

Nucleophilic substitution reactions of (η^6 -fluorotoluene) $\text{Cr}(\text{CO})_3$ and (η^6 -fluoroanisole) $\text{Cr}(\text{CO})_3$ toward phenylacetylide, fluorenyl, indolinyllithium and carbazolinyllithium: crystal structures of tricarbonyl[η^6 -(1,2-diphenylethynyl)benzene]chromium and tricarbonyl[η^6 -(1,4-fluorenyl)toluene]chromium

Fung-E Hong^{*}, Shih-Chun Lo, Ming-Woei Liou, Lung-Fang Chou, Chu-Chieh Lin

Department of Chemistry, National Chung Hsing University, Taichung 40227, Taiwan

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Abstract

Tricarbonyl[η^6 -(1,2-diphenylethynyl)benzene]chromium (**8a**) was obtained along with tricarbonyl[η^6 -(2-phenylethynyl)anisole]chromium (**7b**) and tricarbonyl[η^6 -(3-phenylethynyl)anisole]chromium (**7a**) from the reaction of tricarbonyl(η^6 -2-fluoroanisole)chromium (**4c**) with lithium phenylacetylide (**3**). The formation of ortho- and meta-products, **7b**, **8a** and **7a**, produced in the above reaction demonstrates that the reaction was by no means through a straightforward nucleophilic substitution mechanism. These results provided support for the mechanism proposed by Pauson and Brookhart, in which the nucleophile attacked the carbon atom of the phenyl ring not bearing the leaving group, followed by hydrogen migration and finally elimination of the leaving group to achieve aromaticity. **8a** was obtained presumably from the reaction of **7b** with excess **3**. Compounds were characterized by mass, infrared, ^1H , ^{13}C NMR spectra. The molecular structure of **8a** has been determined by X-ray diffraction studies. Crystal data are as follows: orthorhombic, P_{BCA} , $a = 18.690(2)$ Å, $b = 10.666(2)$ Å, $c = 20.463(2)$ Å, $V = 4079.3(8)$ Å³, $Z = 8$, $R = 4.41\%$, $R_w = 5.56\%$.

Tricarbonyl(η^6 -4-fluorenyl)toluene]chromium (**10**) was obtained as the only separated product from the reaction of tricarbonyl(η^6 -4-fluorotoluene)chromium (**5**) with fluorenyllithium. The X-ray crystal structure of **10** was determined: monoclinic, $P2_1/c$, $a = 12.318(1)$ Å, $b = 11.498(1)$ Å, $c = 13.585(2)$ Å, $\beta = 100.35(1)^\circ$, $V = 1892.8(5)$ Å³, $Z = 4$, $R = 3.63\%$, $R_w = 5.65\%$. Tricarbonyl(η^6 -4-fluorenylanisole)chromium (**11a**), tricarbonyl(η^6 -3-fluorenylanisole)chromium (**11b**) and tricarbonyl(η^6 -2-fluorenylanisole)chromium (**11c**) were also produced in moderate to good yields. Moreover, tricarbonyl(η^6 -4-indolinyllithium)chromium (**12**) and tricarbonyl(η^6 -4-carbazolinyllithium)chromium (**14**) were synthesized from the reaction of **5** with indolinyllithium and carbazolinyllithium, respectively. Tricarbonyl(η^6 -4-indolinylanisole)chromium (**13a**), tricarbonyl(η^6 -3-indolinylanisole)chromium (**13b**) and tricarbonyl(η^6 -2-indolinylanisole)chromium (**13c**) were obtained in high yields from the direct nucleophilic substitution reactions of related compounds.

Keywords: Cr; Li

1. Introduction

Our previous work has shown that tricarbonyl(η^6 -diphenylacetylene)chromium (**1**) could be obtained from the reaction of tricarbonyl(η^6 -fluorobenzene)chromium (**2**) with lithium phenylacetylide (**3**) [1].

Several **2**-related compounds, **4**, **5** and **6**, were also prepared and carried out nucleophilic substitution reac-

tions under the same reaction condition [2]. The unique result of obtaining meta- and ortho-products, **7a** and **7b**, rather than para-product was noteworthy. Their reaction pathways were more complicated than direct $\text{S}_{\text{N}}\text{Ar}$ mechanism and could seemingly be rationalized by a mechanism, modified from that of Pauson and Brookhart [3], in which nucleophilic attack took place on a carbon atom of the phenyl ring not bearing the leaving group, followed by hydrogen migration and finally elimination of the leaving group to achieve aromaticity.

However, our earlier studies had also shown that the reactions of tricarbonyl(η^6 -fluoroarene)chromium

^{*} Corresponding author.

with oxygen-containing nucleophile, lithium butoxide, seemed to undergo a direct nucleophilic substitution at the fluorine-attached carbon atom under the same reaction. Obviously, the reaction pathways were different for the reactions of $(\eta^6\text{-fluorobenzene})\text{Cr}(\text{CO})_3$ derivatives toward butoxyl group from that toward phenylacetylide.

The regiochemistry of nucleophilic addition to $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ compounds is still quite confusing. While some literature have showed that carbanion addition reactions were under kinetic control and their regioselectivities were interpreted by charge/orbital control and/or influenced by the nature of nucleophiles, other evidence has suggested that there could be a reversible process in the cyclohexadienyl intermediate, namely under thermodynamic control [4–6]. It is, therefore, of interest to us to extend the investigation of reactions of $(\eta^6\text{-fluorobenzene})\text{Cr}(\text{CO})_3$ derivatives with phenylacetylide (**3**) and other nucleophiles such as fluorenyl lithium, indolyl lithium and carbazolyl lithium, to help better understand their pathways and also provide a synthetic method of constructing carbon–arene and nitrogen–arene bonds since these kinds of compound, after removal of the $\text{Cr}(\text{CO})_3$ fragment, are of importance in various biologically active natural products and/or as basic components of templates in molecular recognition [7].

2. Results and discussion

As reported previously, **7a** and **7b** could be obtained from the reaction of **4a** and lithium phenylacetylide (**3**) [1]. Tricarbonyl $[\eta^6\text{-(1,2-diphenylethynyl)benzene}]$ chromium (**8a**), apart from **7a** and **7b**, was obtained with small quantity, 7%, while reacting **4c** with excess **3** [8,9]. The molecular structure of **8a** has been studied by X-ray diffraction determination (Fig. 1). The bond lengths of C(41), C(42) and C(51), C(52) are 1.184 and 1.186 Å respectively. The bond angles of C(41), C(42), C(43) and C(51), C(52), C(53) are 178.4 and 177.6° respectively, (Tables 1, 2 and 3). Accordingly, C(41)–C(42) and C(51)–C(52) bonds are typical triple bonds.

Hunter and co-workers pointed out that the planarity of the arene ring can be distorted by a substituent [10]. An inward distortion $\delta d < 0$, will take place when the substituent is an electron-withdrawing group. In contrast, an outward distortion $\delta d > 0$, is expected for an electron-donating substituent [11]. The above rule is obeyed unless a very bulky substituent is present. Since the phenylacetylide substituent and the arene are joined by conjugated multiple bonds, the former may act as a π electron-donating group in this case. Accordingly, outward distortion shall be found for these two phenylacetylide substituents. Indeed, an outward distortion was observed for one phenylacetylide substituent in **8a**.

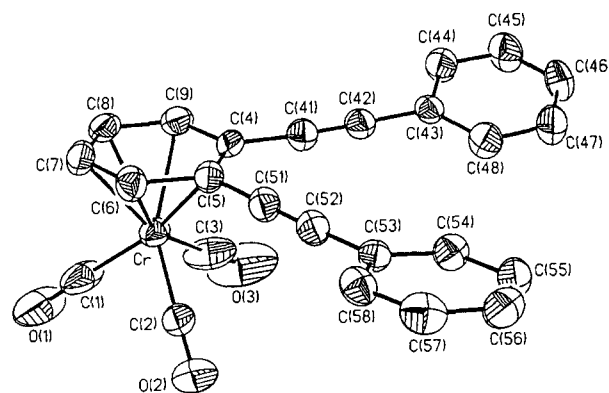


Fig. 1. ORTEP drawing with the numbering scheme of **8a**. Hydrogen atoms were omitted for clarity.

However, a negligible amount of distortion was observed for the other one (Table 3). It seems reasonable for these two phenylethynyl substituents to split a little bit and thus avoid the repulsion from the two neighboring phenyl rings.

The conformation of $\text{Cr}(\text{CO})_3$ in $\text{areneCr}(\text{CO})_3$ is another subject of extensive studies [12]. Generally, an anti-eclipsed form is expected for $\text{areneCr}(\text{CO})_3$ with an electron withdrawing substituent. In contrast, a syn-eclipsed form is expected for $\text{areneCr}(\text{CO})_3$ with an electron donating substituent. However, it will be distorted to a nearly staggered conformer when the substituent is very bulky. As for the disubstituted $\text{areneCr}(\text{CO})_3$ complexes, there are various possible forms. According to Muettterties et al., a staggered

Table 1
Crystal data of **8a**

Formula	$\text{C}_{25}\text{H}_{14}\text{CrO}_3$
Formula weight	414.4
Crystal system	Orthorhombic
Space group	Pbca
a (Å)	18.690(2)
b (Å)	10.666(2)
c (Å)	20.463(2)
V (Å ³)	4079.3(8)
Z	8
D_c (g cm ⁻³)	1.349
$\lambda(\text{Mo K}\alpha)$ (Å)	0.71073
μ (mm ⁻¹)	0.583
Range (deg)	4.0 to 50.0
Scan type	$2\theta - \theta$
No. of reflections collected	7923
No. of independent reflections	3626 ($R_{\text{int}} = 1.40\%$)
No. of observed reflections	2273 ($F > 4.0\sigma(F)$)
No. of refined parameters	262
R_f^a for significant reflections	0.0441
R_w^b for significant reflections	0.0556
GoF ^c	1.22

^a $R_f = [\sum(F_o - F_c)/\sum F_o]$. ^b $R_w = \sum w^{1/2}(F_o - F_c)/\sum w^{1/2}F_o$.
^c $\text{GoF} = [\sum w(F_o - F_c)^2/(N_{\text{rlns}} - N_{\text{params}})]^{1/2}$. $W^{-1} = \sigma^2(F) + 0.0010F^2$.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for **8a**

Atom	x	y	z	U_{eq}^a
Cr	93(1)	1878(1)	3943(1)	60(1)
C(1)	-190(3)	369(5)	3612(3)	129(3)
O(1)	-345(2)	-594(4)	3403(3)	214(3)
C(2)	860(2)	1055(4)	4302(2)	68(1)
O(2)	1342(2)	563(3)	4546(2)	101(1)
C(3)	635(3)	2162(5)	3210(2)	111(2)
O(3)	975(3)	2362(7)	2761(2)	202(3)
C(4)	83(2)	3940(3)	4138(2)	57(1)
C(5)	176(2)	3285(3)	4734(2)	57(1)
C(6)	-330(2)	2357(3)	4921(2)	67(1)
C(7)	-906(2)	2077(4)	4515(2)	77(2)
C(8)	-995(2)	2697(4)	3928(2)	75(2)
C(9)	-506(2)	3619(4)	3735(2)	68(1)
C(41)	566(2)	4906(3)	3938(2)	66(1)
C(42)	943(2)	5756(3)	3798(2)	64(1)
C(43)	1394(2)	6806(4)	3641(2)	57(1)
C(44)	1194(2)	7658(4)	3165(2)	77(2)
C(45)	1633(3)	8866(3)	3031(2)	91(2)
C(46)	2249(3)	8840(3)	3358(2)	84(2)
C(47)	2454(2)	8022(4)	3828(2)	84(2)
C(48)	2028(2)	6999(4)	3968(2)	76(2)
C(51)	771(2)	3556(3)	5148(2)	61(1)
C(52)	1261(2)	3798(4)	5494(2)	61(1)
C(53)	1836(2)	4124(3)	5929(2)	53(1)
C(54)	2356(2)	4974(4)	5740(2)	68(1)
C(55)	2891(2)	5311(4)	6167(2)	75(2)
C(56)	2911(2)	4804(4)	6778(2)	78(2)
C(57)	2408(2)	3956(4)	6968(2)	78(2)
C(58)	1871(2)	3616(3)	6551(2)	64(1)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

conformation is preferred for an ortho-substitution areneCr(CO)₃ complex with two identical substituents [12a]. This is the case in **8a**. The conformation of the Cr(CO)₃ fragment in **8a** is nearly staggered (Fig. 2).

Interestingly, the closely related compound, tricarbonyl[η^6 -(1,3-diphenylethynyl)benzene]chromium (**8b**), was not found in the above reaction of **4c** and **3**. Furthermore, **8a** could be obtained in slightly higher yield, 27%, by reacting purified **7b** with lithium phenylacetylide (**3**). Under the same reaction condition, **8b** was, however, not yielded from the reaction of **7a** with **3** [13]. (More detailed results have been summarized in Table 4.) These results are in accord with our previous observation, in which **8a** was supposed to be produced from the reaction of the formed **7b** undergoing further reaction with excess lithium phenylacetylide [14,15].

On the contrary, only with excess of lithium phenylacetylide could tricarbonyl(η^6 -2-phenylethynyl-toluene)chromium (**9**) be obtained from the reaction of tricarbonyl(η^6 -4-fluorotoluene)chromium (**5**) and lithium phenylacetylide (**3**) in high yields, 74%, under similar reaction condition as described above [16]. The expected para-product was not obtained either. Unlike meta-dominant products observed in the former reaction of **4** with **3**, it is the ortho-complex that was formed as the only separated product. This result also conflicted with the meta-preferable compounds in the addition reactions of carbanions to tricarbonyl(η^6 -toluene)chromiums [17].

With various orientations and yields, the seemingly unusual random distribution of products was quite confusing at the first glance, see Table 4. However, Bodner and Todd had closely studied a series of areneCr(CO)₃ compounds and stated that the ratio and the orientation of the products were affected both by the kind of substituent(s) and its(their) position(s) on the ring [18]. For example, both -OMe and -F substituents will activate the *meta*-carbon atom in the ring, and the -Me group will, in contrast, activate the *ortho*-carbon atom, which is different from the general observation [17] of

Table 3
Selected bond distances (\AA) and angles (deg)

Cr-C(1)	1.825(6)	Cr-C(2)	1.834(4)
Cr-C(3)	1.835(5)	Cr-C(4)	2.235(3)
Cr-C(5)	2.212(3)	Cr-C(6)	2.212(4)
Cr-C(7)	2.214(4)	Cr-C(8)	2.215(4)
Cr-C(9)	2.211(4)	C(1)-O(1)	1.149(7)
C(2)-O(2)	1.155(5)	C(3)-O(3)	1.137(7)
C(4)-C(5)	1.416(5)	C(5)-C(6)	1.422(5)
C(6)-C(7)	1.393(6)	C(7)-C(8)	1.381(7)
C(8)-C(9)	1.400(5)	C(4)-C(9)	1.418(5)
C(4)-C(41)	1.429(5)	C(5)-C(51)	1.428(7)
C(41)-C(42)	1.184(5)	C(42)-C(43)	1.439(5)
C(51)-C(52)	1.186(5)	C(52)-C(53)	1.438(5)
C(1)-Cr-C(2)	87.3(2)	C(2)-Cr-C(3)	88.6(2)
C(1)-Cr-C(3)	90.1(3)	Cr-C(1)-O(1)	177.7(4)
Cr-C(2)-O(2)	177.7(4)	Cr-C(3)-O(3)	178.5(6)
C(4)-C(41)-C(42)	175.9(4)	C(5)-C(51)-C(52)	179.1(4)
C(5)-C(4)-C(41)	121.6(3)	C(4)-C(5)-C(51)	120.5(3)
C(41)-C(42)-C(43)	178.4(4)	C(51)-C(52)-C(53)	177.6(4)

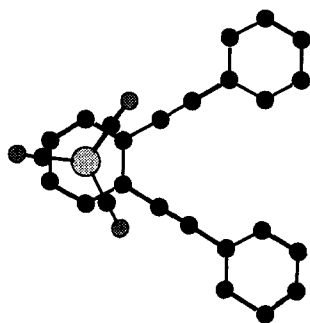


Fig. 2. Top view of **8a**. Hydrogen atoms have been omitted for clarity.

the meta-position activated by electron donating groups, e.g. $-\text{OMe}$ and $-\text{Me}$. Moreover, the degree of this activation is in the order of $-\text{OMe} > -\text{Me} > -\text{F}$. By taking **5** as an example (Table 4, entry 6), carbon atoms on the positions adjacent to the $-\text{Me}$ group are activated by both $-\text{Me}$ and $-\text{F}$ groups in this case as indicated in Scheme 1. Phenylacetylide, therefore, attacked on the according *ortho*-carbon atom of the arene ring, followed by undergoing Brookhart's pathway and led to *ortho*-product in major quantity. Closely examining the resulting major proportion of **7a** in the reactions of **4** and **3** (entries 1, 2 and 3), one finds that Bodner and

Table 4

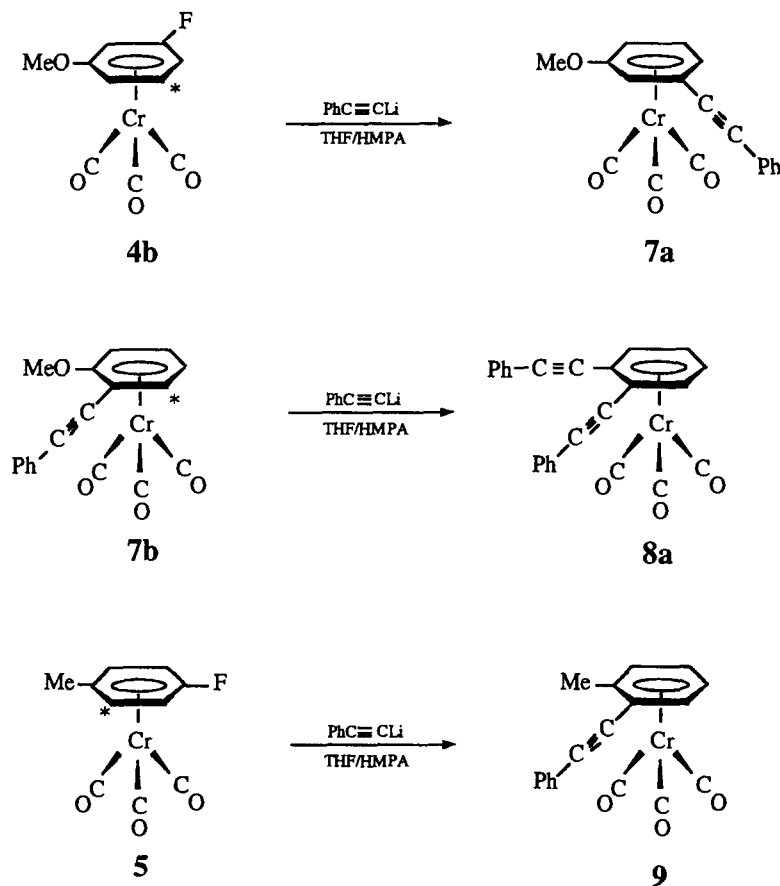
The distribution of products from the reactions of tricarbonyl(η^6 -fluoroarene)chromium with **3**^a

Entry	Reactant	Product		
		<i>ortho</i> -	<i>meta</i> -	<i>para</i> -
1	4a	7b (21%)	7a (32%)	— ^b
2	4b	— ^b	7a (22%)	— ^b
3	4c	7b (8%)/ 8a (7%)	7a (20%)	— ^b
4	7b	8a (27%)	— ^b	— ^b
5	7a	— ^b	— ^c	— ^b
6	5	9 (74%) ^d	— ^b	— ^b

^a 2.25 equivalent was used except entry 6 (see Ref. [16]). ^b Not obtained. ^c **7a** was recovered almost quantitatively. ^d 2.00 equivalent used.

Todd's rule seemed to be obeyed. In addition, the results of obtaining **8a** instead of **8b** from **7b** with **3** (entry 4) and no desired **8a** or **8b** yielded directly from **7a** with **3** (entry 5) suggested that phenylethynyl group activated the *ortho*-position in the arene ring just like methyl group did.

The Bodner and Todd rule seemed to be suitable for explaining the positions predominately attacked by lithium phenylacetylide while toward (η^6 -fluoroarene)chromium, as described above. However, this rule apparently could not rationalize the fact of the direct



Scheme 1. (Carbons labeled with an asterisk represent the activated positions.)

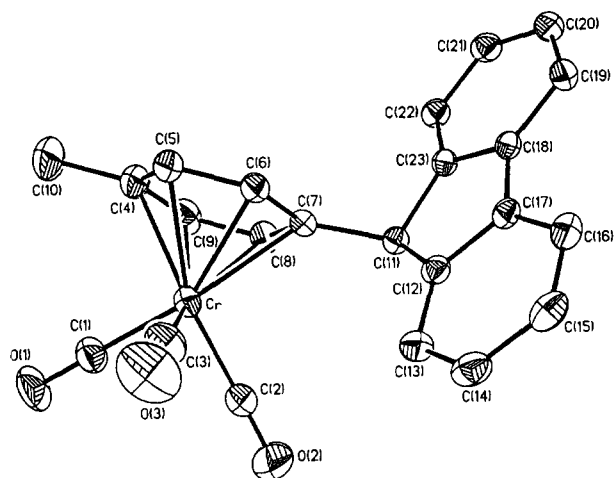


Fig. 3. ORTEP drawing with the numbering scheme of **10**. Hydrogen atoms were omitted for clarity.

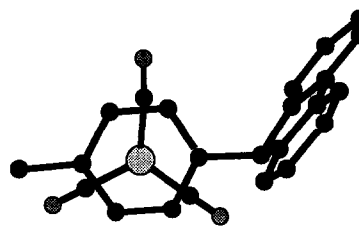


Fig. 4. Top view of **10**. Hydrogen atoms have been omitted for clarity.

substitution of fluoride by butoxyl group. Therefore, efforts to vary the nucleophiles such as fluorenyl lithium, indolinyl lithium and carbazolinyllithium to approach tricarbonyl(η^6 -fluoroarene)chromium have been made; these are summarized in Table 5.

Interestingly, only the para-product, tricarbonyl(η^6 -4-fluorenyltoluene)chromium (**10**), was obtained from the reaction of fluorenyl lithium with **5** (Table 5, entry 1). **10** was characterized by mass, infrared, and ^1H , ^{13}C NMR spectra. Its X-ray diffraction studies supported this structure, in which the two substituents, methyl and fluorenyl, are at the para position (Figs. 3 and 4). The dihedral angle between the fluorenyl and arene $\text{Cr}(\text{CO})_3$ -ring is quite large (Tables 6, 7 and 8) [19]. Besides, the orientation of the $\text{Cr}(\text{CO})_3$ fragment in **10** is nearly staggered.

The formation of para-compound **10** was very similar with the results of the butoxyl case. However, this was apparently in conflict with the Bodner and Todd rule, in which the ortho-position was predicted to be activated both by $-\text{Me}$ and $-\text{F}$ groups in **5** (Scheme 1). Similarly, reactions of **4a**, **4b** and **4c** with fluorenyl lithium, (entries 2, 3 and 4) respectively afforded tricarbonyl(η^6 -

4-fluorenylanisole)chromium (**11a**), tricarbonyl(η^6 -3-fluorenylanisole)chromium (**11b**) and tricarbonyl(η^6 -2-fluorenylanisole)chromium (**11c**) in moderate to good yields. These results also suggested that they did not follow the Bodner and Todd rule, which should have the major distribution at the meta position.

Moreover, direct nucleophilic displacement reactions were also observed while employing nitrogen-containing nucleophiles [20] such as indolinyl lithium, and carbazolinyllithium [21] lithium. Tricarbonyl(η^6 -4-indolinyltoluene)chromium (**12**) was obtained in much higher yields, 80%, (entry 5). Tricarbonyl(η^6 -4-indolinylanisole)chromium (**13a**), tricarbonyl(η^6 -3-indolinylanisole)chromium (**13b**) and tricarbonyl(η^6 -2-indolinylanisole)chromium (**13c**) were obtained from the reactions of **4a**, **4b** and **4c** with deprotonated indole in yields of 85%, 95% and 96% (entries 6, 7 and 8) respectively. In addition, with a bulkier nucleophile, carbazolinyllithium, tricarbonyl(η^6 -4-carbazolinylltoluene)chromium (**14**) was obtained with slightly lower yields, 37%, from the reaction of **5** (entry 9).

As illustrated in Table 5, it has been suggested that all these reactions underwent direct nucleophilic displacement reactions. This is consistent with our previous studies of direct nucleophilic substitution by an oxygen-containing nucleophile, lithium butoxide, and is definitely distinct from that of phenylacetylide with numerous distribution (Table 4). It is quite puzzling that the Todd rule could be applied to the cases when the nucleophile is phenylacetylide but is no longer valid for other nucleophiles such as butoxyl, fluorenyl, indolinyl

Table 5
Nucleophilic substitution reactions of tricarbonyl(η^6 -fluoroarene)chromium with fluorenyl lithium, indolinyl lithium and carbazolinyllithium

Entry	Reactant	Nucleophile	Product/position	Yield(%)	SM(%) ^a
1	5	fluorenyl	10 /para-	49	12
2	4a	fluorenyl	11a /para-	36	31
3	4b	fluorenyl	11b /meta-	51	20
4	4c	fluorenyl	11c /ortho-	81	— ^b
5	5	indolinyl	12 /para-	80	2
6	4a	indolinyl	13a /para-	85	— ^b
7	4b	indolinyl	13b /meta-	95	— ^b
8	4c	indolinyl	13c /ortho-	96	— ^b
9	5	carbazolinyll	14 /para-	37 ^c	34

^a Amount of unreacted starting material recovered. ^b Not determined. ^c In which 8% was 4-carbazolinylltoluene (**15**), resulting from **14** after releasing $\text{Cr}(\text{CO})_3$ moiety.

Table 6
Crystal data of 10

Formula	C ₂₃ H ₁₆ CrO ₃
Formula weight	392.4
Crystal system	Monoclinic
Space group	P2 ₁ /c
a (Å)	12.318(1)
b (Å)	11.498(1)
c (Å)	13.585(2)
β (deg)	100.35(1)
V (Å ³)	1892.8(5)
Z	4
D _c (g cm ⁻³)	1.377
λ(Mo K α) (Å)	0.71073
μ(mm ⁻¹)	0.624
Range (deg)	4.0 to 50.0
Scan type	2θ - θ
No. of reflections collected	6889
No. of independent reflections	3286 (R _{int} = 2.26%)
No. of observed reflections	2857 (F > 4.0σ(F))
No. of refined parameters	244
R _f ^a for significant reflections	0.0363
R _w ^b for significant reflections	0.0565
GoF ^c	1.40

^a $R_f = [\sum(F_o - F_c)/\sum F_o]$. ^b $R_w = \sum w^{1/2}(F_o - F_c)/\sum w^{1/2}F_o$.
^c GOF = $[\sum w(F_o - F_c)^2 / (N_{\text{reflms}} - N_{\text{params}})]^{1/2}$. $W^{-1} = \sigma^2(F) + 0.0010F^2$.

and carbazolynyl. Although this seemingly implied that phenylacetylide cases were under kinetic control with major distribution by the Todd rule, and other nucleophiles such as butoxyl, fluorenyl, indolynyl and carbazolynyl were under thermodynamic control without following the Todd prediction, the formation of ortho-complexes, **11c** and **13c**, or meta-compounds, **11b** and **13b**, rather than para-ones, **11a** and **13a**, suggested that it is not so proper to interpret them in terms of thermodynamics as in terms of the nature of the nucleophiles.

At present there seem to be no appropriate rules that could thoroughly rationalize all these experimental results. Nevertheless, these reactions have provided a mild and convenient synthetic method for constructing nitrogen-arene and carbon-arene bonds.

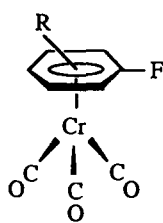
Table 7
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^3$) for 10

Atom	x	y	z	U _{eq} ^a
Cr	6398(1)	841(1)	6771(1)	38(1)
C(1)	4945(2)	575(2)	6828(2)	54(1)
O(1)	4035(2)	384(2)	6873(2)	84(1)
C(2)	6562(2)	-743(2)	6722(2)	54(1)
O(2)	6643(2)	-1743(2)	6697(2)	87(1)
C(3)	6686(2)	764(3)	8144(2)	63(1)
O(3)	6852(3)	728(3)	9002(2)	113(1)
C(4)	5924(2)	2545(2)	6003(2)	57(1)
C(5)	6824(2)	2720(2)	6771(2)	54(1)
C(6)	7803(2)	2064(2)	6832(2)	41(1)
C(7)	7901(2)	1223(2)	6108(2)	36(1)
C(8)	6982(2)	1030(2)	5334(2)	44(1)
C(9)	6017(2)	1682(2)	5279(2)	56(1)
C(10)	4881(2)	3254(3)	5921(3)	86(1)
C(11)	8965(2)	569(2)	6085(2)	33(1)
C(12)	9697(2)	279(2)	7078(1)	35(1)
C(13)	9457(2)	-368(2)	7871(2)	45(1)
C(14)	10294(2)	-581(2)	8681(2)	51(1)
C(15)	11351(2)	-167(2)	8692(2)	48(1)
C(16)	11600(2)	478(2)	7908(2)	42(1)
C(17)	10760(2)	708(2)	7096(2)	34(1)
C(18)	10782(2)	1347(2)	6165(1)	33(1)
C(19)	11632(2)	1952(2)	5843(2)	41(1)
C(20)	11418(2)	2479(2)	4911(2)	46(1)
C(21)	10384(2)	2405(2)	4312(2)	45(1)
C(22)	9532(2)	1808(2)	4629(2)	39(1)
C(23)	9739(2)	1276(2)	5565(1)	32(1)

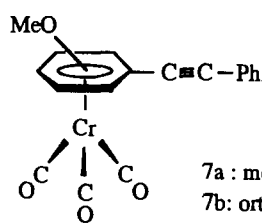
^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 8
Selected bond distances (Å) and angles (deg)

Cr-C(1)	1.831(3)	Cr-C(2)	1.834(3)
Cr-C(3)	1.837(3)	Cr-C(4)	2.248(3)
Cr-C(5)	2.223(2)	Cr-C(6)	2.220(2)
Cr-C(7)	2.243(2)	Cr-C(8)	2.210(2)
Cr-C(9)	2.218(3)	C(1)-O(1)	1.154(3)
C(2)-O(2)	1.155(3)	C(3)-O(3)	1.147(4)
C(4)-C(10)	1.509(4)	C(7)-C(11)	1.516(3)
C(1)-Cr-C(2)	87.2(1)	C(2)-Cr-C(3)	89.2(1)
C(1)-Cr-C(3)	87.7(1)	Cr-C(1)-O(1)	178.6(2)
Cr-C(2)-O(2)	178.5(3)	Cr-C(3)-O(3)	179.0(3)
C(5)-C(4)-C(10)	122.0(3)	C(9)-C(4)-C(10)	120.2(2)
C(6)-C(7)-C(11)	122.8(2)	C(8)-C(7)-C(11)	119.0(2)



- 4a: R = OMe; para
 4b: R = OMe; meta
 4c: R = OMe; ortho
 5: R = Me; para
 6: R = CO₂Me; para



- 7a: meta
 7b: ortho

3. Experimental section

3.1. Apparatus and materials

All operations were performed in a nitrogen-flushed glove box or in a vacuum system. Freshly distilled solvents were used. All processes of separation of the products were performed by centrifugal thin-layer chromatography (TLC, Chromatotron, Harrison model 8924). ^1H and ^{13}C NMR spectra were recorded (Varian-300 spectrometer) at 300 and 75.46 MHz respectively; chemical shifts are reported in ppm relative to internal TMS. IR spectra of solution in CHCl_3 were recorded on a Hitachi 270-30 spectrometer. Mass spectra were recorded on a Joel JMS-SX/SX 102A GC/MS/MS spectrometer.

3.2. General procedure for preparations of $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$, (10–14)

Into a 50 ml flask was placed indole (125 mg, 1.063 mmol, 2.0 eq), which was evacuated under reduced pressure for 10 min and then filled with $\text{N}_2(\text{g})$. The reaction flask was followed by adding 1.6 ml of anhydrous THF and cooled to -78°C (acetone– $\text{N}_2(\text{l})$ -bath). Next, *n*-BuLi (1.60 M, 0.4 ml, 0.638 mmol, 1.2 eq) was added drop by drop to the cold reaction flask. The deprotonation process was carried out at that temperature for 1.2 h and then HMPA added (0.56 ml, 3.190 mmol, 6.0 eq). 30 min later, a solution of tricarbonyl(η^6 -4-fluorotoluene)chromium (**5**) (131 mg, 0.532 mmol) in 1.0 ml of anhydrous THF was added slowly to the cold reaction mixture. The reaction was well stirred at -78°C for another 3 h and gently warmed to 20°C during the next 16 h.

Subsequently, the resulting yellow solution was filtered through a small amount of silica gel. The filtrate was evaporated under reduced pressure to yield crude product. On purification with centrifugal thin-layer chromatography (eluent: hexane), a yellow band of tricarbonyl(η^6 -4-indolinyltoluene)chromium (**12**) was isolated (145 mg, 79.7%). In addition, a small amount (3 mg, 2.3%) of unreacted tricarbonyl(η^6 -4-fluorotoluene)chromium (**5**) was recovered.

12: ^1H NMR (CDCl_3): δ 2.25 (s, 3H, Me), 5.41 (d, $J = 6.6$ Hz, 2H, areneCr(CO) $_3$), 5.79 (d, $J = 6.6$ Hz, 2H, areneCr(CO) $_3$), 6.66 (d, $J = 3.2$ Hz, 1H, vinyl-H for indoliny), 7.25 (m, 3H, vinyl-H for indoliny and arene in indoliny), 7.63 (m, 2H, arene in indoliny); ^{13}C NMR (CDCl_3): δ 20.009 (3C, Me), 89.697 (2C, areneCr(CO) $_3$), 92.476 (2C, areneCr(CO) $_3$), 105.257 (1C, C=C), 106.767 (1C, *ipso* of areneCr(CO) $_3$), 110.423 (1C, C=C), 113.917 (1C, *ipso* of areneCr(CO) $_3$), 121.727, 121.276, 123.180, 128.307 (4C, arene in indoliny), 129.791 (1C, *ipso* of arene in indoliny), 136.374 (1C, *ipso* of arene in indoliny), 232.744 (3C,

3CO); IR(CHCl_3): $\nu_{(\text{CO})}$ 1908, 1976 cm^{-1} ; MS m/z 343 (P^+).

8a: ^1H NMR (CDCl_3): δ 5.32, 5.63 (m, 4H, areneCr(CO) $_3$), 7.36, 7.53 (m, 10H, Ph); ^{13}C NMR (CDCl_3): δ 84.770 (2C, $-\text{C}\equiv\text{C}-$), 89.826 (2C, areneCr(CO) $_3$), 92.434 and 92.888 (2C, *ipso* of areneCr(CO) $_3$), and 2C, $-\text{C}\equiv\text{C}-$), 93.743 (2C, areneCr(CO) $_3$), 122.057 (2C, *ipso* of arene), 128.457 (4C, arene), 129.134 (2C, arene), 131.991 (4C, arene), 231.853 (3C, CO); IR(CHCl_3): $\nu_{(\text{CO})}$ 1986(s), 1917(s) cm^{-1} ; MS m/z 414(P^+);

9: ^1H NMR (CDCl_3): δ 2.42 (s, 3H, Me), 5.24 (m, 2H, areneCr(CO) $_3$), 5.37 (d, $J = 6.2$ Hz, 1H, areneCr(CO) $_3$), 5.70 (d, $J = 6.4$ Hz, 1H, areneCr(CO) $_3$), 7.40 (m, 3H, Ph), 7.56 (m, 2H, Ph); ^{13}C NMR (CDCl_3): δ 19.970 (1C, Me), 84.325 (1C, $-\text{C}\equiv\text{C}-$), 89.052 (1C, areneCr(CO) $_3$), 90.004 (1C, *ipso* of areneCr(CO) $_3$), 92.069 (1C, areneCr(CO) $_3$), 92.185 (1C, $-\text{C}\equiv\text{C}-$), 92.621 (1C, areneCr(CO) $_3$), 96.502 (1C, areneCr(CO) $_3$), 110.575 (1C, *ipso* of areneCr(CO) $_3$), 121.995 (2C, *ipso* of arene), 128.439 (2C, arene), 129.000 (1C, arene), 131.813 (2C, arene), 232.663 (3C, CO); IR(CDCl_3): $\nu_{(\text{CO})}$ 1908, 1980 cm^{-1} .

10: ^1H NMR (CDCl_3): δ 2.17 (s, 3H, Me), 4.75 (s, 1H, H in fluorenyl), 5.10 (d, $J = 6.1$ Hz, 2H, areneCr(CO) $_3$), 5.26 (d, $J = 6.1$ Hz, 2H, areneCr(CO) $_3$), 7.40 (m, 4H, arene in fluorenyl), 7.69 (d, $J = 7.0$ Hz, 2H, arene in fluorenyl), 7.78 (d, $J = 7.0$ Hz, 2H, arene in fluorenyl); ^{13}C NMR (CDCl_3): δ 20.136 (3C, Me), 50.883 (1C, CH in fluorenyl), 92.571 (2C, areneCr(CO) $_3$), 93.597 (2C, areneCr(CO) $_3$), 109.270 (1C, *ipso* of areneCr(CO) $_3$), 110.363 (1C, *ipso* of areneCr(CO) $_3$), 120.201 (2C, arene in fluorenyl), 125.412 (2C, arene in fluorenyl), 127.630 (2C, arene in fluorenyl), 128.293 (2C, arene in fluorenyl), 141.015 (2C, *ipso* of arene in fluorenyl), 144.660 (2C, *ipso* of arene in fluorenyl), 233.830 (3C, 3CO); IR(CHCl_3): $\nu_{(\text{CO})}$ 1894, 1970 cm^{-1} ; MS m/z 392 (P^+).

11a: ^1H NMR (CDCl_3): δ 3.65 (s, 3H, OMe), 4.65 (s, 1H, H in fluorenyl), 5.04 (d, $J = 6.8$ Hz, 2H, areneCr(CO) $_3$), 5.34 (d, $J = 6.8$ Hz, 2H, areneCr(CO) $_3$), 7.38 (m, 4H, arene in fluorenyl), 7.66 (d, $J = 7.2$ Hz, 2H, arene in fluorenyl), 7.76 (d, $J = 7.2$ Hz, 2H, arene in fluorenyl); ^{13}C NMR (CDCl_3): δ 50.643 (1C, CH in fluorenyl), 55.610 (3C, OMe), 77.819 (2C, areneCr(CO) $_3$), 93.618 (2C, areneCr(CO) $_3$), 106.480 (1C, *ipso* of areneCr(CO) $_3$), 114.100 (1C, *ipso* of areneCr(CO) $_3$), 120.099 (2C, arene in fluorenyl), 125.449 (2C, arene in fluorenyl), 127.549 (2C, arene in fluorenyl), 128.217 (2C, arene in fluorenyl), 140.848 (2C, *ipso* of arene in fluorenyl), 144.782 (2C, *ipso* of arene in fluorenyl), 233.437 (3C, 3CO); MS m/z 408 (P^+).

11b: ^1H NMR (CDCl_3): δ 3.74 (s, 3H, OMe), 4.95 (m, 1H, areneCr(CO) $_3$), 5.06 (s, 1H, H in fluorenyl), 5.68 (m, 2H, areneCr(CO) $_3$), 5.85 (m, 1H,

areneCr(CO)₃), 6.70 (m, 1H, arene in fluorenyl), 6.89 (m, 2H, arene in fluorenyl), 7.39 (m, 4H, arene in fluorenyl), 7.68 (m, 1H, arene in fluorenyl); MS *m/z* 408 (P⁺).

11c: ¹H NMR (CDCl₃): δ 3.94 (s, 3H, OMe), 4.66 (s, 1H, H in fluorenyl), 4.70 (m, 1H, areneCr(CO)₃), 5.13 (d, *J* = 6.6 Hz, 1H, areneCr(CO)₃), 5.45 (m, 2H, areneCr(CO)₃), 7.22 (m, 1H, arene in fluorenyl), 7.36 (m, 1H, arene in fluorenyl), 7.45 (m, 3H, arene in fluorenyl), 7.77 (m, 2H, arene in fluorenyl), 7.98 (m, 1H, arene in fluorenyl); MS *m/z* 408 (P⁺).

13a: ¹H NMR (CDCl₃): δ 3.76 (s, 3H, OMe), 5.26 (d, *J* = 6.6 Hz, 2H, areneCr(CO)₃), 5.89 (d, *J* = 6.6 Hz, 2H, areneCr(CO)₃), 6.61 (d, *J* = 2.6 Hz, 1H, vinyl-H for indoliny), 7.21 (m, 3H, vinyl-H for indoliny and arene in indoliny), 7.50 (d, *J* = 8.0 Hz, 1H, arene in indoliny), 7.64 (d, 1H, *J* = 7.6 Hz, arene in indoliny); ¹³C NMR (CDCl₃): δ 55.984 (3C, OMe), 76.706 (2C, areneCr(CO)₃), 91.820 (2C, areneCr(CO)₃), 104.682 (1C, C = C), 108.456 (1C, *ipso* of areneCr(CO)₃), 109.889 (1C, C = C), 129.410 (1C, *ipso* of areneCr(CO)₃), 121.016, 121.568, 123.001, 128.991 (4C, arene in indoliny), 123.860 (1C, *ipso* of arene in indoliny), 141.382 (1C, *ipso* of arene in indoliny), 232.245 (3C, 3CO); IR(CHCl₃): ν_(CO) 1905, 1980 cm⁻¹; MS *m/z* 359 (P⁺).

13b: ¹H NMR (CDCl₃): δ 3.82 (s, 3H, OMe), 5.04 (dd, *J* = 6.6, 1.8 Hz, 1H, areneCr(CO)₃), 5.38 (dd, *J* = 6.6, 1.0 Hz, 1H, areneCr(CO)₃), 5.67 (m, 1H, areneCr(CO)₃), 5.76 (dd, *J* = 6.6, 6.6 Hz, 1H, areneCr(CO)₃), 6.69 (d, *J* = 2.8 Hz, 1H, vinyl-H for indoliny), 7.28 (m, 3H, vinyl-H for indoliny and arene in indoliny), 7.68 (m, 2H, arene in indoliny); ¹³C NMR (CDCl₃): δ 55.859 (3C, OMe), 74.685, 75.246, 80.943, 93.200 (4C, areneCr(CO)₃), 105.902 (1C, C = C), 111.118 (1C, C = C), 119.095 (1C, *ipso* of areneCr(CO)₃), 130.059 (1C, *ipso* of areneCr(CO)₃), 121.532, 121.764, 123.259, 127.540 (4C, arene in indoliny), 135.783 (1C, *ipso* of arene in indoliny), 142.975 (1C, *ipso* of arene in indoliny), 232.734 (3C, 3CO); IR(CHCl₃): ν_(CO) 1976, 1900 cm⁻¹; MS *m/z* 359 (P⁺).

13c: ¹H NMR (CDCl₃): δ 3.75 (s, 3H, OMe), 5.01 (dd, *J* = 6.8, 5.4 Hz, 1H, areneCr(CO)₃), 5.23 (d, *J* = 6.6 Hz, 1H, areneCr(CO)₃), 5.63 (ddd, *J* = 6.8, 6.4, 1.4 Hz, 1H, areneCr(CO)₃), 5.97 (d, *J* = 6.6 Hz, 1H, areneCr(CO)₃), 6.63 (d, *J* = 3.6 Hz, 1H, vinyl-H for indoliny), 7.25 (m, 4H, vinyl-H for indoliny and arene in indoliny), 7.66 (dd, *J* = 6.2, 2.0 Hz, 1H, arene in indoliny); ¹³C NMR (CDCl₃): δ 56.171 (3C, OMe), 73.386, 83.587, 93.823, 96.698 (4C, areneCr(CO)₃), 103.534 (1C, C = C), 110.067 (1C, C = C), 102.831 (1C, *ipso* of areneCr(CO)₃), 129.249 (1C, *ipso* of areneCr(CO)₃), 120.687, 121.310, 122.529, 131.786 (4C, arene in indoliny), 137.608 (1C, *ipso* of arene in indoliny), 139.406 (1C, *ipso* of arene in indoliny),

232.156 (3C, 3CO); IR(CHCl₃): ν_(CO) 1905, 1980 cm⁻¹; MS *m/z* 359 (P⁺).

14: ¹H NMR (CDCl₃): δ 2.30 (s, 3H, Me), 5.48 (d, *J* = 6.7 Hz, 2H, areneCr(CO)₃), 5.83 (d, *J* = 6.7 Hz, 2H, areneCr(CO)₃), 7.34 (dd, *J* = 7.4 and 7.7 Hz, 2H, arene in carbazoliny), 7.52 (dd, *J* = 7.4 and 8.2 Hz, 2H, arene in carbazoliny), 7.83 (d, *J* = 8.2 Hz, 2H, arene in carbazoliny), 8.11 (d, *J* = 7.7 Hz, 2H, arene in carbazoliny); ¹³C NMR (CDCl₃): δ 20.066 (3C, Me), 90.261 (2C, areneCr(CO)₃), 92.945 (2C, areneCr(CO)₃), 106.100 (1C, *ipso* of areneCr(CO)₃), 110.910 (2C, arene in carbazoliny), 112.479 (1C, *ipso* of areneCr(CO)₃), 120.472 (2C, arene in carbazoliny), 121.191 (2C, arene in carbazoliny), 124.347 (2C, *ipso* of arene in carbazoliny), 126.473 (2C, arene in carbazoliny), 140.108 (2C, *ipso* of arene in carbazoliny), 232.789 (3C, 3CO); IR(CHCl₃): ν_(CO) 1904, 1978 cm⁻¹; MS *m/z* 393 (P⁺).

15: ¹H NMR (CDCl₃): δ 2.51 (s, 3H, Me), 7.30 (m, 2H), 7.43 (m, 8H), 8.17 (m, 2H); ¹³C NMR (CDCl₃): δ 21.172 (3C, Me), 109.783 (2C, arene), 119.716 (2C, arene), 120.259 (2C, arene), 123.241 (2C, *ipso*), 125.849 (2C, arene), 127.015 (2C, arene), 130.487 (2C, arene), 135.017 (1C, *ipso*), 137.394 (1C, *ipso*), 141.088 (2C, *ipso*); MS *m/z* 257 (P⁺).

3.3. Crystal structure determination of **8a** and **10**

A red parallelepiped crystal of **8a** with size of 0.2 × 0.4 × 0.5 mm³ and a yellow parallelepiped crystal of **10** with size of 0.4 × 0.6 × 0.7 mm³ were used for X-ray diffraction measurements. The intensities were collected on a Siemens R3m/V diffractometer equipped with graphite-monochromated Mo Kα radiation, λ = 0.71073 Å. The positions of heavy atoms in the structure were determined by direct methods, and the remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least squares techniques. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were considered to ride on carbon atoms with a C–H bond length 0.96 Å, and the temperature factors were fixed at 0.08 Å². The hydrogen atoms were included for structure factor calculation in the final cycles. All refinements and calculations were carried out with the Siemens SHELXTL PLUS software package on a MicroVAX 3100 computer.

The crystallographic data of the complex **8a** and **10** are summarized in Tables 1 and 6. Atomic coordinates of **8a** and **10** are given in Tables 2 and 7 respectively.

4. Supplementary material available

Tables of thermal parameters, bond lengths and angles, anisotropic thermal parameters, and H atom coordinates for **8a** and **10** are available from the authors.

Acknowledgment

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