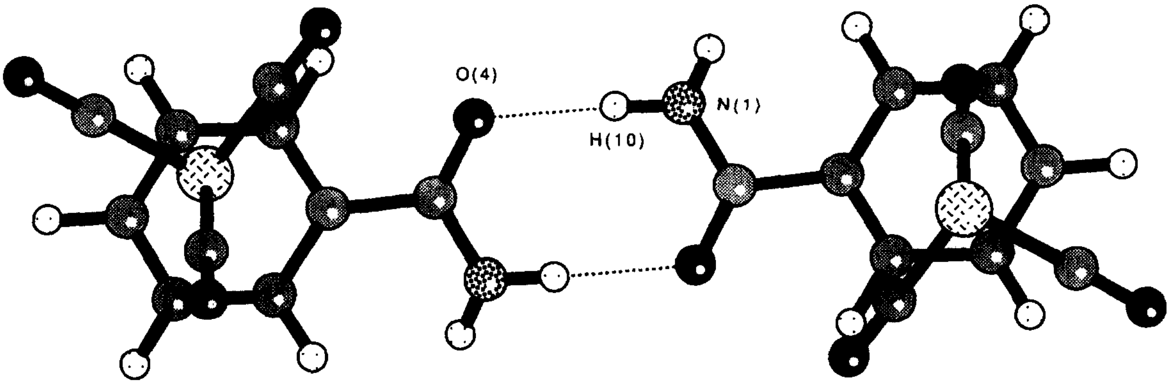


Fig. 4. Hydrogen bonding in [Cr(CO)$_3${η^6-C$_6$H$_5$C(O)NH$_2$}] (3).

the complexed ring. This shift reflects the diamagnetic effect of the Cr(CO)$_3$ group [3]. The methylene proton signals in **2** are easily assigned, as are the aromatic proton signals of H^2 and H^6 (doublet at 5.58 ppm), and of H^4 (pseudotriplet at 5.50 ppm, one proton intensity). Standard *ortho* (6.10 Hz) coupling constants are observed. Related shifts are observed in the ^{13}C resonances for the complexed moiety compared to those of the free amide. The quaternary carbon atom C^1 is the most deshielded and other carbon atom resonances are assigned from the ^{1}H–^{13}C correlation diagram (Fig. 1). The C^4 atom resonance (δ^{13}C = 93.15 ppm) corresponds to the triplet (δ^1H = 5.50 ppm) in the proton spectrum. The resonance of C^2 and C^6 atoms (95.93 ppm) correlates to the doublet H^2, H^6 centred at 5.58 ppm while that of C^3 and C^5 atoms (96.03 ppm) correlates with the pseudo triplet at 5.69 ppm.

The assignments for (benzamide)tricarbonylchromium (**1**) are reported in Table 1. However, the sequences observed for the proton and carbon shifts are different from those for **2**. The H^{2}H^4 protons appear the most deshielded probably due to close proximity of the amide carbonyl group.

Slow crystallization from a diluted dichloromethane solution afforded pure arene complexes (**3**, **4**) free of adduct molecules, and X-ray analysis definitively proved that these complexes are dinuclear. The complexes were also separated from excess of amide by sublimation (see Experimental section).

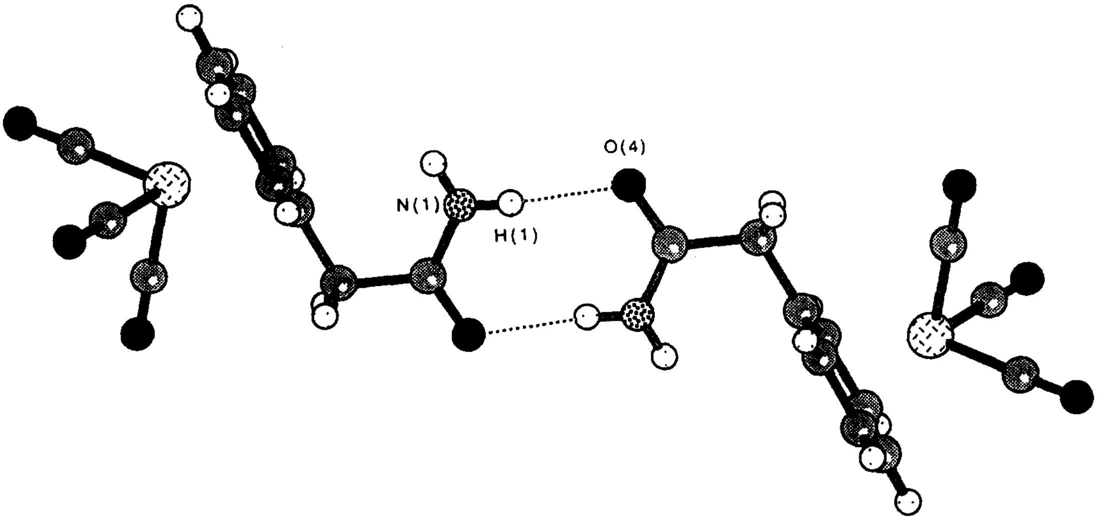


Fig. 5. Hydrogen bonding in [Cr(CO)$_3${η^6-C$_6$H$_5$CH$_2$C(O)NH$_2$}] (4).

TABLE 2. Selected bond lengths and bond angles for $Cr(CO)_3(\eta^6$-$C_6H_5C(O)NH_2)$ (**3**) and $Cr(CO)_3(\eta^6$-$CH_2C(O)NH_2)$ (**4**) with estimated deviations in parentheses [a]

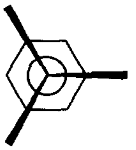
3		4	
bond lengths (Å)			
Cr–ph	1.698	Cr–ph	1.708
Cr–C(1)	1.834(3)	Cr–C(1)	1.839(3)
Cr–C(2)	1.851(2)	Cr–C(2)	1.840(3)
Cr–C(3)	1.833(2)	Cr–C(3)	1.836(3)
Cr–C(4)	2.210(2)	Cr–C(4)	2.219(2)
Cr–C(5)	2.196(2)	Cr–C(5)	2.205(2)
Cr–C(6)	2.220(3)	Cr–C(6)	2.194(3)
Cr–C(7)	2.210(3)	Cr–C(7)	2.209(3)
Cr–C(8)	2.211(3)	Cr–C(8)	2.216(4)
Cr–C(9)	2.202(2)	Cr–C(9)	2.218(3)
C(1)–O(1)	1.156(4)	C(1)–O(1)	1.155(4)
C(2)–O(2)	1.138(4)	C(2)–O(2)	1.143(3)
C(3)–O(3)	1.151(3)	C(3)–O(3)	1.148(4)
hydrogen bonding:			
O(4)···N(1)	2.899(3)	O(4)···N(1)	2.928(3)
O(4)···H(10)	1.95	O(4)···H(1)	2.05
N(1)–H(10)	0.95	N(1)–H(1)	0.88
angles (deg)			
C(1)–Cr–C(2)	89.4(2)	C(1)–Cr–C(2)	88.8(1)
C(1)–Cr–C(3)	88.9(1)	C(1)–Cr–C(3)	89.2(1)
C(2)–Cr–C(3)	88.8(2)	C(2)–Cr–C(3)	88.2(1)
C(1)–Cr–ph	125.2	C(1)–Cr–ph	126.5
C(2)–Cr–ph	125.9	C(2)–Cr–ph	125.9
C(3)–Cr–ph	126.7	C(3)–Cr–ph	126.0
Cr–C(1)–O(1)	178.3(2)	Cr–C(1)–O(1)	179.5(3)
Cr–C(2)–O(2)	178.4(3)	Cr–C(2)–O(2)	177.9(3)
Cr–C(3)–O(3)	178.7(2)	Cr–C(3)–O(3)	179.0(2)

[a] ph is the centre of gravity of the phenyl ring.

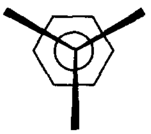
2.1. *Description and discussion of the structures of $(ArX)Cr(CO)_3$; (3, $X = CONH_2$ and $4 = CH_2CONH_2$)*

Complexes **3** and **4** exhibit the expected three-legged piano-stool geometries with η^6-bonded arene rings (Figs. 2 and 3 and Table 2). Hydrogen bonding N–H···O between the amido-groups of two adjacent molecules is observed in both structures (Figs. 4 and 5). The overall solid state structures of **3** and **4** are thus dimers.

The arene-$Cr(CO)_3$ conformations are assessed by the dihedral angles Cr–ph–C(4)/ph–Cr–C–O (ph is the centre of gravity of the C(4)–C(9) carbon atoms of the arene ring). For the *syn*-eclipsed conformation (A) the sum of three dihedral angles should have a value of 120° (the minimum attainable) with the smallest Cr–ph–C(4)/ph–Cr–CO angle equal to 0°, whereas the corresponding values for symmetrical staggered conformation (B) should be 150° (highest attainable) and 30°, respectively. The observed sums and smallest individual values of dihedral angles are 140.2° and 21.8° for **3**, and 143.9° and 26.3° for **4**, respectively, indicating a strong preference for staggered conformation. These values are close to those (139° and 26°) observed in an acetylbenchrotrene complex bearing the moderate π-acceptor substituent C(O)Me [4]. They are clearly far from the values for *syn*-eclipsed conformations found in the presence of strongly π-donating NH_2 (0°) and more weakly π-donating OMe (8.8°) [1].



A



B

To check the effect of the π-type influence of our substituents on the rest of the $[(\eta^6\text{-arene})Cr(CO)_3]$ complex, we considered some structural parameters defined by Hunter *et al.* [1]: the average chromium-carbonyl distance (d_{Cr-CO}), the chromium-arene centroid (ph) distance (D_{cent}), the difference between Cr–C_{ipso} (C(4)) bond length and the average of the other Cr–C(H) bond lengths (δd), the distance of the *ipso*-carbon (C(4)) from the least-squares plane defined by *ortho* (C(5), C(9)) and *meta* (C(6), C(8))-carbon atoms (δp), the distance of the α-substituent atom (C(10)) from this plane (δp_α) together with the corresponding parameter corrected for the C_{ipso}–X (C(4)–C(10)) distance ($\delta p_{\alpha'}$), and the dihedral angle θ between the least-squares planes defined by the *ipso* (C(4)) and *ortho* (C(5), C(9)) carbon atoms and the *ortho* (C(5), C(9)) and *meta* (C(6), C(8)) carbon atoms. The values of these parameters for **3** and **4**, together with those reported for monosubstituted benchrotrenes [1] are given in Table 3.

These data indicate that both the $C(O)NH_2$ (in **3**) and $CH_2C(O)NH_2$ (in **4**) behave as poorer π-donors than NEt_2, NH_2 and OMe, and, with the exception of D_{cent}, they are also poorer π-acceptors than C(O)Me. Two parameters (d_{Cr-CO} and δd) suggest that they are poorer π-acceptors than CO_2Me and poorer π-donors than Me, but the four other parameters (δp, δp_α, $\delta p_{\alpha'}$ and θ) are confusing, showing that Me is for example a better π-acceptor than CO_2Me. Two (δp and θ) indicate $C(O)NH_2$ to be a better π-donor than $CH_2C(O)$-NH_2, but two others (δp_α and $\delta p_{\alpha'}$) suggest the contrary.

However, as already mentioned by Hunter *et al.* [1], any distortion of the arene towards $Cr(CO)_3$ is relatively small with π-acceptor compared to π-donors. Thus, a lack of regular trends for CO_2Me and Me and our $C(O)NH_2$ and $CH_2C(O)NH_2$ substituents is not surprising. Moreover, hydrogen bonding in the structures of **3** and **4** may induce supplementary distortions in the arene rings with greater displacements of C(4) and C(10) (in the positive sense in the Hunter conven-

TABLE 3. Structural and substituent parameters for $[(\eta^6\text{-}C_6H_5X)Cr(CO)_3]$

X	d_{Cr-CO}	D_{cent}	δd	δp	δp_α	$\delta p_{\alpha'}$	Θ	$\Delta\pi$ (complex) ppm	$\Delta\pi$ (free arene) ppm
$C(O)NH_2$ [a]	1.839	1.698	0.002	0.017	0.006	0.005	1.40	3.61	4.23
$CH_2C(O)NH_2$ [a]	1.838	1.708	0.011	−0.002	0.022	0.019	−0.24	−2.88	−2.79
C(O)Me [b]	1.845	1.717	−0.065	−0.038	−0.039	−0.034	−1.04	4.70	4.70
CO_2Me [b]	1.842	1.719	−0.004	0.009	0.015	0.014	0.40	4.99	4.40
Me [b]	1.824	1.725	0.027	−0.012	−0.006	−0.005	−0.15	−2.94	−2.90
OMe [b]	1.827	1.740	0.038	0.021	0.068	0.065	1.90	−10.04	−6.70
NH_2 [b]	1.825	1.724	0.133	0.088	0.212	0.204	5.78	−16.13	−12.00
NEt_2 [b]	1.813	1.728	0.155	0.096	0.215	0.210	5.89	−16.47	−13.60

[a] This work; [b] ref. 1.

tion) than expected solely from electronic reasoning at the molecular level. This may mean that our ligands are better π-acceptors than inferred from structural parameters.

To complete a description of the structures of **3** and **4**, we note that there is a slight twist of the C(10)(O)N plane with respect to that of the arene (C(4)–C(9))—12.8(3)° in **3** and that the dihedral angle C(4) through C(9)/C(10)C(11)(O)N is equal to 84.5 (10)° in **4**. Other structural parameters are normal.

Another approach for estimating the π-donor and π-acceptor properties of aromatic substituents is derived from ^{13}C NMR data. The ^{13}C NMR chemical shifts of the *para*-carbon atom of aromatic rings are sensitive to the total electron density on the molecule [1]. The π-donor and π-acceptor characters in η^6-arene tricarbonyl chromium complexes ($\Delta\pi$) can be defined as proportional to the difference (in ppm) between the chemical shifts of the *para*- and *meta*-carbon atoms in the monosubstituted complexes ($\Delta\pi = \delta para - \delta meta$). From the experimental results, it is clear that strong electron π-releasing substituents have large negative $\Delta\pi$-values, whereas π-accepting substituents have positive $\Delta\pi$-values (Table 3). Our ^{13}C NMR measurements in Tables 1 and 3 clearly indicate that $C(O)NH_2$ behaves as a poorer π-acceptor than C(O)Me or CO_2Me and also that $CH_2C(O)NH_2$ is a poorer π-donor than NH_2 or OMe, roughly comparable to Me.

The two studies reported lead to similar conclusions about the relation between structural distortions in substituted arenechromium tricarbonyl complexes and electronic effects of the substituents. The results are consistent with literature data [1].

3. Experimental section

Chromium hexacarbonyl was sublimed prior to use at 90°C/15 mmHg through a layer of microwave-activated alumina. Decalin was purified by passing it through a layer of microwave-activated silica 40/100 mesh (of about 10% of the volume of the decalin). Chromatography was performed with chromatography grade silica. ^1H and ^{13}C NMR spectra were obtained with Bruker instruments AC 200 (^{13}C resonances were measured at 50.32 MHz and ^1H-^{13}C correlations were carried out using the POWGATE program. Melting points were measured on a Kofler hot-stage apparatus and are uncorrected. Infrared spectra were measured as Nujol films.

3.1. (η^6-Benzamide)tricarbonylchromium (3)

Benzamide (250 mg, 2.06 mmol) and chromium hexacarbonyl (1 g, 4.54 mol) were placed into a 50 ml flask fitted with an anti-sublimation condenser [5]. Decalin (75 ml) was poured into the flask and the mixture was heated under reflux for 45 min. The mixture was then cooled to −18°C and the precipitate was filtered off, affording a colourless filtrate. The unreacted starting material was then sublimed at 0.1 mmHg and 70–80°C during 5 h. Crystallization of the residue from ethyl acetate-hexane afforded 10 mg (19%) of (η^6-benzamide)tricarbonylchromium, m.p. 125–127°C. Analysis: Found: C, 46.94; H, 2.71; N, 5.33. $C_{11}H_9CrNO_4$: Calc. C, 46.71; H, 2.74; N, 5.45%. ^1H-NMR (acetone, ppm): 7.2(br, 2H, $CONH_2$); 6.30(d, H^2, H^6); 5.65(pt, H^3, H^5); 5.80(pt, H^4). IR (Nujol; cm^{-1}) 1982, 1905, 1880–νCO {$Cr(CO)_3$}; 1645–νCO ($CONH_2$).

3.2. Tricarbonyl(η^6-phenylacetamide)chromium (4)

The appropriate reagents in the same molar quantities were treated as above yielding 110 mg (20%) of tricarbonyl(η^6-phenylacetamide)chromium, m.p. 161–163°C. Analysis: Found: C, 48.49; H, 3.26; N, 4.68. $C_{12}H_{11}CrNO_4$: Calc. C, 48.72; H, 3.35; N, 5.17%. ^1H-NMR (acetone, ppm): 3.3(s, 2H, CH_2); 5.45(pt, H^4);

TABLE 4. Crystallographic data for $Cr(CO)_3(\eta^6\text{-}C_6H_5C(O)NH_2)$ (3) and $Cr(CO)_3(\eta^6\text{-}C_6H_5CH_2C(O)NH_2)$ (4)

	3	4
chem formula	$C_{10}CrH_7NO_4$	$C_{11}CrH_9NO_4$
fw	257.16	271.19
colour	orange	yellow
cryst size (mm)	0.45 × 0.25 × 0.2	0.35 × 0.25 × 0.08
cryst system	triclinic	monoclinic
space group	$P1$	$C2/c$
a, Å	6.6418(8)	26.647(3)
b, Å	7.213(1)	6.739(2)
c, Å	11.343(3)	12.494(2)
α, deg	85.72(2)	90.0
β, deg	82.89(2)	95.58(1)
γ, deg	71.70(1)	90.0
V, Å^3	512	2233
Z	2	8
ρcalc, g/cm^3	1.667	1.615
$F(000)$	260	1104
μ(Mo Kα), cm^{-1}	10.54	9.99
radiation	Mo Kα; λ = 0.7107 Å	Mo Kα; λ = 0.7107 Å
scan type	ω-2θ	ω-2θ
scan range, deg in ω	0.8 + 0.34 tan θ	0.8 + 0.34 tan θ
hkl: lower limit	−8, −8, −2	−1, −1, −15
upper limit	8, 8, 14	32, 8, 15
sin(θ max)/λ	0.62	0.62
tot. no of reflcns	2506	2970
no of unique reflcns $I > 3\sigma(I)$	1824	1698
no. variables	145	160
R	0.033	0.032
R_w	0.036	0.043
G.O.F.	1.50	1.54
absorption correction (ψ scan)		
transmission min	91.0171	
max	99.7263	
max Δ/σ (final cycle)	0.03	0.02
resid density, e/Å^3	0.31	0.35

5.56(d, H^2, H^6); 5.69(pt, H^3, H^5). IR (cm^{-1}) 1960, 1885, 1860-νCO {$Cr(CO)_3$}; 1695-νCO ($CONH_2$).

3.3. The complex of (η^6-benzamide)tricarbonylchromium and benzamide (1)

A procedure analogous to that for the preparation of (η^6-benzamide)tricarbonylchromium was used, the product being isolated by chromatography on an SiO_2 column (2-methylpentane-ethylacetate as eluent), yield 0.8 g (23%). NMR and IR in Table 1. Analysis: Found: C, 53.57; H, 3.64; N, 7.02; Calculated for $[(PhCONH_2)Cr(CO)_3]PhCONH_2$: C, 53.97; H, 3.64; N, 7.40%.

3.4. The complex of tricarbonyl(η^6-phenylacetamide)chromium and phenylacetamide (2)

The analogous procedure to that used for **1** gave 0.55 g (37%) of **2**. NMR and IR in Table 1. Analysis: Found: C, 56.68; H, 4.51; N, 6.93; Calculated for $[(PhCH_2CONH_2)Cr(CO)_3]PhCH_2CONH_2$: C, 56.16; H, 4.46; N, 6.89%.

3.5. Crystal structure analyses

Crystals of **3** (orange: 0.45 × 0.25 × 0.2 mm) and **4** (yellow: 0.35 × 0.25 × 0.08 mm) were mounted on an Enraf-Nonius CAD4 diffractometer. The crystal data and data collection parameters are summarized in Table 4. The unit cells were determined and refined from 25 randomly selected reflections obtained by CAD4 automatic routines. Intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction (ψ scan) was made for **3**. The Enraf-Nonius SDP library [6] was used for data reductions of both structures. The solution and refinement of the structure of **4** was performed with the SDP library and the SHELX76 programs [7] were used in the case of **3**. Neutral-atom scattering factors and anomalous dis-

TABLE 5. Positional parameters and B_{eq} [a] values for [Cr(CO)$_3${η^6-$C_6H_5C(O)NH_2$}] (**3**) and [Cr(CO)$_3${η^6-$C_6H_5CH_2C(O)NH_2$}] (**4**)

Atom	x	y	z	B(Å^2)
(a) [Cr(CO)$_3${η^6-$C_6H_5C(O)NH_2$}] (**3**)				
Cr	0.18241(4)	0.13750(4)	0.21451(2)	2.193(9)
O(1)	−0.0304(5)	0.2355(3)	−0.0093(2)	6.85(7)
O(2)	0.4994(4)	−0.2144(3)	0.1033(2)	5.88(6)
O(3)	−0.1004(3)	−0.1072(3)	0.2958(2)	4.17(4)
O(4)	−0.2498(3)	0.2970(3)	0.4863(2)	4.62(5)
N(1)	−0.3396(3)	0.5722(3)	0.3731(2)	3.86(5)
C(1)	0.0548(4)	0.1960(3)	0.0763(2)	3.73(6)
C(2)	0.3806(4)	−0.0789(4)	0.1450(2)	3.63(5)
C(3)	0.0107(3)	−0.0147(3)	0.2646(2)	2.71(4)
C(4)	0.0225(3)	0.3579(3)	0.3490(2)	2.69(4)
C(5)	0.0803(4)	0.4528(3)	0.2429(2)	3.00(5)
C(6)	0.2950(4)	0.3983(4)	0.1905(2)	3.71(6)
C(7)	0.4485(4)	0.2458(4)	0.2429(2)	3.92(6)
C(8)	0.3930(4)	0.1490(4)	0.3484(2)	3.70(5)
C(9)	0.1817(3)	0.2024(4)	0.4012(2)	3.07(5)
C(10)	−0.2011(3)	0.4076(3)	0.4083(2)	2.87(5)
ph [b]	0.2368	0.3010	0.2958	
(b) [Cr(CO)$_3${η^6-$C_6H_5CH_2C(O)NH_2$}] (**4**)				
Cr	0.59996(1)	0.16744(6)	0.04712(3)	2.343(7)
O(1)	0.68947(8)	0.2173(4)	−0.0778(2)	5.85(5)
O(2)	0.5349(1)	0.3307(4)	−0.1401(2)	5.62(6)
O(3)	0.58222(8)	−0.2336(3)	−0.0505(2)	4.41(5)
O(4)	0.77055(6)	0.1707(3)	0.3667(2)	4.10(4)
N(1)	0.69629(8)	0.2921(4)	0.4038(2)	3.67(5)
C(1)	0.6549(1)	0.1988(4)	−0.0298(2)	3.42(6)
C(2)	0.5600(1)	0.2719(5)	−0.0676(2)	3.41(6)
C(3)	0.58931(9)	−0.0788(4)	−0.0136(2)	2.96(5)
C(4)	0.64943(8)	0.1985(4)	0.1997(2)	2.52(5)
C(5)	0.6166(1)	0.0393(4)	0.2090(2)	3.16(5)
C(6)	0.5640(1)	0.0659(5)	0.1880(2)	3.75(6)
C(7)	0.5444(1)	0.2513(6)	0.1593(2)	3.87(6)
C(8)	0.5771(1)	0.4124(5)	0.1502(2)	3.56(6)
C(9)	0.62925(9)	0.3875(4)	0.1697(2)	3.01(5)
C(10)	0.70560(9)	0.1729(5)	0.2231(2)	3.59(6)
C(11)	0.72629(9)	0.2110(4)	0.3384(2)	2.82(5)
ph [b]	0.5968	0.2258	0.1793	

[a] B values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3) [$a^{2*}B(1,1) + b^{2*}B(2,2) + c^{2*}B(3,3) + ab(\cos\gamma)^*B(1,2) + ac(\cos\beta)^*B(1,3) + bc(\cos\alpha)^*B(2,3)$]. [b] ph is the centre of gravity of the phenyl ring.

persion corrections were those given by Cromer and Waber [8]. The structures were solved and refined by conventional three-dimensional Patterson, difference Fourier, and full-matrix least-squares methods. All non-hydrogen atoms in the structures of **3** and **4** were refined with anisotropic temperature factors. The hydrogen atoms of phenyl rings in **3** and **4** were placed in calculated positions riding on the carbon atoms bearing them. Those of the amido groups were located from difference Fourier maps and included in the final calculations with isotropic temperature factors. Final positional parameters of non-hydrogen atoms are given in Table 5.

3.6. Supplementary material available

Tables of general displacement parameters U, full distances and angles, positional parameters of hydrogen atoms and least-squares planes (9 pages) are obtained from the Cambridge Crystallographic Data Centre, and these, together with observed and calculated structure factors for **3** and **4** (18 pages) may be obtained from the authors.

References

1 A.D. Hunter, L. Shilliday, W.S. Furey and M.J. Zaworotko, *Organometallics, 11* (1992) 1550 and references therein.

2 M. Hudecek, M.V. Gajda and S. Toma, *J. Organomet. Chem., 413* (1991) 155.

3 A. Mangini and F. Taddei, *Inorg. Chim. Acta., 2* (1968) 8.

4 Y. Dusausoy, J. Protas, J. Besançon and J. Tirouflet, *C. R. Acad. Sci., Ser. C, 270* (1970) 1792.

5 M. Hudecek and S. Toma, *J. Organomet. Chem., 393* (1990) 115.

6 B.A. Frenz, The Enraf-Nonius CAD4-SDP. A real time for Concurrent X-ray Data Collection and Crystal Structure Determination in Computing in Crystallography, M. Schemk, R. Olthof-Hazekamp, M. Van Koningsveld and G.C. Bassi (eds.), Delft University, Holland, 1978.

7 G.M. Sheldrick, SHELX76, University of Cambridge, UK, 1976.

8 D.T. Cromer and J.T. Waber, *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, UK, 1975, Vol. IV.