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Systematic X-ray Crystallographic Study of the Structural Manifestations of π-Donor and π-Acceptor Substituent Effects in Substituted (η^6-Arene)Cr(CO)$_3$ Complexes[1,2]

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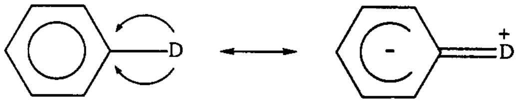
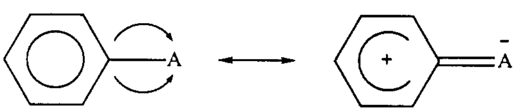
The new X-ray crystal structures of five (η^6-arene)Cr(CO)$_3$ complexes having one or two π-donor or π-acceptor substituents on their benzene rings are reported and are compared with the structures of the related (η^6-arene)Cr(CO)$_3$ complexes reported in the literature. It is found that the π-donor substituents and the ipso-carbon atoms to which they are attached are bent away from the Cr(CO)$_3$ fragments while the π-acceptor substituents and the ipso-carbon atoms to which they are attached are approximately in the arene plane or are bent slightly toward the Cr(CO)$_3$ fragments. The magnitudes and directions of these distortions of the arene planarity are found *not* to be dependent on the steric bulk of the substituent for any but the most bulky substituents. Rather, these distortions appear to be due primarily to electronic effects and a model is proposed to explain these distortions in terms of the π-donor and/or π-acceptor character of the arene substituents. The new X-ray structures reported are those of (η^6-C$_6$H$_5$(NH$_2$))Cr(CO)$_3$ (C$_9$H$_7$CrNO$_3$: a = 7.0425 (12) Å, b = 9.572 (4) Å, c = 7.4694 (11) Å, β = 110.798 (12)°, V = 470.7 (2) Å^3; monoclinic; $P2_1/m$; Z = 2), (η^6-C$_6$H$_5$(OMe))Cr(CO)$_3$ (C$_{10}$H$_8$CrO$_4$: a = 7.2485 (6) Å, b = 11.6331 (12) Å, c = 12.0276 (10) Å, V = 1014.20 (14) Å^3; orthorhombic; $P2_12_12_1$; Z = 4), (η^6-1,4-C$_6$H$_4$(NMe$_2$)$_2$)Cr(CO)$_3$ (C$_{13}$H$_{16}$CrN$_2$O$_3$: a = 8.2210 (16) Å, b = 16.7202 (13) Å, c = 9.1900 (19) Å, β = 90.879 (10)°, V = 1263.1 (4) Å^3; monoclinic; $P2_1/n$; Z = 4), (η^6-1,4-C$_6$H$_4$(OMe)$_2$)Cr(CO)$_3$ (C$_{11}$H$_{10}$CrO$_5$: a = 7.859 (3) Å, b = 8.140 (9) Å, c = 19.014 (7) Å, β = 98.930 (20)°, V = 1216.5 (7) Å^3; monoclinic; $P2_1/c$; Z = 4), and (η^6-1,4-C$_6$H$_4$(CO$_2$Me)$_2$)Cr(CO)$_3$ (C$_{13}$H$_{10}$CrO$_7$: a = 8.8537 (14) Å, b = 20.2488 (11) Å, c = 7.5823 (12) Å, β = 92.724 (8)°, V = 1357.8 (3) Å^3; monoclinic; $P2_1/c$; Z = 4).

Introduction

The study of the interactions between substituents and arenes has been a central theme in physical organic chemistry.[3] Thus, the importance of π-symmetry interactions, e.g.



1a 1b



2a 2b

(where D = a π-donor substituent such as NMe$_2$ and A = a π-acceptor substituent such as NO$_2$) is well recognized and they are known to give rise to a variety of changes in the reactivity,[4] spectroscopic properties,[5] bonding,[6] and structures[7] of these species which can be used to detect and quantify these interactions. However, for arenes bonded in an η^6-fashion to transition-metal centers in complexes such as (η^6-arene)Cr(CO)$_3$,[8] the spectroscopic,[9,10]

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(1) (a) Substituent Interactions in η^6-Arene Complexes. 1. (b) For part 2, see: Hunter, A. D.; Mozol, V.; Cai, S. D. *Organometallics*, submitted for publication.

(2) Parts of this work have been presented orally: (a) Hunter, A. D.; Mozol, V.; Santarsiero, B. D. 73rd Canadian Chemical Conference, Halifax, Nova Scotia, July 1990; Abstract 614 IN-F14. (b) Hunter, A. D.; Chukwu, R.; Mozol, V.; Ristic-Petrovic, D. 200th National Meeting of the American Chemical Society, Washington, DC Aug 1990; Abstract INOR 121.

(3) (a) Maskill, H. *The Physical Basis of Organic Chemistry*; Oxford University Press: New York, 1985; pp 202–215, 442–473. (b) Exner, O. In *Advances in Linear Free Energy Relationships*; Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1972; pp 1–69. (c) Hind, J. *Physical Organic Chemistry*; McGraw-Hill: New York, 1962; pp 81–103.

(4) See, for example: (a) March, J. *Advanced Organic Chemistry, Reactions, Mechanisms, and Structure*, 3rd ed.; John Wiley and Sons: New York, 1985; pp 453–462. (b) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry, Part A: Structure and Mechanisms*, 3rd ed.; Plenum: New York, 1990; pp 196–209.

(5) See, for example: (a) Levy, G. C.; Lichter, R. L.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*; John Wiley and Sons: New York, 1980. (b) Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic: New York, 1972. (c) Memory, J. D.; Wilson, N. K. *NMR of Aromatic Compounds*; John Wiley and Sons: New York, 1982. (d) Nelson, G. L.; Levy, G. C.; Cargioli, J. D. *J. Am. Chem. Soc.* **1972**, *94*, 3089–3094. (e) Ewing, D. F. *Org. Magn. Reson.* **1979**, *12*, 499–524. (f) Katritzky, A. R.; Topsom, R. D. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 87–100. (g) Nelson, G. L.; Williams, E. A. *Prog. Phys. Org. Chem.* **1976**, *12*, 229–342. (h) Bromilow, J.; Brownlee, R. T. C.; Craik, D. J.; Sadek, M.; Taft, R. W. *J. Org. Chem.* **1980**, *45*, 2429–2440. (i) Hugel, H. M.; Kelly, D. P.; Spear, R. J.; Bromilow, J.; Brownlee, R. T. C.; Craik, D. J. *Aust. J. Chem.* **1979**, *32*, 1511–1519. (j) Brownlee, R. T. C.; Sadek, M. *Aust. J. Chem.* **1981**, *34*, 1593–1602. (k) Bromilow, J.; Brownlee, R. T. C.; Topsom, R. D.; Taft, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 2020–2022. (l) Maciel, G. E.; Natterstad, J. J. *J. Chem. Phys.* **1965**, *42*, 2427–2435.

(6) (a) Dillow, G. W.; Kebarle, P. *J. Am. Chem. Soc.* **1989**, *111*, 5592–5596. (b) Chowdhury, S.; Kishi, H.; Dillow, G. W.; Kebarle, P. *Can. J. Chem.* **1989**, *67*, 603–610. (c) Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290–4301. (d) Ferguson, G.; Robertson, J. M. *Adv. Phys. Org. Chem.* **1963**, *1*, 203–281. (e) Hehre, W. J.; Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* **1976**, *12*, 159–187. (f) Turner, D. W. *Adv. Phys. Org. Chem.* **1966**, *4*, 31–71. (g) Jug, K.; Koster, A. M. *J. Am. Chem. Soc.* **1990**, *112*, 6772–6777 and references cited therein.

(7) See, for example: (a) Allen, F. H.; Kennard, O.; Taylor, R. *Acc. Chem. Res.* **1983**, *16*, 146–153. (b) Domenicano, A.; Vaciago, A.; Coulson, C. A. *Acta Crystallogr., Sect. B* **1975**, *31*, 221–234. (c) Skancke, A. In *Fluorine-Containing Molecules*; Liebman, J. F., Greenberg, A., Dolbier, W. R., Jr., Eds.; VCH Publishers: New York, 1988; pp 43–64.

(8) For general reviews on (η^6-arene)Cr(CO) chemistry see, for example: (a) Solladié-Cavallo, A. *Polyhedron* **1985**, *4*, 901–927. (b) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499–525. (c) Silverthorn, W. E. *Adv. Organomet. Chem.* **1975**, *13*, 47–137. (d) Senoff, C. V. *Coord. Chem. Rev.* **1980**, *32*, 111–191.

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Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

compd	$(C_6H_5NH_2)Cr(CO)_3$	$(C_6H_5OMe)Cr(CO)_3$	$[1,4\text{-}C_6H_4(NMe_2)_2]Cr(CO)_3$	$[1,4\text{-}C_6H_4(OMe)_2]Cr(CO)_3$	$[1,4\text{-}C_6H_4(CO_2Me)_2]Cr(CO)_3$
color	yellow	yellow	yellow	yellow	orange
fw	229.2	244.2	300.3	274.2	330.2
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P2_1/m$	$P2_12_12_1$	$P2_1/n$	$P2_1/c$	$P2_1/c$
temp, °C	17	17	17	17	17
cell constants[a]					
a, Å	7.0425 (12)	7.2485 (6)	8.2210 (16)	7.859 (3)	8.8537 (14)
b, Å	9.572 (4)	11.6331 (12)	16.7202 (13)	8.2410 (9)	20.2488 (11)
c, Å	7.4694 (11)	12.0276 (10)	9.1900 (19)	19.014 (7)	7.5823 (12)
β, deg	110.798 (12)		90.879 (10)	98.930 (20)	92.724 (8)
cell vol, Å^3	470.7 (2)	1014.20 (16)	1263.1 (4)	1216.5 (7)	1357.8 (3)
F(000)	232	496	624	560	672
Z	2	4	4	4	4
D_{calc}, g cm^{-3}	1.62	1.60	1.58	1.50	1.62
μ_{calc}, cm^{-1}	11.6	10.9	8.9	9.2	8.5
scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
radiation	Mo K_α	Mo K_α	Mo K_α	Mo K_α	Mo K_α
max cryst dimens, mm	0.15 × 0.25 × 0.60	0.40 × 0.85 × 1.00	0.30 × 0.40 × 0.70	0.20 × 0.30 × 0.80	0.45 × 0.50 × 1.00
scan width	0.80 + 0.35 tan θ	0.80 + 0.35 tan θ	0.80 + 0.35 tan θ	0.80 + 0.35 tan θ	0.80 + 0.35 tan θ
transm range	0.921, 0.999	0.790, 0.999	0.907, 0.998	0.790, 0.997	0.979, 0.998
decay of stds	±1%	±1%	±1%	±1%	±1%
reflns measd	953	1057	2373	2207	2564
2θ range, deg	2–50	2–50	2–50	2–50	2–50
no. of unique reflns	879	1057	2236	2145	2382
no. of reflns obsd[b]	819	935	1609	1172	2019
computer programs[c]	NRCVAX[d]	NRCVAX[d]	NRCVAX[d]	NRCVAX[d]	NRCVAX[d]
structure soln	direct	direct	direct	direct	direct
no. of params	88	137	172	154	190
weight modifier, *k*	0.000 02	0.000 025	0.000 02	0.000 03	0.000 015
GOF	4.07	2.59	3.21	2.00	3.69
R	0.029	0.031	0.042	0.049	0.031
R_w	0.037	0.033	0.049	0.043	0.038
final diff map, e/Å^3	0.17	0.34	0.26	0.30	0.21

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ for 24 reflections $\theta > 15°$. [b] $I > 3\sigma(I)$. Corrections: Lorentz–polarization and absorption (empirical ψ scan). [c] Neutral scattering factors and anomalous dispersion corrections from: *Internal Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. 4. [d] An Interactive Program System for Structure Analysis: Gabe, E. J.; Le Page, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

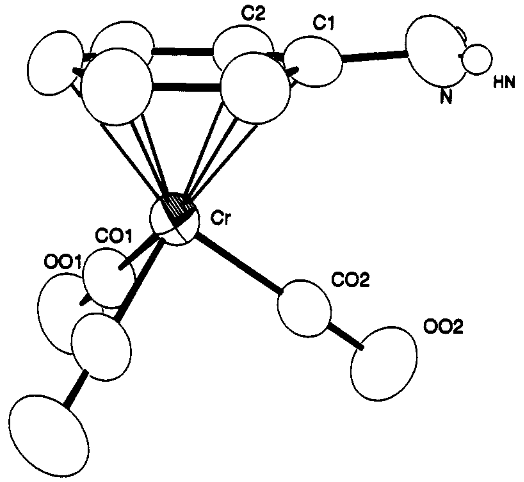

Figure 1. ORTEP plot for the complex (η^6-$C_6H_5(NH_2)$)$Cr(CO)_3$.

electrochemical,[11] electronic,[12] and especially structural[13] consequences of the analogous π-symmetry interactions are more poorly understood. Therefore, when we observed that the arene rings in (η^6-arene)$Cr(CO)_3$ complexes having

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(9) For infrared spectroscopic studies on (η^6-arene)$Cr(CO)_3$ complexes see ref 1b and, for example: Neuse, E. W. *J. Organomet. Chem.* **1975**, *99*, 287–295 and work cited therein.

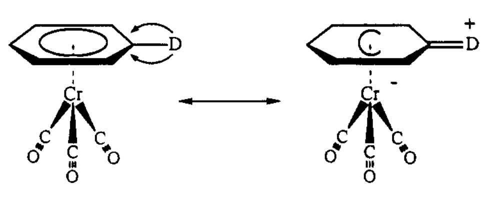
(10) For ^{13}C NMR studies on (η^6-arene)$Cr(CO)_3$ complexes, see ref 1b and, for example: (a) Bodner, G. M.; Todd, L. J. *Inorg. Chem.* **1974**, *13*, 360–363. (b) Roques, B. P. *J. Organomet. Chem.* **1977**, *136*, 33–37 and work cited therein.

(11) For electrochemical studies of (η^6-arene)$Cr(CO)_3$ complexes see, ref 1b and: Connelly, N. G.; Geiger, W. E. *Adv. Organomet. Chem.* **1984**, *23*, 1–93 and references cited therein.

(12) For molecular orbital studies on (η^6-arene)$Cr(CO)_3$ complexes see, refs 8b, 12f, and: (a) Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546–7557. (b) Ono, I.; Mita, S.; Kondo, S.; Mori, N. *J. Organomet. Chem.* **1989**, *367*, 81–84. (c) Allen, G. C.; Butler, I. S.; Kirby, C. *Inorg. Chim. Acta* **1987**, *134*, 289–292. (d) Modelli, A.; Distefano, G.; Guerra, M.; Jones, D. *J. Am. Chem. Soc.* **1987**, *109*, 4440–4443. (e) Byers, B. P.; Hall, M. B. *Organometallics* **1987**, *6*, 2319–2325. (f) Rogers, R. D.; Atwood, J. L.; Albright, T. A.; Lee, W. A.; Rausch, M. D. *Organometallics* **1984**, *3*, 263–270. (g) Chinn, J. W.; Hall, M. B. *J. Am. Chem. Soc.* **1983**, *105*, 4930–4941. (h) Albright, T. A.; Hofmann, P.; Hoffmann, R.; Lillya, C. P.; Dobosh, P. A. *J. Am. Chem. Soc.* **1983**, *105*, 3396–3341. (i) Semmelhack, M. F.; Garcia, J. L.; Cortes, D.; Farina, R.; Hong, R.; Carpenter, B. K. *Organometallics* **1983**, *2*, 467–469. (j) Albright, T. A. *Acc. Chem. Res.* **1982**, *15*, 149–155. (k) Aroney, M. J.; Copper, M. K.; Englert, P. A.; Pierens, R. K. *J. Mol. Struct.* **1981**, *77*, 99–108. (l) Albright, T. A.; Carpenter, B. K. *Inorg. Chem.* **1980**, *19*, 3092–3087. (m) Albright, T. A.; Hoffmann, R. *Chem. Ber.* **1978**, *111*, 1578–1590. (n) Hoffmann, R.; Albright, T. A.; Thorn, P. L. *Pure Appl. Chem.* **1978**, *50*, 1–9. (o) Ceccon, A.; Gentiloni, M.; Romanin, A.; Venzo, A. *J. Organomet. Chem.* **1977**, *127*, 315–324. (p) Elian, M.; Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Inorg. Chem.* **1976**, *15*, 1148–1155. (q) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058–1076. (r) Khandkarova, V. S.; Gubin, S. P.; Kvasov, B. A. *J. Organomet. Chem.* **1970**, *23*, 509–515. (s) Müller, J. *J. Organomet. Chem.* **1969**, *18*, 321–325. (t) Brown, D. A.; Rawlinson, R. M. *J. Chem. Soc. A* **1969**, 1534–1537. (u) Carroll, D. G.; McGlynn, S. P. *Inorg. Chem.* **1968**, *7*, 1285–1290. (v) Rooney, D.; Chaiken, J.; Driscoll, D. *Inorg. Chem.* **1987**, *26*, 3939–3945. (w) Solladie-Cavallo, A.; Wipff, G. *Tetrahedron Lett.* **1980**, 3047–3050.

organometallic substituents (e.g. (η^6-1,3,5-$C_6H_3Fp_3$)$Cr(CO)_3$ where Fp = (η^5-C_5H_5)$Fe(CO)_2$)[14] were very nonplanar,[15] we were not initially sure if this was due to some unique aspect of the Fe–Cr interaction[14a] or whether it was simply a manifestation of the π-donor character of the Fe–aryl bond.[14b–d,17] The nature of various anomalies in the spectroscopic and electrochemical data for these complexes[14b–d] along with the close relationship between the effects of NO_2 and $Cr(CO)_3$ groups on the chemistry of arenes[8b] suggested to us that the latter explanation was the correct one.[18] To confirm this hypothesis, we decided to carry out a systematic investigation to quantify the effects of main-group π-donor and π-acceptor substituents[19] on the planarity of the arene rings in (η^6-arene)-$Cr(CO)_3$ complexes. The results from such a study were also expected to add an additional novel measure of the magnitudes of these π-symmetry interactions to the physical organic repertoire.

The molecular orbital calculations which have been reported for (η^6-arene)$Cr(CO)_3$ complexes have not generally addressed the consequences of arene nonplanarity or its relationship to substituent π-donor and π-acceptor interactions.[12,20] Fortunately, the qualitative effects of any significant degree of π-donation or π-acceptance in these complexes are readily predictable in elementary valence bond terms, as they are for the uncomplexed arenes. Thus, π-donation from a substituent, D, would be expected to result in the contribution of a second resonance form (i.e. **3b**) to the electronic structures of these complexes, i.e.



3a **3 b**

having an exocyclic double bond, a positive charge localized on D, and a negative charge localized on the $Cr(CO)_3$ fragment.[21] The anionic $Cr(CO)_3$ center in the charge-separated zwitterionic (cyclohexadienyl)$Cr(CO)_3$ resonance form would have an 18-electron configuration and would therefore be expected to repel the electron density of the exocyclic double bond. Hence, the π-donor substituent and its ipso-carbon atom would be expected to bend away from the $Cr(CO)_3$ center. This would result in the loss of arene planarity as the contribution from resonance form **3b** to

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(13) For the crystallographic studies of the noncyclic (η^6-arene)$Cr(CO)_3$ complexes used in this work, see: (a) Bailey, M. Y.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 1314–1319. (b) Rees, B.; Coppers, P. *Acta Crystallogr., Sect. B* **1973**, *29*, 2516–2528. (c) Bailey, M. F.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 1314–1319. (d) Rees, B.; Coppens, P. *J. Organomet. Chem.* **1972**, *42*, C102–C104. (e) Le Maux, P.; Saillard, J. Y.; Grandjean, D.; Jaouen, G. *J. Org. Chem.* **1980**, *45*, 4526–4528. (f) Saillard, J. Y.; Grandjean, D.; Le Maux, P.; Jaouen, G. *Nouv. J. Chim.* **1981**, *5*, 153–160. (g) Dusausoy, Y.; Protas, J.; Besancon, J.; Tirouflet, J. *C. R. Acad. Sci., Ser. C* **1970**, *270*, 1792–1794. (h) Wasserman, H. J.; Wovkulich, M. J.; Atwood, J. D.; Churchill, M. R. *Inorg. Chem.* **1980**, *19*, 2831–2834. (i) Van Meurs, F.; Van Koningsveld, H. *J. Organomet. Chem.* **1976**, *118*, 295–303. (j) Fukui, M.; Ikeda, T.; Oishi, T. *Chem. Pharm. Bull.* **1983**, *31*, 466. (k) Van Meurs, F.; Van Koningsveld, H. *J. Organomet. Chem.* **1977**, *131*, 423–428. (l) Abraham, F.; Nowogrocki, G.; Brocard, J.; Lebibi, J.; Bremard, C. *Acta Crystallogr., Sect. C* **1984**, *40*, 1181–1183. (m) Van Der Helm, D.; Loghry, R. A.; Hanlon, D. J.; Hagen, A. P. *Cryst. Struct. Commun.* **1979**, *8*, 899–903. (n) Halet, J. F.; Saillard, J. Y.; Caro, B.; Le Bihan, J. Y.; Top, S.; Jaouen, G. *J. Organomet. Chem.* **1984**, *267*, C37–C40. (o) Le Bihan, J. Y.; Senechal-Tocquer, M. C.; Senechal, D.; Gentric, D.; Caro, B.; Halet, J. F.; Saillard, J. Y.; Jaouen, G.; Top, S. *Tetrahedron* **1988**, *44*, 3565–3574. (p) Schubert, U.; Hornig, H. *J. Organomet. Chem.* **1984**, *273*, C11–C16. (q) Carter, O. L.; McPhail, A. T.; Sim, G. A. *J. Chem. Soc. A* **1967**, 1619–1626. (r) Saillard, J. Y.; Grandjean, D. *Acta Crystallogr., Sect. B* **1976**, *32*, 2285–2289. (s) Ceccon, A.; Giacometti, G.; Venzo, A.; Ganis, P.; Zanotti, G. *J. Organomet. Chem.* **1981**, *205*, 61–69. (t) Schöllkopf, K.; Stezowski, J. J.; Effenberger, F. *Organometallics* **1985**, *4*, 922–929. (u) Xiaoguang, Y.; Jinshun, H.; Jinling, H. *J. Struct. Chem.* **1985**, *4*, 52. (v) Schubert, U.; Dötz, K. H. *Cryst. Struct. Commun.* **1979**, *8*, 989–994. (w) Denise, B.; Goumont, R.; Parlier, A.; Rudler, H.; *J. Organomet. Chem.* **1989**, *337*, 89–104. (x) Chung, T. M.; Lee, Y. A.; Chung, Y. K.; Jung, I. N. *Organometallics* **1990**, *9*, 1976–1979. (y) Dusausoy, Y.; Protas, J. *J. Organomet. Chem.* **1975**, *94*, 47–53. (z) Boutonnet, J. C.; Levisalles, J.; Rose-Munch, F.; Rose, E.; Precigoux, G.; Leroy, F. *J. Organomet. Chem.* **1985**, *290*, 153–164. (aa) Blagg, J.; Davies, S. G.; Goodfellow, C. L.; Sutton, K. H. *J. Chem. Soc., Perkin Trans. I* **1987**, 1805–1811. (bb) Dusausoy, Y.; Protas, J.; Besancon, J.; Tirouflet, J. *Acta Crystallogr., Sect. B* **1973**, *29*, 469–4476. (cc) Dusausoy, Y.; Protas, J.; Besancon, J.; Tirouflet, J. *Acta Crystallogr., Sect. B* **1972**, *28*, 3183–3188. (dd) Dusausoy, Y.; Protas, J.; Besancon, J. *J. Organomet. Chem.* **1973**, *59*, 281–292. (ee) Bush, M. A.; Dullforce, T. A.; Sim, G. A. *J. Chem. Soc. D* **1969**, 1491–1493. (ff) Dusausoy, Y.; Lecomte, C.; Protas, J.; Besancon, J. *J. Organomet. Chem.* **1973**, *63*, 321–327. (gg) Carter, O. L.; McPhail, A. T.; Sim, G. A. *J. Chem. Soc. A* **1967**, 228–236. (hh) Dötz, K. H.; Tiriliomis, A.; Harms, K. *J. Chem. Soc., Chem. Commun.* **1989**, 788–790. (ii) Van Meurs, F.; Van Koningsveld, H. *J. Organomet. Chem.* **1974**, *78*, 229–235. (jj) Gilday, J. P.; Widdowson, D. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1235–1237. (kk) Rose-Munch, F.; Rose, E.; Semra, A. *J. Organomet. Chem.* **1989**, *363*, 103–121. (ll) Wright, M. E. *J. Organomet. Chem.* **1989**, *376*, 353–358. (mm) Boutonnet, J. C.; Rose-Munch, F.; Rose, F.; Jeannin, Y.; Robert, F. *J. Organomet. Chem.* **1985**, *297*, 185–190. (nn) Levisalles, J.; Rose-Munch, F.; Rose, E.; Semra, A.; Oricain, J. G.; Jeannin, Y.; Robert, F. *J. Organomet. Chem.* **1983**, *328*, 109–122. (oo) Rose-Munch, F.; Rose, E.; Semra, A. *J. Organomet. Chem.* **1989**, *363*, 123–130. (pp) Rose-Munch, F.; Rose, E.; Semra, A.; Mignon, L.; Garcia-Oricain, J. *J. Organomet. Chem.* **1989**, *363*, 297–309. (qq) Yoshifuji, M.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Chem. Commun.* **1985**, 1109–1111. (rr) Bailey, M. F.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 1298–1306. (ss) Byers, B. P.; Hall, M. B. *Inorg. Chem.* **1987**, *26*, 2186–2188. (tt) Hunter, G.; Iverson, D. J.; Mislow, K.; Blount, J. F. *J. Am. Chem. Soc.* **1980**, *102*, 5942–5943. (uu) Iverson, D. J.; Hunter, G.; Blunt, J. F.; Damewood, J. R., Jr.; Mislow, K. *J. Am. chem. Soc.* **1981**, *103*, 6073–6083. (vv) Downton, P. A.; Mailvaganam, B.; Frampton, C. S.; Sayer, B. G.; McGlinchey, M. J. *J. Am. Chem. Soc.* **1990**, *112*, 27–32.

(14) (a) Hunter, A. D. *Organometallics* **1989**, *8*, 1118–1120. (b) Hunter, A. D.; McLernon, J. L. *Organometallics* **1989**, *8*, 2679–2688. (c) Richter-Addo, G. B.; Hunter, A. D. *Inorg. Chem.* **1989**, *28*, 4063–4065. (d) Richter-Addo, G. B.; Hunter, A. D.; Wichrowska, N. *Can. J. Chem.* **1989**, *68*, 41–48.

(15) In the X-ray crystal structures of the complexes (η^6-1,3,5-$C_6H_3Fp_3$)$Cr(CO)_3$,[14a,b] (η^6-1,4-C_6H_4MeFp)$Cr(CO)_3$,[16] (η^6-C_6H_5((η^5-C_5H_4Me)$Fe(CO)_2$))$Cr(CO)_3$,[16] and (η^6-C_6H_5((η^5-indenyl)$Fe(CO)_2$))Cr-$(CO)_3$[16] it can be seen that all of the Fp substituents (where Fp = (η^5-C_5H_5)$Fe(CO)_2$) and the ipso-carbon atoms to which they are attached are bent substantially away from the $Cr(CO)_3$ centers.

(16) Li, J.; Hunter, A. D.; Santarsiero, B. D.; Bott, S. G.; Atwood, J. L. Unpublished observations.

(17) Organometallic fragments such as Fp are reasonably good π-donors,[14b,d] see: (a) Hunter, A. D.; Szigety, A. B. *Organometallics* **1989**, *8*, 2670–2679. (b) Chukwu, R.; Hunter, A. D.; Santarsiero, B. D. *Organometallics* **1991**, *10*, 2141–2152. (c) Chukwu, R.; Hunter, A. D.; Santarsiero, B. D.; Bott, S. G.; Atwood, J. L.; Chassaignac, J. *Organometallics*, in press. (d) Stewart, R. P.; Treichel, P. M. *J. Am. Chem. Soc.* **1970**, *92*, 2710–2718. (e) Bolton, E. S.; Knox, G. R.; Robertson, C. G. *J. Chem. Soc., Chem. Commun.* **1969**, 664. (f) Nesmeyanov, A. N.; Leshcheva, I. F.; Polovyanyuk, I. V.; Ustynyuk, Y. A. *J. Organomet. Chem.* **1972**, *37*, 159–165. (g) Butler, I. R.; Lindsell, W. E. *J. Organomet. Chem.* **1984**, *262*, 59–68. (h) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585–591.

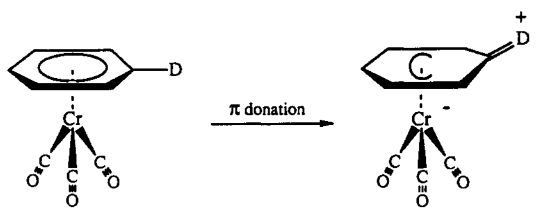
(18) For a detailed discussion of the spectroscopic and especially the electrochemical consequences of adding π-donor and/or π-acceptor substituents to the arene rings of (η^6-arene)$Cr(CO)_3$ complexes and the relationship of this data to our bonding model, see ref 1b.

(19) The structures of complexes having transition-metal substituents either as σ-bonded to the arene (e.g. (η^6-1,4-C_6H_4MeFp)$Cr(CO)_3$) or as part of the arene substituent (e.g. in (μ_2-η^6,η^6-biphenyl)$(Cr(CO)_3)_2$) have the same general structural dependence upon substituent π-donor/π-acceptor character described for the main-group substituents. However, given the added complications of describing their bonding and the possible involvement of direct intermetallic interactions, they will be discussed in detail in a separate manuscript.[16]

(20) In paracyclophane complexes, the alkyl groups are observed to bend away from the $Cr(CO)_3$ fragment due to the cyclophane ring strain. This was modeled by distorting the structure of (η^6-1,4-$C_6H_4Me_2$)$Cr(CO)_3$ toward a boat conformation which resulted in increased hyperconjugation (i.e. π-donation) to the chromium center.[12b]

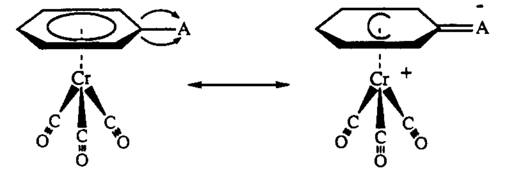
(21) The spectroscopic and electrochemical studies presented in ref 1b unambiguously demonstrate that a substantial portion of the electron-density transferred by π-symmetry interactions with the substituents becomes localized on the $Cr(CO)_3$ center.

the electronic structure of the complex was increased, i.e.



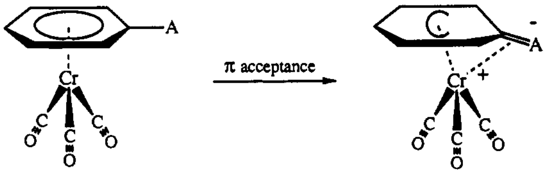
(1)

In the extreme, such a π-donor interaction would produce a cyclohexadienyl complex in which the exocyclic double bond was completely nonbonding with respect to, and bent away from, Cr(CO)$_3$.[22] Indeed, this hypothesis is in accord with the calculated structure for the hypothetical species $[(\eta^5\text{-}C_6H_5{=}CR_2)Cr(CO)_3]^-$.[23] With π-acceptor substituents, an analogous π-symmetry interaction might be expected, i.e.



4a **4b**

However, here the exocyclic double bond would be expected to bend toward, and thus bond to, the 16-electron cationic Cr(CO)$_3$ (reestablishing the favored 18-electron count), i.e.



(2)

as has been predicted for the related species $[(\eta^7\text{-}C_6H_5{=}CR_2)Cr(CO)_3]^+$.[23] However, any contribution from resonance form **4b** to the overall bonding of the complex, and hence any structural distortion of the arene toward Cr(CO)$_3$, would be expected to be relatively small compared to the π-donor case (for conventional (η^6-arene)Cr(CO)$_3$ complexes) both for the obvious steric reasons and because such bending would be expected to result in decreased electron density on the already relatively electron-poor Cr(CO)$_3$ center.[21,24,25]

In this paper, we report the results of a systematic study of the influence of π-donor and π-acceptor substituents on arene geometry in (η^6-arene)Cr(CO)$_3$ complexes.[18] In particular, we have characterized by X-ray crystallography a series of five (η^6-arene)Cr(CO)$_3$ complexes having one or two π-donor or π-acceptor substituents and we compare their structural data with that of the related (η^6-arene)Cr(CO)$_3$ complexes reported in the literature having from zero to six π-donor and/or π-acceptor substituents. The dramatic structural distortions found in the arenes are then explained in terms of the valence bond model outlined above.

Experimental Section

X-ray Crystal Structure Determinations for the Complexes (η^6-C$_6$H$_5$X)Cr(CO)$_3$ (Where X = OMe and NH$_2$) and (η^6-1,4-C$_6$H$_4$X$_2$)Cr(CO)$_3$ (Where X = NMe$_2$, OMe, and CO$_2$Me). Single crystals of five (η^6-arene)Cr(CO)$_3$ complexes[26] having one or two strongly π-donor and/or π-acceptor substituents, listed above, were grown from saturated solutions (CH$_2$Cl$_2$/hexanes) at $\approx$-9 °C. Crystals suitable for X-ray examination were mounted and sealed in glass capillaries and were optically centered in the X-ray beam on an Enraf-Nonius CAD4 automated diffractometer. Details of data collection and structure solution parameters are presented in Table I. Structure solution proceeded routinely for all five compounds. For complex 2 (i.e. X = OMe), the enantiomer was indentified by η-refinement. Ring hydrogen atoms were placed in calculated positions (d_{C-H} = 1.08 Å) and were assigned isotropic temperature factors equivalent to those calculated for the carbon atom to which they are bonded. Methyl hydrogen atoms were located via inspection of difference Fourier maps and were fixed to the attached carbon atoms. The only hydrogen atoms that were refined were the N-*H* hydrogen atoms of (η^6-C$_6$H$_5$(NH$_2$))Cr(CO)$_3$, which were refined with isotropic temperature factors. Final fractional coordinates and equivalent isotropic thermal parameters are given in Table II. All crystallographic calculations were conducted with the PC version of the NRCVAX program package which was locally implemented on IBM compatible 80486 computers.[27]

X-ray Structural Reports from the Literature. An online search of the Cambridge Crystallographic Data Base, CCDB, was carried out during Oct 1989 by Dr. Bernard D. Santarsiero of the University of Alberta Structure Determination Laboratory for complexes having (η^6-arene)–Cr linkages. In addition, the structures of any additional relevant (η^6-arene)Cr(CO)$_3$ complexes of which the authors were aware were included. In total, we were able to find reports of X-ray crystal structure determinations for over 100 different (η^6-arene)Cr(CO)$_3$ complexes. Some of these complexes were omitted from further consideration because there were insufficient data available for any detailed analysis (usually because only a figure depicting the molecule was reported in the paper and no data were deposited in the CCDB).[28] Many of the remaining complexes had polycyclic arenes (e.g. naphthalenes, steroids, etc.) on the Cr(CO)$_3$ centers. These were not used further in studies of arene planarity due to the possible confounding influences of ring strain. The remaining 46 (η^6-arene)Cr(CO)$_3$ complexes having monocyclic aromatic ligands to which were

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[22] For examples of cyclohexadienyl complexes with noncoordinated exocyclic double bonds, see: (a) Lacoste, M.; Rabao, H.; Astruc, D.; Ardoin, N.; Varet, E.; Saillard, J. Y.; Le Beuze, A. *J. Am. Chem. Soc.* **1990**, *112*, 9548–9557. (b) Crocker, L. S.; Mattson, B. M.; Heinekey, D. M. *Organometallics* **1990**, *9*, 1011–1016. (c) Crocker, L. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1989**, *111*, 405–406. (d) Ceccon, A.; Gambaro, A.; Venzo, A. *J. Chem. Soc., Chem. Commun.* **1985**, 540–542. (e) Ceccon, A.; Gambaro, A.; Venzo, A. *J. Organomet. Chem.* **1984**, *275*, 209–222. (f) Ceccon, A.; Gambaro, A.; Romanin, A. M.; Venzo, A. *J. Organomet. Chem.* **1983**, *254*, 199–205. (g) Lacoste, M.; Varret, F.; Toupet, L.; Astruc, D. *J. Chem. Soc.* **1987**, *109*, 6504–6506. (h) Rieke, R. D.; Henry, W. P.; Arney, J. S. *Inorg. Chem.* **1987**, *26*, 420–427. (i) Milligan, S. N.; Rieke, R. D. *Organometallics* **1983**, *2*, 171–173.

[23] In the calculations for these species, the exocyclic double bond was predicted to bend toward Cr(CO)$_3$ by 11° for $[(C_6H_5{=}CR_2)Cr(CO)_3]^+$ and away from Cr(CO)$_3$ in $[(C_6H_5{=}CR_2)Cr(CO)_3]^-$, see: (a) Albright, T. A.; Hoffmann, R.; Hofmann, P. *Chem. Ber.* **1978**, *111*, 1591–1602. (b) Hoffmann, R.; Hofmann, P. *J. Am. Chem. Soc.* **1976**, *98*, 598–603 and references cited therein. For leading references to $[(C_6H_5{=}CR_2)Cr(CO)_3]^+$ complexes and their chemistry, see: (c) Top, S.; Jaouen, G.; Sayer, B. G.; McGlinchey, M. J. *J. Am. Chem. Soc.* **1983**, *105*, 6426–6429 and references cited therein.

[24] With more electron-rich complexes (e.g. (η^6-arene)Cr(PR$_3$)$_3$ and (η^6-arene)$_2$Cr) however, the relative contributions from resonance forms **4b** and **3b** to the overall electronic structure would be expected to increase and decrease, respectively.

[25] In practice, the extreme difficulty encountered in synthesizing substituted (η^6-arene)Cr(CO)$_3$ complexes having strongly π-accepting substituents (e.g. NO$_2$)[3] is an additional factor making the *observation* of the structural consequences for π-acceptance interactions in (η^6-arene)Cr(CO)$_3$ complexes more difficult.[1b]

[26] These complexes were prepared and characterized as described elsewhere.[1b] Thus, the electron-poor complex (η^6-1,4-C$_6$H$_4$(CO$_2$Me)$_2$)Cr(CO)$_3$ was prepared by the reaction of Cr(CO)$_6$ and 1,4-C$_6$H$_4$(CO$_2$Me)$_2$ in refluxing Bu$_2$O while the other four complexes were prepared by the reaction of Cr(CO)$_6$ and the appropriate arene in refluxing Bu$_2$O/THF.[1b]

[27] An interactive system of programs for structure analysis: Gabe, E. J.; Le Page, Y.; Charland, J. P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

[28] The X-ray structure analysis of (η^6-C$_6$H$_5$OMe)Cr(CO)$_3$·C$_6$H$_3$(NO$_2$)$_3$ was not included because of its high *R* value (13.7%) and because the charge-transfer interaction with C$_6$H$_3$(NO$_2$)$_3$ might have perturbed its structure, see: Carter, O. L.; McPhail, A. T.; Sim, G. A. *J. Chem. Soc. A* **1966**, 822–838.

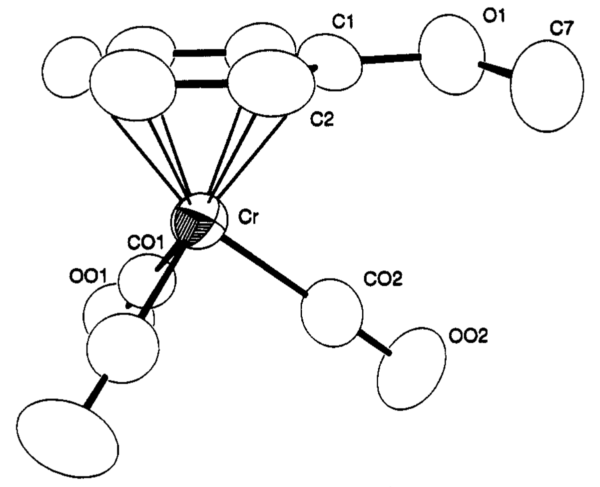


Figure 2. ORTEP plot for the complex (η^6-$C_6H_5(OMe)$)$Cr(CO)_3$.

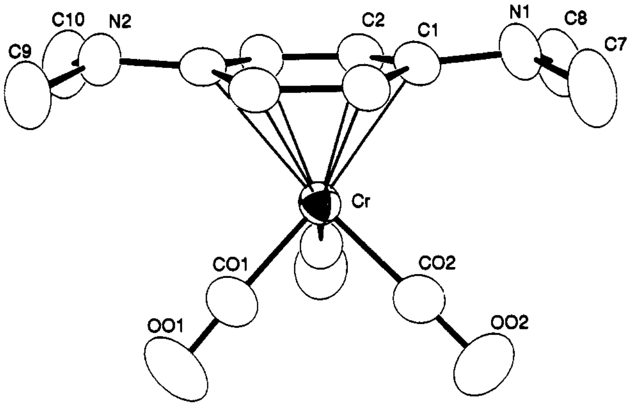


Figure 3. ORTEP plot for the complex (η^6-1,4-$C_6H_4(NMe_2)_2$)$Cr(CO)_3$.

attached between zero and six main-group substituents were used in our study of arene planarity in these complexes.[13,19] Where possible, the requisite bond lengths, angles, least-squares planes, and torsion angles were taken from the primary literature sources. Where not available for these sources, the relevant atomic positions and unit cell parameters were used to calculate these data.[27]

Results

The X-ray crystal structures of 46 (η^6-arene)$Cr(CO)_3$ complexes having monocyclic arene ligands and main-group substituents have been reported previously.[8,13,19] However, the majority of these are not suitable for a quantitative analysis of π-donor and π-acceptor effects on the structures of the aromatic rings because the π-donor or π-acceptor character of their substituents *in the η^6-complexes* cannot be readily established from the data in the literature or because steric effects prevent their arene substituents from adopting the appropriate orientations required to maximize π-symmetry interactions. This leaves only 15 complexes that are even partially satisfactory for our studies of deviations from arene planarity in these complexes. We have therefore crystallographically characterized five additional complexes having π-donating or π-accepting substituents of known strength (i.e. (η^6-C_6H_5X)$Cr(CO)_3$ (where X = NH_2 and OMe) and (η^6-1,4-$C_6H_4X_2$)$Cr(CO)_3$ (where X = NMe_2, OMe, and CO_2Me)). Each of the complexes exhibited the expected three-legged piano stool structures having η^6-bonded arene rings (Figures 1–5 and Table III). The relative arene–$Cr(CO)_3$ conformations of each of these complexes were consistent with theoretical predictions and the structures of related derivatives.[12,13] Thus, the two (η^6-C_6H_5X)$Cr(CO)_3$ complexes having a single π-donor substituent (i.e. NH_2 and OMe) have the syn-eclipsed conformation (**5**) predicted by

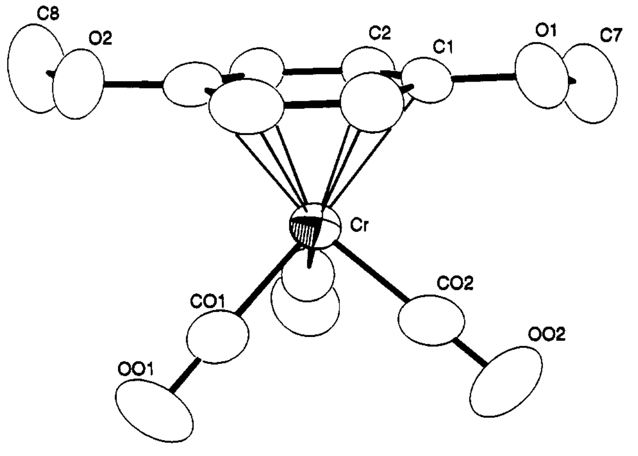


Figure 4. ORTEP plot for the complex (η^6-1,4-$C_6H_4(OMe)_2$)$Cr(CO)_3$.

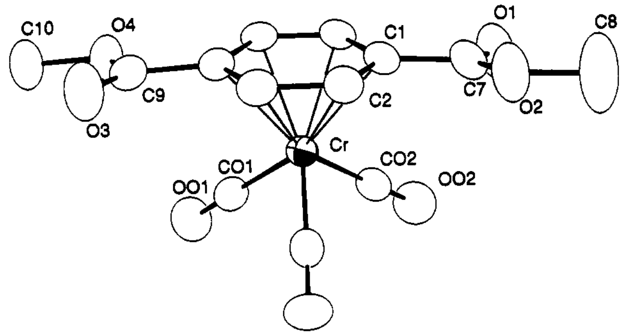
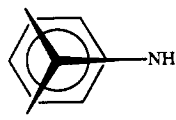


Figure 5. ORTEP plot for the complex (η^6-1,4-$C_6H_4(CO_2Me)_2$)$Cr(CO)_3$.



5

theory,[12a,g,i,w] with torsion angles of 0 and 8.8°, respectively (i.e. the expected torsion angle is 0°). Similarly, the para-disubstituted (η^6-1,4-$C_6H_4X_2$)$Cr(CO)_3$ complexes having two π-donor or two π-acceptor substituents (i.e. X = NMe_2 and OMe or CO_2Me, respectively) adopt the predicted symmetrically staggered conformations, i.e.

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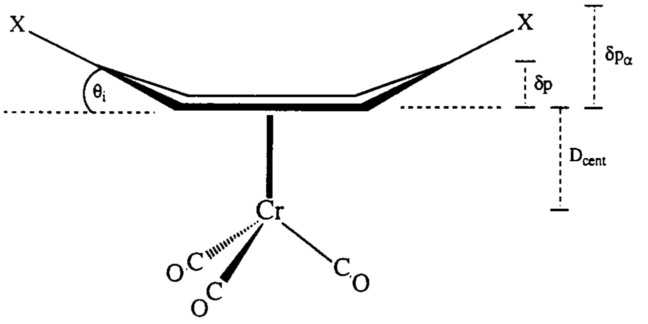
having average torsion angles of 23.7, 18.4, and 23.8°, respectively (the ideal value is 30°).[8b,12a] Features of these structures related to the π-donor and π-acceptor character of the substituents are summarized in Table IV and are discussed below along with the X-ray structural data for the related (η^6-arene)$Cr(CO)_3$ complexes having either monosubstituted or para-disubstituted arene rings.[13]

To measure the effects of the π-symmetry interactions on the rest of the (η^6-arene)$Cr(CO)_3$ complex, we have used a number of different structural parameters. Relevant bond length parameters include the C_{ipso}–substituent bond length, d_{C-X}, the average chromium to carbonyl bond distance, d_{Cr-CO}, the average carbonyl C–O bond distance, d_{CrC-O}, and the distance between the chromium atom and the arene centroid, D_{cent}. To measure deviations in arene planarity and the bending of the α-substituent atoms away from Cr(CO)$_3$, we have chosen a set of standard parameters, δd, δp, δp_α, $\delta p_{\alpha'}$, and θ_i. The parameter δd is defined as the difference between the Cr–C$_{ipso}$ bond length and the average of the other Cr–C(H) bond lengths, in angstroms, i.e.

$$\delta d = d_{Cr-C_{ipso}} - d_{Cr-C(H)_{av}} \quad (3)$$

The parameters δp and δp_α are defined as the distances that the ipso-carbon atoms and the α-substituent atoms, respectively, are lifted out of the least-squares plane defined by the four ortho- and meta-carbon atoms for the (η^6-C_6H_5X)Cr(CO)$_3$ and (η^6-1,4-C_6H_4XY)Cr(CO)$_3$ complexes,[29] in angstroms, i.e.



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The paramter $\delta p_{\alpha'}$ is the value of δp_α corrected for the arene–substituent bond length, i.e.

$$\delta p_{\alpha'} = \delta p_\alpha(1.301\ \text{Å}/d_{C_{ipso}-X}) \quad (4)$$

(where 1.301 Å is the shortest $d_{C_{ipso}-X}$ distance we have measured) and is particularly useful for substituents having C–X bond lengths in excess of 2 Å (as with transition-metal substituents).[19] The parameter θ_i is defined as the angle between the least-squares planes defined by the ipso- and ortho-carbon atoms of the arene and the least-squares plane defined by the ortho- and meta-carbon atoms of the arene, in degrees; see above. These five parameters are defined such that they have positive values when the substituents and their ipso-carbon atoms are displaced away from the Cr(CO)$_3$ centers. Thus, our model predicts that they will have positive values for π-donor and negative values for π-acceptor substituents.

A wide variety of parameters are available to measure the π-donor and/or π-acceptor character of aromatic substituents in addition to their characteristic inductive effects (which we will estimate from Taft's σ_I parameter for the *uncomplexed* arenes).[3] One of the more convenient, if less well-known, scales is derived from ^{13}C NMR data and is based on the observation that the ^{13}C NMR chemical shifts of the para-carbon atoms of aromatic rings are quite sensitive (≈160–300 ppm/electron) to the total electron density on the arene.[5,10a] Inductive and through-space substituent effects are thought to be relatively small and of very similar magnitude for the meta- and para-carbon atoms of both free and η^6-complexed arenes.[5l,10a,14b,d,17a] It has therefore been suggested that one can obtain an estimate of the π-donor or π-acceptor character of the substituents by correcting the ^{13}C NMR chemical shifts of their para-carbon atoms using those of the meta-carbon atoms.[5l,10a] The resulting measure of π-donor and π-acceptor character in (η^6-arene)Cr(CO)$_3$ complexes, Δ_π, is defined[10a] as the difference (in ppm) between the measured chemical shifts of the para- and meta-substituted carbon atoms in the monosubstituted complexes, e.g.

$$\Delta_\pi = \delta_{para} - \delta_{meta} \quad (5)$$

which places both π-donor and π-acceptor interactions on the same scale. Strongly π-donating substituents are observed to have large negative $\Delta\pi$ values, while strongly π-accepting substituents have large positive $\Delta\pi$ values (see Table V).[10a,14b,d,17a] Since more conventional measures of π-donor and π-acceptor character (e.g. Taft's σ^+ and σ^- parameters)[3] for substituents on η^6-arene *complexes* are not available in the literature for a sufficiently broad range of substituents and since this $\Delta\pi$ parameter is so easily measured, we will use it as our scale of the π-donor and π-acceptor character of the substituents in (η^6-arene)Cr(CO)$_3$ complexes.

Discussion

The X-ray crystallographic data summarized in Table IV for the mono-substituted derivatives, (η^6-C_6H_5X)Cr(CO)$_3$, clearly indicate that there is a substantial dependence of the structures of the arene ligands in these complexes on the π-donor and π-acceptor character of the substituents and that these distortions in the arene are in accord with predictions of the valence bond rationale presented above. Thus, inspection of this data indicates that π-donor substituents and their ipso-carbon atoms are bent away from Cr(CO)$_3$ while π-acceptor substituents and their ipso-carbon atoms are in the plane of the arene or are bent slightly toward Cr(CO)$_3$ (as is found for the hydrogen atoms in (η^6-C_6H_6)Cr(CO)$_3$).[8,12p,13a–d] Furthermore, the observed magnitudes of these structural distortions appear to be dependent primarily upon the magnitude of the π-donor or π-acceptor abilities of the substituents. For example, the very strongly π-donating NH_2 and NEt_2[12e,f] substituents (Δ_π = −16.13 and −16.47 ppm, respectively) show similarly large distortions from planarity (e.g. δd = 0.133 Å, δp = 0.088 Å, δp_α = 0.212 Å, $\delta p_{\alpha'}$ = 0.204, and θ_i = 5.78° for X = NH_2) with the two NR_2 substituents and their ipso-carbon atoms being bent strongly away from the Cr(CO)$_3$ group while the more weakly π-donating OMe substituent ($\Delta\pi$ = −10.04 ppm) in (η^6-C_6H_5(OMe))Cr(CO)$_3$ shows a smaller structural distortion (i.e. δd = 0.038 Å, δp = 0.021 Å, δp_α = 0.068 Å, $\delta p_{\alpha'}$ = 0.065, and θ_i = 1.90°) in the same direction. In contrast, those substituents having moderate π-acceptor character (e.g. CO_2Me, C(O)Me, and $SiMe_3$ where Δ_π = 4.99, 4.7, and 4.66 ppm, respectively)[13g,m,q,r] remain approximately in the arene plane and/or are bent slightly toward the Cr(CO)$_3$ groups (e.g. δd = 0.015 Å, δp = −0.013 Å, δp_α = −0.027 Å, $\delta p_{\alpha'}$ = −0.019, and θ_i = −0.59° for X = $SiMe_3$) which is in accord with our model. Considering the dominant role often invoked for steric effects in explaining the bending of aromatic substituents away from Cr(CO)$_3$ groups in the literature, it is particularly interesting to note that for almost all of the monosubstituted (η^6-arene)Cr(CO)$_3$ complexes reported, the observed structural distortions of the arene rings can generally be explained without reference to steric effects. Thus, the NEt_2 and CO_2Me substituents have similar sizes but their arene rings exhibit opposite structural distortions (Table IV) and even the sterically bulky $SiMe_3$ substituent and its ipso-carbon atom in (η^6-C_6H_5($SiMe_3$))Cr(CO)$_3$ are bent somewhat toward the Cr(CO)$_3$ group. Clearly, electronic rather than steric effects dominate the observed structural distortions for most conventional arene substituents, even those such as $SiMe_3$ which are moderately bulky. However, it is not surprising that with very bulky

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[29] Whereas the C_4 plane illustrated in 7 was found to be close to planarity in all compounds studied (deviations <0.01 Å), the corresponding C_5 cyclohexadienyl and C_6 arene planes were found to be planar to within 0.01 Å in only about 20% of the cases studied.

Table II. Fractional Atomic Coordinates (x, y, z) and B_{iso} for the Complexes[a]

	x	y	z	B_{iso}		x	y	z	B_{iso}
$(\eta^6\text{-}C_6H_5(NH_2))Cr(CO)_3$									
Cr	0.97106 (8)	$^1/_4$	0.16669 (7)	3.23 (3)	C1	0.6443 (5)	$^1/_4$	−0.0689 (5)	4.28 (18)
C01	1.1623 (4)	0.3793 (3)	0.2907 (3)	4.31 (12)	C2	0.6862 (4)	0.3759 (4)	0.0324 (4)	4.82 (14)
O01	1.2880 (4)	0.4567 (3)	0.3726 (3)	6.81 (12)	C3	0.7450 (5)	0.3746 (4)	0.2344 (4)	5.63 (16)
C02	1.0623 (5)	$^1/_4$	−0.0342 (5)	4.15 (17)	C4	0.7676 (7)	$^1/_4$	0.3383 (6)	6.2 (3)
O02	1.1200 (5)	$^1/_4$	−0.1615 (4)	6.91 (19)	N	0.5696 (6)	$^1/_4$	−0.2650 (5)	5.36 (22)
$(\eta^6\text{-}C_6H_5(OMe))Cr(CO)_3$									
Cr	0.16467 (10)	0.03761 (6)	0.92937 (6)	3.50 (3)	C2	−0.0956 (7)	0.0040 (5)	1.0263 (4)	4.70 (25)
C01	0.3403 (8)	0.0925 (4)	0.8353 (4)	4.25 (22)	C3	−0.0049 (8)	0.1003 (6)	1.0687 (4)	5.9 (3)
O01	0.4554 (5)	0.1237 (3)	0.7763 (3)	6.14 (21)	C4	0.0401 (8)	0.1945 (5)	1.0040 (5)	5.6 (3)
C02	0.2026 (7)	−0.1037 (5)	0.8645 (4)	4.66 (24)	C5	−0.0017 (8)	0.1915 (4)	0.8910 (5)	5.1 (3)
O02	0.2266 (6)	−0.1912 (3)	0.8236 (3)	7.13 (23)	C6	−0.0922 (7)	0.0977 (5)	0.8436 (4)	4.37 (23)
C03	0.3467 (7)	0.0071 (4)	1.0297 (4)	4.47 (23)	O1	−0.2351 (5)	−0.0808 (3)	0.8592 (3)	5.94 (19)
O03	0.4651 (6)	−0.0095 (4)	1.0914 (3)	6.98 (22)	C7	−0.2651 (9)	−0.1850 (5)	0.9141 (6)	7.5 (4)
C1	−0.1417 (6)	0.0050 (4)	0.9109 (4)	4.21 (21)					
$(\eta^6\text{-}1,4\text{-}C_6H_4(NMe_2)_2)Cr(CO)_3$									
Cr	0.32066 (9)	0.84998 (4)	0.02437 (8)	2.48 (3)	C4	0.1064 (6)	0.9315 (3)	0.0929 (5)	2.69 (19)
C01	0.4165 (6)	0.8510 (3)	0.1909 (5)	3.76 (24)	C5	0.2388 (5)	0.9763 (3)	0.0420 (5)	2.60 (20)
O01	0.4807 (6)	0.8494 (3)	0.2958 (4)	6.20 (23)	C6	0.2963 (5)	0.9645 (3)	−0.0898 (5)	2.47 (19)
C02	0.5205 (6)	0.8303 (3)	−0.0454 (5)	3.39 (23)	C7	0.4192 (7)	0.9395 (4)	−0.3529 (6)	5.0 (3)
O02	0.6501 (5)	0.81837 (24)	−0.0875 (4)	5.21 (20)	C8	0.2356 (8)	0.8245 (4)	−0.3806 (6)	4.9 (3)
C03	0.2862 (6)	0.7420 (3)	0.0470 (5)	3.30 (23)	C9	0.1250 (6)	1.0015 (4)	0.3099 (6)	4.6 (3)
O03	0.2645 (5)	0.67549 (22)	0.0632 (4)	5.20 (21)	C10	−0.0639 (8)	0.8887 (4)	0.2775 (6)	5.2 (3)
C1	0.2257 (6)	0.9070 (3)	−0.1762 (5)	2.70 (21)	N1	0.2719 (5)	0.89958 (24)	−0.3108 (4)	3.29 (20)
C2	0.1079 (5)	0.8555 (3)	−0.1201 (5)	2.84 (20)	N2	0.0408 (5)	0.94824 (24)	0.2173 (4)	3.35 (19)
C3	0.0499 (5)	0.8681 (3)	0.0125 (5)	2.83 (20)					
$(\eta^6\text{-}1,4\text{-}C_6H_4(OMe)_2)Cr(CO)_3$									
Cr	0.29848 (11)	0.73994 (14)	0.10443 (5)	2.95 (5)	C3	0.0174 (7)	0.7986 (8)	0.0827 (4)	3.6 (3)
C01	0.4140 (8)	0.7269 (11)	0.1961 (4)	4.8 (4)	C4	0.0899 (9)	0.9098 (8)	0.1342 (4)	3.8 (3)
O01	0.4867 (7)	0.7163 (9)	0.2527 (3)	7.7 (3)	C5	0.2369 (10)	0.9998 (9)	0.1231 (4)	4.0 (4)
C02	0.4984 (8)	0.6863 (8)	0.0713 (4)	3.8 (3)	C6	0.2982 (8)	0.9893 (8)	0.0581 (4)	3.6 (3)
O02	0.6224 (6)	0.6501 (6)	0.0506 (3)	6.2 (3)	C7	0.2379 (10)	0.7575 (13)	−0.1069 (4)	7.0 (5)
C03	0.2478 (10)	0.5257 (10)	0.1080 (5)	4.1 (4)	C8	−0.1074 (11)	0.8425 (11)	0.2115 (4)	7.6 (5)
O03	0.2181 (7)	0.3883 (6)	0.1100 (3)	6.3 (3)	O1	0.2844 (6)	0.8879 (6)	−0.0577 (3)	5.1 (3)
C1	0.2183 (8)	0.8876 (8)	0.0045 (4)	3.6 (3)	O2	0.0354 (6)	0.9351 (6)	0.19791 (25)	5.1 (3)
C2	0.0814 (7)	0.7872 (8)	0.0167 (3)	3.5 (3)					
$(\eta^6\text{-}1,4\text{-}C_6H_4(CO_2Me)_2)Cr(CO)_3$									
Cr	0.99820 (4)	0.369126 (19)	0.17457 (5)	2.524 (17)	C5	1.0256 (3)	0.47569 (12)	0.2344 (4)	2.94 (11)
C01	0.8367 (3)	0.38539 (13)	0.0135 (4)	3.36 (12)	C6	1.1687 (3)	0.44757 (13)	0.2225 (4)	3.04 (11)
O01	0.7386 (3)	0.39450 (12)	−0.0858 (3)	5.32 (11)	C7	1.3611 (3)	0.36005 (16)	0.3004 (4)	3.82 (14)
C02	1.1093 (3)	0.33786 (15)	−0.0104 (4)	3.43 (12)	C8	1.5391 (4)	0.28342 (23)	0.4134 (7)	8.12 (24)
O02	1.1783 (3)	0.31894 (12)	−0.1237 (3)	5.41 (12)	C9	0.7612 (3)	0.47280 (14)	0.3573 (4)	3.35 (12)
C03	0.9176 (3)	0.28511 (14)	0.1979 (4)	3.25 (12)	C10	0.5816 (3)	0.54702 (17)	0.2318 (5)	4.98 (16)
O03	0.86490 (25)	0.23400 (10)	0.2099 (3)	4.87 (11)	O1	1.44013 (25)	0.37453 (12)	0.1832 (3)	5.50 (12)
C1	1.2099 (3)	0.39134 (14)	0.3263 (4)	3.06 (11)	O2	1.39385 (23)	0.31523 (12)	0.4241 (3)	5.23 (11)
C2	1.1072 (3)	0.36472 (14)	0.4441 (4)	3.17 (12)	O3	0.67512 (24)	0.45359 (12)	0.4617 (3)	5.02 (11)
C3	0.9624 (3)	0.39282 (14)	0.4545 (3)	3.15 (12)	O4	0.73282 (21)	0.51954 (10)	0.2371 (3)	3.92 (9)
C4	0.9198 (3)	0.44722 (13)	0.3477 (3)	2.88 (11)					

[a] Estimated standard deviations refer to the last digit printed, and B_{iso} is the mean of the principle axes of the thermal ellipsoids.

substituents in complexes such as $(\eta^6\text{-}C_6H_5(CHBu^t_2))Cr(CO)_3$[13i] (of unknown π-donor character), steric effects *appear* to cause substantial distortions of the $CHBu^t_2$ substituent and its ipso-carbon atom away from the $Cr(CO)_3$ center.

For those monosubstituted $(\eta^6\text{-}C_6H_5X)Cr(CO)_3$ and para-disubstituted $(\eta^6\text{-}1,4\text{-}C_6H_4X_2)Cr(CO)_3$ complexes for which the π-donor or π-acceptor characters of the substituents have been quantified[1b] (i.e. where X = NEt_2,[13e,f] NH_2, OMe, Me,[13k,30] $SiMe_3$,[13m] C(O)Me,[13g] and CO_2Me[13q,r]), one can evaluate the dependence of the structural distortion parameters on $\Delta\pi$ in a more quantitative fashion. In Figure 6, the dependence of a representative structural distortion parameter (i.e. δp) on the magnitude of $\Delta\pi$ is shown. As can be seen from the data in Table V, four parameters (i.e. δp, δp_α, $\delta p_{\alpha'}$, and θ_i) show a qualitatively similar and high dependence upon $\Delta\pi$ (i.e. for *linear* least-squares regression analyses $R = 0.93$ or 0.94) while δd shows a somewhat lower correlation (i.e. $R = 0.87$). However, for the reasons noted above for the relatively electron-poor $Cr(CO)_3$ center, a quadratic expression might be expected to provide a better fit to the data and this is also consistent with the experimental data (i.e. Figure 6). In either case, the largest structural changes clearly occur for the strongest π-donor substituents, as was expected.[24] In Figure 7, δp is plotted as a function of Taft's inductive parameter for the substituents on uncomplexed arenes, σ_I,[3] and it can be seen that, as we expected, these two parameters show little dependence on one another (Table V). By way of comparison, it would be interesting to determine the maximum distortion in the arene planarity that would be expected if resonance form **3b** became the sole contribution to the bonding in monosubstituted π-donor complexes, $(\eta^6\text{-}C_6H_5D)Cr(CO)_3$ (cf. the hypothetical com-

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[30] The methyl group and related alkyls are weak but significant π-donors (i.e. $\Delta_\pi = -2.9$ ppm), see: (a) Libit, L.; Hoffmann, R. *J. Am. Chem. Soc.* **1974**, *96*, 1370–1383. (b) Calhorda, M.; Carrondo, M. A. A. F. de C. T.; Dias, A. R.; Galvao, A. M.; Garcia, M. H.; Martins, A. M.; Minas da Piedade, M. E.; Pinheiro, C. I.; Romao, C. G.; Martinho Simoes, J. A.; Veiros, L. F. *Organometallics* **1991**, *10*, 483–494.

Table III. Selected Interatomic Distances (Å) and Angles (deg)

	$(C_6H_5NH_2)Cr(CO)_3$	$(C_6H_5OMe)Cr(CO)_3$	$[C_6H_4(NMe_2)_2]Cr(CO)_3$	$[C_6H_4(OMe)_2]Cr(CO)_3$	$[C_6H_4(CO_2Me)_2]Cr(CO)_3$
Cr–C1	2.349 (3)	2.264 (5)	2.207 (5)	2.262 (6)	2.199 (3)
Cr–C2	2.248 (3)	2.252 (6)	2.182 (4)	2.227 (6)	2.220 (3)
Cr–C3	2.188 (3)	2.203 (5)	2.248 (5)	2.236 (6)	2.213 (3)
Cr–C4	2.209 (4)	2.225 (5)	2.322 (5)	2.292 (6)	2.189 (3)
Cr–C5	2.188 (3)	2.207 (6)	2.223 (5)	2.236 (7)	2.216 (3)
Cr–C6	2.248 (3)	2.241 (5)	2.192 (4)	2.236 (7)	2.209 (3)
Cr–C01	1.822 (3)	1.818 (6)	1.710 (5)	1.840 (7)	1.865 (3)
Cr–C02	1.830 (4)	1.840 (6)	1.803 (5)	1.836 (7)	1.861 (3)
Cr–C03	1.822 (3)	1.823 (6)	1.840 (5)	1.814 (8)	1.857 (3)
C01–O01	1.149 (3)	1.154 (7)	1.093 (6)	1.141 (9)	1.137 (4)
C02–O02	1.159 (5)	1.144 (6)	1.156 (6)	1.146 (9)	1.144 (4)
C03–O03	1.149 (3)	1.151 (7)	1.136 (6)	1.158 (9)	1.141 (4)
C1–X1	1.369 (5)	1.357 (6)	1.305 (6)	1.364 (8)	1.502 (4)
X1–R1	0.77 (3)	1.398 (7)	1.440 (7)	1.434 (11)	1.194 (4)
X1–R2	0.77 (3)		1.439 (7)		1.327 (4)
C4–X2			1.301 (6)	1.362 (9)	1.502 (4)
X2–R3			1.406 (7)	1.413 (10)	1.190 (4)
X2–R4			1.433 (7)		1.330 (4)
Cr–C01–O01	177.3 (3)	177.5 (5)	177.6 (5)	178.8 (8)	179.0 (3)
Cr–C02–O02	180.0	179.5 (5)	178.5 (5)	178.8 (6)	179.51 (25)
Cr–C03–O03	177.3 (3)	177.8 (5)	178.9 (4)	178.9 (7)	178.32 (25)
C2–C1–X1	120.41 (17)	123.8 (4)	120.2 (4)	123.3 (6)	121.8 (3)
C6–C1–X1	120.41 (17)	115.4 (4)	119.3 (4)	116.4 (6)	118.19 (25)
C1–X1–R1	113.0 (22)	119.9 (4)	117.9 (4)	118.1 (5)	123.5 (3)
C1–X1–R2	113.0 (22)		116.4 (4)		111.2 (3)
R1–X1–R2	133 (3)		117.0 (4)		125.3 (3)
C3–C4–X2			119.9 (4)	125.0 (6)	117.88 (24)
C5–C4–X2			120.7 (4)	115.4 (6)	122.22 (24)
C4–X2–R3			117.5 (4)	116.6 (6)	123.3 (3)
C4–X2–R4			116.7 (4)		111.04 (24)
R3–X2–R4			120.0 (4)		125.6 (3)

Table IV. Structural and Substituent Parameters for the (η^6-Arene)Cr(CO)$_3$ Complexes[a,b]

arene	d_{C-X}, Å	d_{Cr-CO}, Å	d_{CrC-O}, Å	D_{cent}, Å	δd, Å	δp, Å	δp_α, Å	$\delta p_{\alpha'}$	θ_i, deg	Δ_π(complex), ppm[c]	Δ_π(free arene), ppm[d]	σ_I(free arene)[e]
$C_6H_5(NEt_2)$[f]	1.356	1.813 (4)	1.159 (2)	1.728	0.155	0.096	0.215	0.210	5.89	−16.47	−13.6	0.10
$C_6H_5(NH_2)$	1.369	1.825 (5)	1.152 (6)	1.724	0.133	0.088	0.212	0.204	5.78	−16.13	−12.0	0.10
$C_6H_5(OMe)$	1.357	1.827 (17)	1.150 (10)	1.740	0.038	0.021	0.068	0.065	1.90	−10.04	−6.7	0.25
$C_6H_5(Me)$[f]	1.501	1.824 (8)	1.151 (8)	1.725	0.027	−0.012	−0.006	−0.005	−0.15	−2.94	−2.9	−0.05
$C_6H_5(SiMe_3)$[f]	1.891	1.840 (4)	1.156 (2)	1.725	0.015	−0.013	−0.027	−0.019	−0.59	4.66	0.0	−0.12
$C_6H_5(C(O)Me)$[f]	1.505	1.845 (41)	1.166 (41)	1.717	−0.065	−0.038	−0.039	−0.034	−1.04	≈4.7	4.7	0.28
$C_6H_5(CO_2Me)$[f]	1.493	1.842 (7)	1.155 (7)	1.719	−0.004	0.009	0.015	0.014	0.40	4.99	4.4	0.30
1,4-$C_6H_4(NMe_2)_2$	1.305	1.784 (5)	1.128 (6)	1.732	−0.004	0.079	0.200	0.199	5.80	−14.68	−11.5	0.10
	1.301				0.111	0.086	0.205	0.205	5.90	−14.68	−11.5	0.10
1,4-$C_6H_4(OMe)_2$	1.362	1.830 (7)	1.148 (9)	1.738	0.058	0.064	0.121	0.116	3.30	−10.04	−6.7	0.25
	1.364				0.028	0.044	0.079	0.073	2.10	−10.04	−6.7	0.25
1,4-$C_6H_4(CO_2Me)_2$	1.502	1.861 (3)	1.141 (4)	1.706	−0.016	−0.017	−0.115	−0.100	−2.95	4.99	4.4	0.30
	1.502				−0.026	−0.032	−0.113	−0.098	−2.93	4.99	4.4	0.30
$C_6H_5(CHBu^t_2)$[f]	1.523	1.826 (4)	1.152 (3)	1.727	0.115	0.074	0.464	0.403	11.84			

[a] These substituent and structural parameters are defined in the text. [b] The structural parameters for each complex are derived from the X-ray crystallographic data cited in Tables I–III and ref 12 in the text. [c] From ref 1b in the text. The estimated π-donor or π-acceptor character of the substituent in the (η^6-arene)Cr(CO)$_3$ complex. [d] Derived from the data in ref 5e in the text. The estimated π-donor or π-acceptor character of the substituent on the uncomplexed arene. [e] Taft's inductive substituent constant for the uncomplexed arene from ref 5f in the text. [f] Parameters calculated from the data presented in the original publications, see refs 13e–g,i,k,m,q,r.

plex $[(\eta^5\text{-}C_6H_5{=}CR_2)Cr(CO)_3]^-$).[23] This value can be estimated from the crystallographic data for the known complexes $(\eta^5\text{-}C_6H_5{=}CPh_2)Re(CO)_3$ and $(\eta^5\text{-}C_5Me_5)_2Fe_2(\mu_2\text{-}\eta^5,\eta^5\text{-}C_6H_5{=}C_6H_5)$ which have η^5-cyclohexadienyl ligands and exocyclic double bonds and in which there is no direct bond between the metal atoms and the ipso-carbon atom to which the exocyclic double bond is attached.[22] For the iron complex, which has a true exocyclic double bond ($d_{C_{ipso}=C_{ipso}}$ is 1.37 Å) and no direct Fe–C_{ipso} bond, the observed θ_i value is 25°.[22g] Since the strongest π-donor substituents (i.e. NR_2) have θ_i values of almost 6°, it appears that they display approximately one-quarter of the structural distortion that would be expected if only one resonance form **3b** (and not resonance form **3a**) were contributing to their bonding!

Those (η^6-arene)Cr(CO)$_3$ complexes having two or more π-donor and/or π-acceptor substituents would also be expected to show structural distortions about their arene rings that might also be understood in valence bond terms. However, now, in addition to the substituent–Cr interactions that they would be expected to exhibit, substituent–substituent interactions would also be expected. Indeed, for noncomplexed arenes, such interactions are known to profoundly influence arene structures, spectra, and physical properties. For example, the π-donor and π-acceptor substituents display substantial synergic interactions for the para- but not the meta-substituted arenes.[31] For the (η^6-arene)Cr(CO)$_3$ complexes, bending of

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(31) For example, π-donor/π-acceptor-substituted arenes such as 1,4-$C_6H_4(NH_2)(NO_2)$ have excellent second-order nonlinear optical properties, see, for example: Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; John Wiley and Sons: New York, 1991; pp 134–143.

Table V. Results of Linear Least-Squares Regression Analyses for the Data (i.e. $Y = mX + b$)

dependent variable[b] Y	independent variable[b] X	slope m	intercept b	corr coeff R
δd, Å	$\Sigma\Delta_\pi$, ppm	−0.0061 Å ppm^{-1}	0.006 Å	0.87
δp, Å	$\Sigma\Delta_\pi$, ppm	−0.0050 Å ppm^{-1}	0.001 Å	0.93
δp_α, Å	$\Sigma\Delta_\pi$, ppm	−0.012 Å ppm^{-1}	0.003 Å	0.93
$SP_{\alpha'}$	$\Sigma\Delta_\pi$, ppm	−0.011 ppm^{-1}	0.007	0.93
θ_i, deg	$\Sigma\Delta_\pi$, ppm	−0.32° ppm^{-1}	0.14°	0.94
δd, Å	$\Sigma\sigma_I$	−0.12 Å	0.05 Å	0.27[c]
SP, Å	$\Sigma\sigma_I$	−0.02 Å	0.03 Å	0.05[c]
Sp_α, Å	$\Sigma\sigma_I$	−0.13 Å	0.08 Å	0.17[c]
$\delta p_{\alpha'}$, Å	$\Sigma\sigma_I$	−0.13 Å	0.08 Å	0.18[c]
θ_i, deg	$\Sigma\sigma_I$	−2.3°	1.9°	0.11[c]

[a] These analyses were carried out using the program KaleidaGraph by Synergy Software. [b] The parameters are defined in the text. [c] The apparent differences in these R values are apparently statistical artifacts as the "fit" of none of the data in these graphs is visually distinguishable.

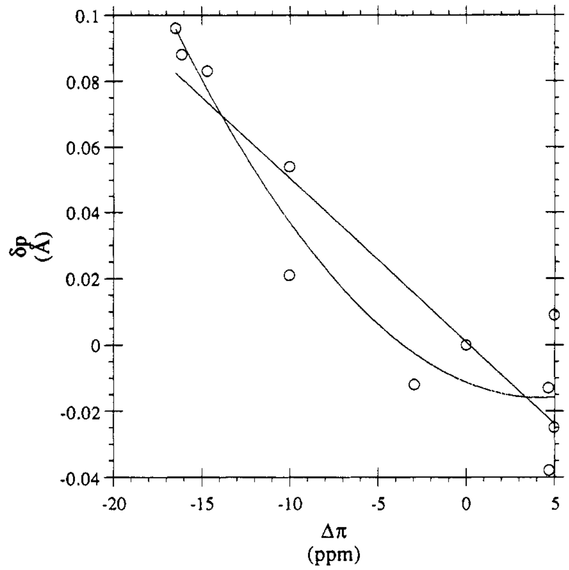


Figure 6. Structural distortion parameter, δp, as a function of substituent π-donor/π-acceptor character, Δ_π, for the (η^6-arene)Cr(CO)$_3$ complexes in Table IV.

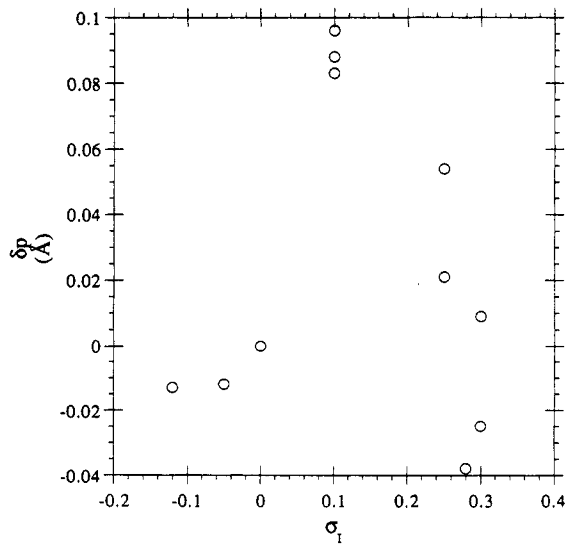
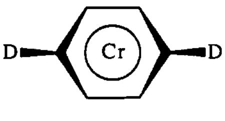


Figure 7. Structural distortion parameter, δp, as a function of substituent inductive character, σ_I, for the (η^6-arene)Cr(CO)$_3$ complexes in Table IV.

the substituents out of the arene plane (see 7) would be expected to decrease the magnitude of the π-symmetry substituent–substituent interactions compared to the case in which the arenes are planar. As for the (η^6-C$_6$H$_5$X)Cr(CO)$_3$ complexes, however, the magnitudes of the structural distortions would be expected to be greater for π-donors than for π-acceptors and to vary as a function of $\Delta\pi$. Thus, π-donor substituents and their ipso-carbon atoms are expected to be bent away from the Cr(CO)$_3$ centers while the π-acceptor substituents and their α-substituent atoms are expected to be in the arene plane or to show a small bending toward the Cr(CO)$_3$ centers. One would therefore expect "boat" and "inverted boat" conformations for the arene ligands of the complexes (η^6-1,4-C$_6$H$_4$D$_2$)Cr(CO)$_3$ and (η^6-1,4-C$_6$H$_4$A$_2$)Cr(CO)$_3$, respectively, i.e.



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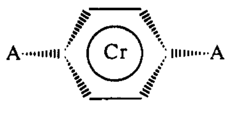

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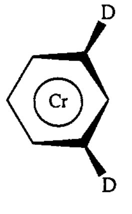
(where the Cr(CO)$_3$ group is below the plane of the paper, D = a π-donor, and A = a π-acceptor). The structural data for the complexes listed in Table IV are in accord with these structural predictions (see Figures 3–5 and Table IV). For example, the "boat" for (η^6-1,4-C$_6$H$_4$(NMe$_2$)$_2$)Cr(CO)$_3$ is substantially deeper than is that for (η^6-1,4-C$_6$H$_4$(OMe)$_2$)Cr(CO)$_3$ since the former has a more negative $\Delta\pi$ value than does the latter (i.e. −14.68 vs −10.04 ppm, respectively). Thus, the average δp value for the NMe$_2$ complex (0.083 Å) is larger than it is for the OMe complex (0.054 Å). Also, the complex (η^6-1,4-C$_6$H$_4$(CO$_2$Me)$_2$)Cr(CO)$_3$, which has two π-acceptor substituents, has an inverted-boat structure with a smaller average distortion (i.e δp = −0.025 Å) than do the (η^6-1,4-C$_6$H$_4$D$_2$)Cr(CO)$_3$ complexes. The other para-substituted complexes whose X-ray crystal structures have been reported, and for which we can estimate reasonable $\Delta\pi$ values, show distortions of arene planarity consistent with the π-donor and/or π-acceptor character of their substituents as described above.

Our model of the π-symmetry interactions in (η^6-arene)Cr(CO)$_3$ complexes can also be used to predict the structural distortions expected for other arene substitution geometries.[32] Thus, for complexes having two or three π-donor substituents (i.e. (η^6-1,3-C$_6$H$_4$D$_2$)Cr(CO)$_3$, (η^6-1,2-C$_6$H$_4$D$_2$)Cr(CO)$_3$, and (η^6-1,3,5-C$_6$H$_3$D$_3$)Cr(CO)$_3$), our model predicts the following distortions in arene planarity.



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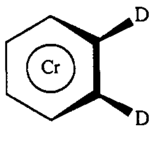

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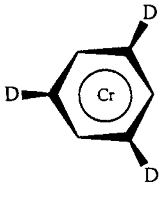

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Again, where the X-ray crystal structures for such species have been reported in the literature,[13] they are fully consistent with these predictions. Thus, the complex (η^6-1,2,3-C$_6$H$_3$(OMe)$_3$)Cr(CO)$_3$ has the expected "two-thirds crown" conformation with the meta-substituent ipso-carbon atoms being bent substantially away from Cr-

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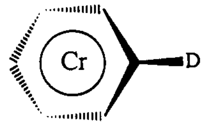
[32] Indeed, we have recently characterized by X-ray crystallography nine additional examples of such complexes having various 1,3-, 1,4- and 1,3,5-substitution geometries around the arene ring, including mixed π-donor/π-acceptor complexes, and in each case they fully support our structural proposals (Hunter, A. D.; Furey, W. S.; Christie, S. D.; Zaworotko, M. J. Unpublished observations). These structures will be fully described in upcoming manuscripts.

$(CO)_3$,[13c,f,33] the ortho-substituted complex (η^6-1,2-$C_6H_4(OMe)_2)Cr(CO)_3$ has the chair conformation expected for such a structure (i.e. $d_{Cr-C(1,2)}$ = 2.30 and 2.30 Å, $d_{Cr-C(3,6)}$ = 2.23 and 2.24 Å, and $d_{Cr-C(4,5)}$ = 2.22 and 2.22 Å),[13z] and the complex (η^6-1,3,5-$C_6H_3(N(CH_2)_4)_3)Cr(CO)_3$ (where $N(CH_2)_4$ = *N*-pyrrolidino which is expected to be an excellent π-donor) exhibits a crownlike geometry (i.e. $d_{Cr-C(ipso)}$ = 2.344 Å (average) and $d_{Cr-C_{ortho}}$ = 2.279 Å (average))[13t] as did the related organometallic derivative described in the Introduction (i.e. (η^6-1,3,5-$C_6H_3Fp_3)Cr(CO)_3$).[14a,b] Finally, this model may also provide an electronic rationale for why the complexes having six alkyl groups (e.g. (η^6-$C_6Me_6)Cr(CO)_3$,[13rr,ss] (η^6-$C_6Et_6)Cr(CO)_3$,[13tt,uu] etc.) have the substituents bent away from $Cr(CO)_3$ even though this geometry creates steric crowding between these alkyl groups. It seems possible that this bending away from the $Cr(CO)_3$ center may not be entirely due to the steric bulk of the $Cr(CO)_3$ center but, rather, it may have a component due to electronic interactions.[30]

An interesting feature of the structures having strongly π-donating substituents is that, in addition to the expected primary distortions to the arenes planarity (i.e. eq 1), secondary distortions to the planarity of the rest of aromatic ring are consistently observed. For example, in the (η^6-$C_6H_5D)Cr(CO)_3$ complexes having sufficiently strongly π-donating substituents (e.g. NH_2 and OMe) one can see that both the ortho- and para-carbons are also lifted slightly with respect to the meta-carbon atoms, i.e.



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(where the hatched wedges indicate the secondary distortions are of smaller magnitude than are the primary distortions (designated as solid wedges)). For example, the complexes (η^6-$C_6H_5(NH_2))Cr(CO)_3$ and (η^6-$C_6H_5(OMe))Cr(CO)_3$ display the expected pattern in their Cr–C(arene) bond distances (i.e. $d_{Cr-C_{ipso}}$ = 2.349 (3) Å, $d_{Cr-C_{ortho}}$ = 2.248 (3) Å, $d_{Cr-C_{meta}}$ = 2.188 (3) Å, and $d_{Cr-C_{para}}$ = 2.209 (4) Å for D = NH_2 and $d_{Cr-C_{ipso}}$ = 2.264 (5) Å, $d_{Cr-C_{ortho}}$ = 2.252 (6) and 2.241 (5) Å, $d_{Cr-C_{meta}}$ = 2.203 (5) and 2.207 (5) Å, and $d_{Cr-C_{para}}$ = 2.225 (5) Å for D = OMe) as does the NEt_2[13e,f] derivative. Although these secondary structural distortions may originate from the preference of the arene carbon atoms for retaining 120° bond angles, a more complete and satisfactory explanation must await a detailed molecular orbital study.

Any π-donor/π-acceptor interactions between the substituents on (η^6-arene)$Cr(CO)_3$ complexes and the rest of the molecule would also be expected to affect the geometry about the substituent atoms. In particular, for maximal π-symmetry interactions, the π-donor and π-acceptor substituents on (η^6-arene)$Cr(CO)_3$ complexes must adopt the correct orientation with respect to the aromatic ring as they must for uncomplexed arenes.[7,10b,12k,34] In addition, any contribution from π-donation and/or π-acceptance would be expected to change the hybridizations and bond lengths on these substituents as well. For example, π-donation would be expected to flatten the pyramidal aryl-NR_2 groups (due to a change in nitrogen's hybridization from sp^3 toward sp^2) and increase the bond angle in aryl–O–Me groups (due to the hybridization of oxygen changing from sp^3 toward sp^2) and should shorten the aryl–N and aryl–O bonds, as appropriate, in each. Similarly, π-acceptance by CO_2Me would be expected to produce analogous but smaller changes (see above), including a shortening of the aryl–C bond and lengthening of the C–O (carbonyl) bond. In fact, data consistent with these suggestions are observed for the complexes that we have crystallographically characterized and for the other complexes reported in the literature.[13,35–37] Thus, the complexes (η^6-$C_6H_5(OMe))Cr(CO)_3$ and (η^6-1,4-$C_6H_4(OMe)_2)Cr(CO)_3$ show (Figures 1–5, Table III) the expected short arene–O bond distances, wide C_{ipso}–O–Me bond angles, and small average torsion angles about this bond (10.6, 14.8, and 1.7°) while the CO_2Me substituents in the complex (η^6-1,4-$C_6H_4(CO_2Me)_2)Cr(CO)_3$ show the expected relatively short C_{ipso}–CO_2Me bonds, long C=O bonds in the CO_2Me group, and coplanar arene and CO_2Me fragments (torsion angles of 11.1 and 6.5°). Finally, the strongly π-donating NR_2 substituents in (η^6-$C_6H_5(NH_2))Cr(CO)_3$ and (η^6-1,4-$C_6H_4(NMe_2)_2)Cr(CO)_3$ have nitrogen atoms which are nearly planar, the latter has torsion angles about the arene–substituent bonds which are close to zero (i.e. 16.6 and 13.5°), and their arene–N bond distances are remarkably short due to the contributions of resonance forms such as **3b** (see Table III for all bond lengths and angles).[38]

This valence bond model has been developed specifically for the relatively electron-poor (η^6-arene)$Cr(CO)_3$ complexes;[37] however, it should be readily applicable to other closely related η^6-arene complexes (e.g. (η^6-arene)$Mo(CO)_3$, (η^6-arene)$W(CO)_3$, and $[(\eta^6\text{-arene})Mn(CO)_3]^+$). In the longer term, it might be worthwhile to investigate the extension of this model in a more systematic fashion to a wider range of η^6-arene complexes and to related ligands (e.g. substituted cyclopentadienyls) to see if π-donor/π-acceptor interactions have similar importance for them.[39] Indeed, preliminary inspections of some structural data for three related classes of η^6-arene complexes (e.g. $[(\eta^6\text{-arene})FeCp]^+$, ($\eta^6$-arene)$_2$V, and ($\eta^6$-arene)$_2$Cr) indicate

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(33) This complex acts as if it were an (η^6-1,3-$C_6H_4D_2)Cr(CO)_3$ species, in terms of our model, because steric hindrance on the middle OMe substituent (by the other two OMe groups) prevents it from adopting an orientation in which it can act as a strong π-donor.

(34) The Karplus relationship tells us that the maximum magnitude of any π-donor/π-acceptor interaction will decrease (as a function of the cosine of the torsion angle) from the maximum to zero as the aryl-substituent angle twists through 90°.

(35) For a polycyclic (η^6-arene)$Cr(CO)_3$ complex having a CO_2Et group on the η^6-arene ring, see: Nechvatal, G.; Widdowson, D. A.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1981**, 1260–1262.

(36) For polycyclic (η^6-arene)$Cr(CO)_3$ complexes having OMe groups on the η^6-arene ring, see: (a) Uemura, M.; Nishikawa, N.; Take, K.; Ohnishi, M.; Hirotsu, K.; Higauchi, T.; Hayashi, Y. *J. Org. Chem.* **1983**, *48*, 2349–2356. (b) Arzeno, H. B.; Barton, D. H. R.; Davies, S. G.; Lusinchi, X.; Meunier, B.; Pascard, C. *Nouv. J. Chim.* **1980**, *4*, 369–375. (c) Cambie, R. C.; Clark, G. R.; Gourdie, A. C.; Rutledge, P. S.; Woodgate, P. D. *J. Organomet. Chem.* **1985**, *297*, 177–184. (d) Dötz, K. H.; Dietz, R.; Von Imhof, A.; Lorenz, H.; Huttner, G. *Chem. Ber.* **1976**, *109*, 2033–2038. (e) Baird, P. D.; Blagg, J.; Davies, S. G.; Sutton, K. H. *Tetrahedron* **1988**, *44*, 171–186.

(37) The related (η^6-$C_6H_5(CO_2Me))Cr(CO)_2L$ complexes show similar effects, see: (a) Saillard, J. Y.; Le Borgne, G.; Grandjean, D. *J. Organomet. Chem.* **1975**, *94*, 409–416. (b) Saillard, J. Y.; Grandjean, D. *Acta Crystallogr., Sect. B* **1978**, *34*, 3772–3775. (c) Saillard, J. Y.; Grandjean, D.; LeBeuze, A.; Simonneaux, G. *J. Organomet. Chem.* **1981**, *204*, 197–205. (d) Andrianov, V. G.; Struchkov, Y. T.; Baranetzkaya, N. K.; Setkina, V. N.; Kursanov, D. N. *J. Organomet. Chem.* **1975**, *101*, 209–214. (e) Harris, G. W.; Albers, M. O.; Boeyens, C. A.; Coville, N. J. *Organometallics* **1983**, *2*, 609–614. (f) Le Maux, P.; Simonneaux, G.; Jaouen, G.; Ouahab, L.; Batail, P. *J. Am. Chem. Soc.* **1978**, *100*, 4312–4314. (g) Van Rooyen, P. H.; Dillen, J. L. M.; Lotz, S.; Schindehutte, M. *J. Organomet. Chem.* **1984**, *273*, 61–68.

(38) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper and Row: New York, 1983; pp 258–259.

(39) A structural study of disubstituted $[(\eta^6\text{-arene})FeCp]^+$ salts reveals significant, but less extreme, structural distortions in the η^6-arene ligands. For example, $[(\eta^6\text{-}1,2\text{-}C_6H_4Cl(NH(CH_2Ph)))FeCp]^+$ has δp_α and θ_i values of 0.18 Å and 4.8°, respectively: Christie, S. D.; Piorko, A.; Zaworotko, M. J. Unpublished observations.

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that they have the arene structures predicted by this model.[39-42]

Conclusions

The analysis of the structural data presented herein supports our proposal that the structural distortions of the arenes and their substituents in (η^6-arene)Cr(CO)$_3$ complexes are largely caused by electronic effects and that, except for the bulkiest substituents, these distortions are best explained in terms of the π-donor and π-acceptor interactions between the substituents and the rest of the molecule. In addition, this model allows one to predict the distortions of the arenes from planarity and the geometries of the substituents with a remarkably high degree of accuracy. Although our simple valence bond model has a high predictive value and is consistent with the published molecular orbital rationale for the bonding in (η^6-arene) complexes, a series of detailed molecular orbital calculations on (η^6-arene)Cr(CO)$_3$ complexes (in which the three-dimensional structures of the substituted arene fragments having various substitution geometries and π-donor/π-acceptor substituents are systematically varied) is certainly required for a more fundamental understanding of the origins of the structural distortions in these species.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada, the University of Alberta, and Saint Mary's University for the financial support of this work. We also thank Dr. Bernard D. Santarsiero of the University of Alberta Structure Determination Laboratory for carrying out the Cambridge Crystallographic Data Base search and Nadia Wichrowska and Vivian Mozol for their experimental assistance.

Registry No. [η^6-C$_6$H$_5$(NH$_2$)]Cr(CO)$_3$, 12108-11-1; [η^6-C$_6$H$_5$(OMe)]Cr(CO)$_3$, 12116-44-8; [η^6-1,4-C$_6$H$_4$(NMe$_2$)$_2$]Cr(CO)$_3$, 46930-56-7; [η^6-1,4-C$_6$H$_4$(OMe)$_2$]Cr(CO)$_3$, 12176-26-0; [η^6-1,4-C$_6$H$_4$(CO$_2$Me)$_2$]Cr(CO)$_3$, 33039-20-2.

Supplementary Material Available: Tables of hydrogen atom coordinates and B_{iso} parameters, anisotropic thermal parameters, bond lengths, and bond angles for the five crystal structures and plots of the data used to generate the least-squares regression analyses described in Table V (25 pages); listings of structure factor amplitudes for the five structures (39 pages). Ordering information is given on any current masthead page.

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(40) For most classes of η^6-arene complexes, only alkyl-substituted derivatives have commonly been prepared. For example, a number of [(η^6-arene)$_2$Fe]$^{2+}$ and [(η^6-arene)Fe(η^5-cyclohexadienyl)]$^+$ complexes have been crystallographically characterized, but they are limited to arenes with alkyl substituents: (a) Cameron, T. S.; Clerk, M. D.; Linden, A.; Sturge, K. C.; Zaworotko, M. J. *Organometallics* 1988, *7*, 2571–2573. (b) Clerk, M. D.; Sturge, K. C.; White, P. S.; Zaworotko, M. J. *J. Organomet. Chem.* 1989, *368*, C33–C37. (c) Atwood, J. L.; Christie, S. D.; Clerk, M. D.; Osmond, D. A.; Sturge, K. C.; Zaworotko, M. J. *Organometallics*, in press. (d) Rogers, R. D.; Sturge, K. C.; Zaworotko, M. J. Unpublished observations.

(41) The complex (η^6-1,4-C$_6$H$_4$F$_2$)$_2$V has boat-shaped arene ligands with the fluorine substituents and the ipso-carbon atoms to which they are attached being bent substantially away from the vanadium atom, see: Radonovich, L. J.; Zuerner, E. C.; Efner, H. F.; Klubunde, K. J. *Inorg. Chem.* 1976, *15*, 2976–2981.

(42) The X-ray structural results for the electron-rich (η^6-arene)$_2$Cr complexes having π-acceptor CF$_3$ substituents are particularly interesting, since, as expected,[24] these substituents and the ipso-carbon atoms to which they are attached are bent substantially toward chromium, see: (a) Larson, S. B.; Seymour, C. M.; Lagowski, J. J. *Acta Crystallogr., Sect. C* 1985, *41*, 1624–1626. (b) Eyring, M. W.; Zuerner, E. C.; Radonovich, L. J. *Inorg. Chem.* 1981, *20*, 3405–3410. (c) Larson, S. B.; Seymour, C. M.; Lagowski, J. J. *Acta Crystallogr., Sect. C* 1987, *43*, 1626–1628. (d) Faggiani, R.; Hao, N.; Lock, C. J. L.; Sayer, B. G.; McGlinchey, M. J. *Organometallics* 1983, *2*, 96–100.

Formation and Substitution of Remote Ester-Functionalized Organocopper Reagents

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Remote ester-functionalized aryl and alkyl organocopper compounds have been produced through the use of a highly reactive form of copper. Methyl 5-bromopentanoate and various alkyl halobenzoates undergo oxidative addition with active copper to produce methyl 5-cupriopentanoate and alkyl cupriobenzoates, respectively, in moderate to good yields. These organocopper reagents will cross-couple with acid chlorides to form the corresponding keto esters and with alkyl halides to produce the corresponding alkylated esters in moderate to good yields. The organocopper compounds could also be converted to their respective homocoupled dimers in varying yields by appropriate oxidative or thermal methods. Methyl 5-cupriopentanoate has a slight tendency to undergo an intramolecular cyclization to form, after aqueous workup, cyclopentanone and methanol.

Introduction

Organocopper compounds[1] are an exceptionally useful class of synthetic reagents primarily due to their ability to undergo substitution reactions[2] with alkyl halides and 1,4-conjugate addition reactions[3] with α,β-unsaturated carbonyl compounds. The α-cuprio esters have been obtained by forming the enolate of the ester followed by treatment with a suitable copper(I) salt.[4] This approach, obviously, cannot be used for reagents in which the car-

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(1) (a) Lipshutz, B. H. *Synthesis* 1987, 325 and references cited therein. (b) Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. A. *Tetrahedron Lett.* 1984, *40*, 5005 and reference cited therein. (c) Posner, G. H. *An Introduction to Synthesis Using Organocopper Reagents*; Wiley: New York, 1980. (d) Bertz, S. H.; Dabbagh, G. *J. Org. Chem.* 1984, *49*, 1119. (e) Bertz, S. H.; Dabbagh, G. *J. Am. Chem. Soc.* 1988, *110*, 3668.

(2) Posner, G. H. *Org. React.* (*N.Y.*) 1975, *22*, 253 and references cited therein.

(3) Posner, G. H. *Org. React.* (*N.Y.*) 1972, *19*, 1 and references cited therein.

(4) (a) Kauffmann, Th.; Beissner, G.; Berg, H.; Koppelmann, E.; Legler, J.; Schonfelder, M. *Agnew. Chem., Int. Ed. Engl.* 1968, *7*, 540. (b) Corey, E. J.; Kuwajima, I. *Tetrahedron Lett.* 1972, 487. (c) Kuwajima, I.; Doi, Y. *Ibid.* 1972, 1163. (d) Rathke, M. W.; Lindert, A. *J. Am. Chem. Soc.* 1971, *93*, 4605.

0276-7333/92/2311-1560$03.00/0