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Electronic Interaction of Tricarbonylchromium-Complexed Benzene with a Facing Aryl Ring in the 1,8-Diarylnaphthalene System

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Abstract: A series of 1,8-diarylnaphthalenes with the face-to-face aryl group(s) coordinated to tricarbonylchromium have been synthesized. Examination of X-ray crystal structures, charge-transfer absorption bands, and CO stretching vibrations has indicated marked π-donor ability for the tricarbonyl(arene)chromium moiety. Copyright © 1996 Elsevier Science Ltd

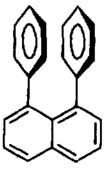
The tricarbonylchromium group is an attractive functional group for the role it plays in changing the reactivity of arene nuclei.[1] It is well known that the aromatic ring of tricarbonyl(arene)chromium complexes is more susceptible to nucleophilic rather than electrophilic substitution reactions indicating a strong electron-withdrawing effect of the tricarbonylchromium group.

Recently, the nature of π-π interactions between stacked aromatic rings has attracted much attention as one of the most important noncovalent interactions.[2] In tricarbonylchromium-complexed meta- and paracyclophanes, it was pointed out that transannular electron release from the non-complexed benzene to another benzene coordinated to tricarbonylchromium could take place.[3] However, in another report no such π-π interaction was observed between the π-systems in tricarbonylchromium-complexed [2.2]metacyclophane;[4] thus, there seems to be some conflict as to the electronic function of the tricarbonylchromium group upon π-π interaction.

The 1,8-diarylnaphthalene system can serve as another model for the study of π-π interaction. While through-space charge-transfer interaction was clearly observed in a series of 1-aryl-8-tropilionaphthalenes,[5] Siegel *et al.* realized that the interactions of stacked phenyl rings in 1,8-diarylnaphthalenes are dominated by the polar/π over charge-transfer effects.[6] Here we wish to report the characteristic electronic interaction observed between 1,8-aryl groups π-coordinated to the tricarbonylchromium function in this system.

First, mono- and bis-coordinated tricarbonylchromium complexes of 1,8-diphenylnaphthalene **2a** and **3** were synthesized by a palladium(0) catalyzed cross-coupling reaction[7] of tricarbonyl(chlorobenzene)chromium with 8-phenyl-1-naphthylboronic acid,[8] and by a direct complexation of **1** with $Cr(CO)_6$ under thermal conditions,[9] respectively.

X-Ray structures of **2a**[10] and **3**[11] are shown in Fig. 1. It is apparent that the two aromatic rings at the 1,8-positions face each other in a nearly parallel arrangement. The structural characteristics are summarized in Table 1.



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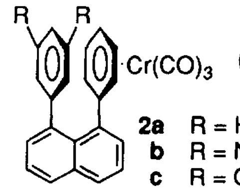
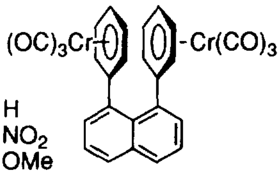


2a R = H
b R = NO_2
c R = OMe
d R = NMe_2

2



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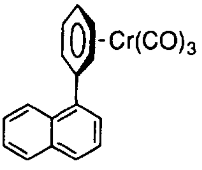

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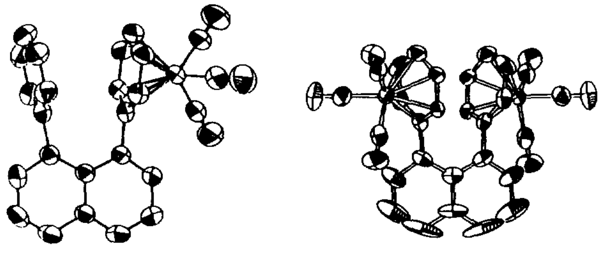
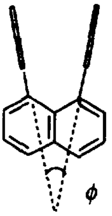


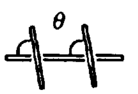
2a **3**

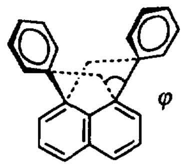
Fig. 1. X-ray crystal structures of **2a** and **3**. All hydrogen atoms are omitted for clarity.

The splayed-out angles (ϕ) of the facing aromatic rings, the rotation angles (θ) for both of the aromatic rings with reference to the basal naphthalene plane, and the dihedral angles (φ) between two single bonds connecting the substituents are quite similar in non-complexed and mono-complexed compounds **1** and **2a**. However, these angles for the bis-complex **3** are considerably different from those of **1** and **2a**. The two chromium-complexed aromatic rings in **3** evidently repel each other as shown by the angle φ which is much larger than those of **1** and **2a**. This must be due to the strongly *repulsive* electronic interaction between the two aromatic rings π-coordinated to tricarbonylchromium. Since the stacked aromatic rings possessing electron-withdrawing groups in the 1,8-diarylnaphthalene system are reported to decrease the *repulsive* interaction

Table 1. Structural characteristics by X-ray crystallography of 1,8-diarylnaphthalene derivertives π-coordinating to tricarbonylchromium complexes







Compound	Angle (°)		
	Splay, ϕ^a	Rotation, θ^b	Dihedral, φ^c
1[d]	20	67	3.4
2a	17	68 [PhCr(CO)3]	2.8
		72 (Ph)	
3	24	54	27.4

[a] Splayed-out angle of the facing aromatic rings. [b] Rotation angle of the substituent rings against the basal naphthalene plane. [c] Dihedral angle btween two single bonds which connect aromatic rings. [d] Data from ref. 5.

between the two arene rings,[3c,6a] the above phenomenon may appear contradictory to the general view that the the tricarbonylchromium moiety exerts an electron-withdrawing ability. This, however, can be explained by taking into consideration that the HOMO[12a] of the chromium-complexed arene is extended to penetrate through the arene's π-cloud so that it can interact repulsively with another π-system at the opposite side of the arene ring.

In order to further confirm such an electronic effect of tricarbonyl(arene)chromium, we synthesized a series of 1-aryl-8-[tricarbonyl(benzene)chromium]naphthalene complexes, **2b-d**. Their electronic spectra are shown in Fig. 2. While the spectra of **2c** and **2d** with electron-donating groups are similar to that of **2a**, only compound **2b** having a highly electron deficient aromatic ring exhibited a longer-wavelength absorption. This band, which is observed neither in **4** nor in 1-(3',5'-dinitrophenyl)naphthalene, exhibits a considerable bathochromic shift upon changing the solvent from acetonitrile to less polar dichloromethane,[13] and is assigned to an intramolecular charge-transfer band with the chromium-complexed benzene acting as a π-donor.

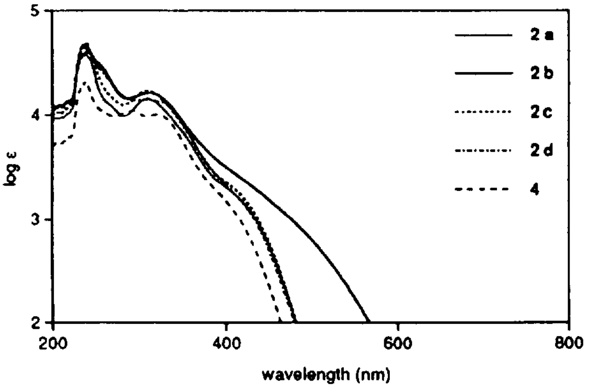


Fig. 2. UV-visible spectra for 8-(aryl)-1-[tricarbonyl(benzene)-chromium]naphthalene (**2a-d**) and **4** in CH_2Cl_2.

Also, the carbonyl stretching frequencies in IR spectra of the compounds **2a-d** support the function of tricarbonylchromium-complexed arene acting as an electron donor (Table 2). Wavenumbers of both symmetric (a_1) and antisymmetric (e) absorptions of the complex **2b** are higher than those of **2a**, **2c**, **2d** and **4** by about 10 cm^{-1}. This phenomenon is attributable to the electron donation from the tricarbonylchromium component to the electron-deficient aromatic ring through the chromium-complexed benzene ring.[14]

Table 2. The comparison of the CO stretching frequencies in IR spectra

	ν(CO) (cm^{-1}) in $CHCl_3$	
Compound	a_1	e
2a (R=H)	1967	1894
2b (R=NO_2)	1976	1908
2c (R=OMe)	1967	1894
2d (R=NMe_2)	1964	1890
4	1967	1894

Thus, in conclusion, all our findings converge into the notion that the tricarbonylchromium moiety can cause the coordinated arene ring to act as a strong π-donor. Although there have been some reports on *inter*molecular charge-transfer interaction of π-(arene)chromium complexes,[12] the present work indicates the first example which clearly demonstrates the π-donor ability of π-(arene)chromium complex through its structural feature as well as spectral data, by the use of structurally well-defined complexes having the *intra*molecular interaction.

The present result is significant in as much as it could redirect the existing avenue of an optically active tricarbonyl(arene)chromium complex with planar chirality and also could lead to the design of new molecules for the development of nonlinear optics based on the π-electron donor and acceptor interaction. Further detailed studies along this line are in progress.

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8. Complex **2a** was obtained in 47% yield by heating a solution of 8-phenyl-1-naphthylboronic acid, tricarbonyl(chlorobenzene)chromium (1.2 equiv), $Pd(PPh_3)_4$ (5 mol %), and Na_2CO_3 (1.2 equiv) in $MeOH-H_2O$ (10:1) at 75 °C for 2.5 h.
9. Bis-chromium complex **3** was obtained in 76% yield by heating a solution of 1,8-diphenylnaphthalene and $Cr(CO)_6$ (4 equiv.) in Bu_2O-THF (10:1) at reflux for 24 h.
10. Crystal data for **2a**: yellow prisms, $C_{24}H_{18}O_3Cr{\bullet}(C_4H_{10})_{1/2}$, FW = 459.48, triclinic, space group $P\bar{1}$, $a = 9.927(1)$ Å, $b = 13.119(1)$ Å, $c = 9.688(2)$ Å, $\alpha = 99.99(1)°$, $\beta = 112.00(1)°$, $\gamma = 93.198(9)°$, $V = 1141.9(3)$ Å^3, $Z = 2$, $D_c = 1.34$ g cm^{-3}, 293 K. Data were collected on a Rigaku AFC7R diffractiometer using $\omega - 2\theta$ scan to a 2θ max of 120.1° with graphite monochromated Cu Kα radiation ($\lambda = 1.54178$ Å). Of 3385 reflections collected, 2035 reflections with $I > 3.0\sigma(I)$ were used in the solution. Structure refined to $R = 0.053$ and $R_w = 0.051$.
11. Crystal data for **3**: yellow prisms, $C_{28}H_{16}O_6Cr_2$, FW = 552.42, orthorhombic, space group $P2_12_12$, a=13.943(1) Å, b=7.852(2) Å, c=10.561(1) Å, V=1156.1(5) Å^3, Z=2, D_c = 1.59 g cm^{-3}, 293 K. Data were collected on a Rigaku AFC7R diffractiometer using $\omega - 2\theta$ scan to a 2θ max of 120.0° with graphite monochromated Cu Kα radiation ($\lambda = 1.54178$ Å). Of 1037 reflections collected, 897 reflections with $I > 3.0\sigma(I)$ were used in the solution. Structure refined to $R = 0.047$ and $R_w = 0.042$.
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