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Nucleophilic substitution reactions of acetylides on substituted tricarbonyl(η^6 -fluoroarene)chromium and reactions of tricarbonyl[η^6 -(2-trimethylsilylethynyl)toluene]chromium and tricarbonyl[η^6 -(*p*-ethynyl-phenylethynyl)benzene]chromium with dicobalt octacarbonyl

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Abstract

Nucleophilic substitution reactions of various acetylides on substituted tricarbonyl(η^6 -fluoroarene)chromiums were pursued. The reaction presumably underwent a more complicated mechanism rather than the direct substitution on the fluorine-bearing carbon. The organometallic compounds (η^6 -C₆H₃R¹R²R³)Cr(CO)₃ (R¹: C≡C-C₆H₄CH₃, R²: *o*-Me, R³: H (**5a**), R¹: C≡C-C₆H₄CH₃, R²: *o*-OMe, R³: H (**5a**), R¹: C≡C-C₆H₄CH₃, R²: *o*-OMe, R³: H (**5a**), R¹: C≡C-C₆H₄CH₃, R²: *o*-OMe, R³: H (**6b**), R¹: C≡CPh, R²: *o*-Me, R³: O-OMe (**8b**), R¹: C≡CPh, R²: *o*-Me, R³: m-OMe, R³: H (**5a**), R¹: C≡CPh, R²: *o*-Me, R³: H (**5b**), R¹: C≡CPh, R²: *o*-Me, R³: H (**12**), R¹: C≡C-C₆H₄C≡CH, R²: *o*-Me, R³: H (**13**)) as well as the organometallic dimmer [{(η^6 -*o*-Me-C₆H₄)Cr(CO)₃(di-ethynyl)] (di-ethynyl): C≡C-C₆H₄C≡C (**14**)) have been synthesized from nucleophilic substitution reactions of tricarbonyl(η^6 -fluoroarene)(chromium) compounds with suitable acetylides. The products have been characterized by spectroscopic means. In addition, (**8b**) and (**8c**) were characterized by X-ray diffraction studies. Further reactions of (**9a**) and (**12**) with appropriate amount of Co₂(CO)₈ yielded μ -alkyne bridged bimetallic complexes, Co₂(CO)₆{ μ -Me₃SiC≡C-(*o*-tolueneC-r(CO)₃}{(**10**) and (Co₂(CO)₆)₂{ μ -HC≡C-C₆H₄-C≡C-(benzene)Cr(CO)₃)}{(**15**), respectively. Both (**10**) and (**15**) were characterized by spectroscopic means as well as single crystal X-ray crystallography. The core of these molecules is quasi-tetrahedron containing a Co₂C₂ unit. A two-dicobalt-fragments coordinated di-enyls complex, (Co₂(CO)₆)₂{ μ -HC≡C-C₆H₄-C≡C-H} (**17**), was synthesized from the reaction of 1,3-diethynylbenzene with Co₂(CO)₈. Crystallographic studies of (**17**) show that it exhibits a distorted Co₂C₂ quasi-tetrahedral geometry. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Nucleophilic substitution; µ-Alkyne bridged bimetallic compounds; Chromium; Cobalt

1. Introduction

Our previous work has shown that the nucleophilic substitution of fluoroarene $Cr(CO)_3$ by acetylide underwent a more complicated reaction mechanism than the direct substitution on the fluorine-bearing carbon [1,2]. As shown in Scheme 1, the expected *para-* product was not isolated in this reaction condition; instead, two unexpected products, *ortho-* and *meta-*, were obtained.

A proposed mechanism, modified from Pauson and Brookhart for a related case, involving hydrogen migration via the metal is consistent with our results [3–5]. According to this mechanism, the nucleophilic attack that took place on a carbon of the phenyl ring does not bear the leaving group, and is followed by hydrogen migration and final elimination of the leaving group to achieve aromaticity. Recently, nucleophilic aromatic substitution reactions via *cine* or *tel-meta* mechanism was proposed. The mechanism involves chromium-hydride and (η^4 -cyclohexadiene) complexes [6–13].

Here, we report more results of the nucleophilic substitution reactions of substituted tricarbonyl(η^6 -fluoro-arene)chromium with various acetylides.

The chemistry of alkyne bridge dimetallic compounds has been examined extensively [14–18]. Among them, the alkyne-bridged dicobalt complexes, $Co_2(CO)_6(\mu$ -RC=CR),

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Scheme 1.

were studied extensively [19–21]. Alkyne bridged dicobalt complexes are believed to be a key step to the productions in the Pauson–Khand reaction [22–26]. The high yields of the alkyne bridged dicobalt complexes and the efficient removal/recovery of the acetylene also makes these complexes acetylene protecting groups [27,28].

The triple bond character of an alkyne is expected to be reduced while attached to an (arene)Cr(CO)₃ group since the Cr(CO)₃ fragment is a strong electron-withdrawing group [29]. It is, therefore, of interest to us to investigate the reactivity of the triple bond in Me₃SiC=C-(o-tolueneCr(CO)₃) and μ -HC=C-C₆H₄-C=C-(benzene)C-r(CO)₃ by allowing them to react with Co₂(CO)₈. Here, we report the results from these reactions.

2. Results and discussion

Compound (**5a**), tricarbonyl[η^6 -(2-(4-methylphenylethynyl))toluene]chromium, and a trace amount of (**5b**) were obtained from the reaction of tricarbonyl[η^6 -4flurotoluene]chromium (**1b**) with deprotonated 4-tolyl acetylene (Scheme 2). It is consistent with our previous observations for this type of nucleophilie [1,2].

Similar results were observed for the reaction shown in Scheme 3. Tricarbonyl[η^6 -(2-(4-methyl-phenylethynyl)-

anisole]chromium compounds (**6a**) and (**6b**) were obtained from the reaction of tricarbonyl[η^6 -4-fluroanisole]chromium (**1c**) with deprotonated 4-tolyl acetylene. The ratio of (**6b**)/(**6a**) is about 3:1 and is in the right region of Bodner and Todd's prediction [30].

More complicated results were obtained when tri-substituted (arene)Cr(CO)₃, (7), was reacted with acetylide as shown in Scheme 4. Tricarbonyl[η^6 -(3-phenylethynyl-5-methyl)anisole]chromium (8c) and tricarbonyl[η^6 -(2-phenylethynyl-3-methyl)anisole]chromium (8b) as well as a trace amount of (8a) were obtained from the reaction. The yields of (8c) and (8b) are 54 and 32%, respectively. The results are consistent with the prediction from Bodner and Todd's rule. It also confirms the fact that the degree of the activation of substituents are in the order of $-OMe \ge -Me \ge -F$.

Both (8b) and (8c) were characterized by spectroscopic means as well as X-ray diffraction studies. (Figs. 1 and 2). Single crystals of $(8c) \cdot 1/2H_2O$, suitable for X-ray structure determination, were recrystallized from CH_2Cl_2 at 4°C. The water molecules presumably enter the system during crystallization.

The bond lengths of C(31)-C(30) is 1.190(10) Å for (8c) (Table 1); it is 1.188(4) Å for C(11)-C(12) in (8b) (Table 2). Accordingly, they are typical triple bonds. The dihedral angle between the phenyl ring and the arene is



Scheme 3.



Scheme 4.



Fig. 1. ORTEP drawing with the numbering scheme of (8b).



Fig. 2. ORTEP drawing with the numbering scheme of (8c). Hydrogen atoms are omitted for clarity.

Table 1 Selected bond distances (Å) and angles (°) of (8b)

	. ,		
Cr(1)–C(1)	1.823(4)	Cr(1)–C(2)	1.833(4)
Cr(1)–C(3)	1.840(4)	Cr(1) - C(13)	2.245(3)
Cr(1) - C(14)	2.269(3)	Cr(1) - C(15)	2.228(3)
Cr(1)–C(16)	2.175(4)	Cr(1) - C(17)	2.213(4)
Cr(1)–C(18)	2.223(3)	O(1) - C(1)	1.161(5)
O(2)–C(2)	1.161(4)	O(3)–C(3)	1.150(5)
O(4)–C(4)	1.430(4)	O(4) - C(14)	1.351(4)
C(10)-C(11)	1.435(4)	C(11)–C(12)	1.188(4)
C(12)-C(13)	1.434(4)		
$C(1) = C_{-}(1) = C(2)$	P(c(1))	$C(1)$ $C_{-}(1)$ $C(2)$	01.0(2)
C(1) - Cr(1) - C(2)	80.0(1)	C(1) - Cr(1) - C(3)	91.0(2)
C(2)-Cr(1)-C(3)	88.8(2)	C(4) - O(4) - C(14)	118.0(2)
Cr(1)-C(1)-O(1)	177.4(3)	Cr(1)-C(2)-O(2)	177.9(3)
Cr(1)-C(3)-O(3)	176.3(4)	C(10)-C(11)-C(12)	177.0(3)
C(11)-C(12)-C(13)	174.8(3)		

Table 2								
Selected	bond	distances	(Å)	and	angles	(°)	of	(8c)

		-	
Cr(2)–C(5)	1.851(10)	Cr(2)–C(6)	1.843(9)
Cr(2) - C(7)	1.817(9)	Cr(2) - C(32)	2.205(7)
Cr(2)–C(33)	2.225(7)	Cr(2)–C(34)	2.298(8)
Cr(2)–C(35)	2.243(8)	Cr(2)–C(36)	2.250(8)
Cr(2)–C(37)	2.226(7)	O(5)–C(5)	1.148(12)
O(6)-C(6)	1.152(11)	O(7)–C(7)	1.192(11)
O(8)-C(8)	1.381(11)	O(8)-C(36)	1.341(11)
C(29)-C(30)	1.440(9)	C(30)–C(31)	1.190(10)
C(31)–C(32)	1.432(10)		
C(5)-Cr(2)-C(6)	91.9(4)	C(5)-Cr(2)-C(7)	86.0(4)
C(6)-Cr(2)-C(7)	88.1(4)	Cr(2) - C(5) - O(5)	180.0(11)
Cr(2) - C(6) - O(6)	177.7(10)	Cr(2) - C(7) - O(7)	179.6(5)
C(29)-C(30)-C(31)	179.2(7)	C(30)-C(31)-C(32)	177.4(7)

about 14° for (8c) and about 1.8° for (8b). These two rings are almost coplanar and thus might gain better delocalization energy among the system.

Tricarbonyl[η^{6} -(2-trimethylsilylethynyl)toluene]chromium (**9a**) as well as the trace amount of the *meta*-product, tricarbonyl[η^{6} -(3-trimethylsilylethynyl)toluene]chromium (**9b**), were obtained from the reaction of (**1b**) with deprotonated trimethylsilylacetylene (Scheme 5). All these results point to the triple bond character of the nucleophile is the major factor causing the unusual substitution mechanism.

Results from Scheme 5 are summarized in Table 3.

With the presence of the strong electron-withdrawing $Cr(CO)_3$ fragment in the (arene) $Cr(CO)_3$, one might expect a diminishing of the triple bond character. However, an alkyne bridged dicobalt complex, $Co_2(CO)_6$ { μ -Me₃SiC=C-(*o*-tolueneCr(CO)₃} (10) was obtained from the reaction of (9a) with $Co_2(CO)_8$ even under room temperature (Scheme 6). It indicates that the triple bond of (9a) is still active enough to bond to the dicobalt center, in spite of the presence of the strongly electron-withdrawing $Cr(CO)_3$ fragment.

Complex (10) was characterized by mass, infrared, ¹H, ¹³C NMR spectra as well as X-ray diffraction studies. The core of this molecule is a quasi-tetrahedral Co_2C_2 unit consistent with most of these types of molecule. Two substituents, SiMe_3 and *o*-tolueneCr(CO)₃ bend away from the metal center (Fig. 3). The bond length of the bridged acetylene in (10) is 1.344 Å which is slightly longer than that of $\text{Co}_2(\text{CO})_5(\text{PPh}_3)\{\mu\text{-PhC}\equiv\text{CH}\}$,



Scheme 5.

Table 3 Nucleophilic substitution reactions of tricarbonyl(η^6 -fluoroarene)chromium with acetylides

Entry	Reactant	Nucleophile	Product	Yield (%)
1	1b	p-Methylbenzylacetylide	5a	77
2	1c	<i>p</i> -Methylbenzylacetylide	6a	18
3	1c	<i>p</i> -Methylbenzylacetylide	6b	59
4	7	Phenylacetylide	8b	32
5	7	Phenylacetylide	8c	54
6	1b	Trimethylsilylacetylide	9a	30
7	1a	<i>p</i> -Ethynl-phenylacetylide	12	37
8	1b	<i>p</i> -Ethynl-phenylacetylide	13	47

Co₂(CO)₄(PPh₃)₂{ μ -PhC≡CH} (Table 4). The bond lengths of the latter two compounds are 1.329 and 1.325 Å, respectively [31]. The elongation of the carbon–carbon bond in the bridged acetylene in (**10**) might due to a better backbonding effect caused by the strong electron-withdrawing Cr(CO)₃ fragment. It is also evidenced by the fact that larger bend away angles, 153.8 and 146.8° for C≡C–SiMe₃ and C≡C–areneCr(CO)₃, respectively, are observed in (**10**). In addition, the bond distances of acetylene to dicobalt center in (**10**) is also longer than most of the related compounds. Co₂(CO)₆{ μ -Me₃SiC≡C–(o-C₆H₅CH₃)} (**11**) was observed as the Cr(CO)₃ decomplexed product from (**10**). The absence of the diagnostic (arene)Cr(CO)₃ peaks in ¹H NMR indicates the loss of the Cr(CO)₃ fragment.

Conjugated oligomers have attracted much attention due to their potential in material science [32,33]. 1,4-Diethynylbenzene, $-C \equiv CC_6H_4C \equiv C-$, has been frequently involved in organic and homometallic polymers as a building block unit. Many attempts have been pursued in order to incorporate organometallic fragments to both sides of this unit [34]. The synthesis of $(o-CH_3-\eta^6-C_6H_4Cr(CO)_3)-C \equiv$ $CC_6H_4C \equiv C-(o-CH_3-\eta^6-C_6H_4Cr(CO)_3)$ (14) provides



Fig. 3. ORTEP drawing with the numbering scheme of (10). Hydrogen atoms are omitted for clarity.

another example of this type of work. It has been prepared by successive reactions as shown in Scheme 7. First, tricarbonyl[η^6 -(*p*-ethynyl-phenylethynyl)benzene]chromium (**12**) was obtained from the nucleophilic substitution of tricarbonyl[η^6 -fluorobenzene]chromium (**1b**) with deprotonated *p*-diethynylbenzene. Then, (*o*-CH₃- η^6 -C₆H₄Cr(CO)₃)-C=CC₆H₄C=C-(*o*-CH₃- η^6 -

 $C_6H_4Cr(CO)_3$) (14) was obtained from the further nucleophilic substitution of (1b) with deprotonated (13).

There are two triple bonds available for the coordination of the dicobalt fragment $\text{Co}_2(\text{CO})_6$ in (12). One might expect that the reduction in reactivity of the triple bond adjacent to the areneCr(CO)₃ moiety is due to a strongly



Table 4 Selected bond distances (Å) and angles (°) of (10)

Co(1)-Co(2)	2.477(1)	C(11)–C(12)	1.344(4)
Co(1)-C(11)	1.956(3)	Co(2) - C(11)	1.990(2)
Co(1)-C(12)	1.996(3)	Co(2)–C(12)	1.997(2)
Co(1)-C(16)	1.822(3)	Co(1)–C(17)	1.792(3)
Co(1)-C(18)	1.815(4)	Co(2)–C(19)	1.819(3)
Co(2)-C(20)	1.782(4)	Co(2)–C(21)	1.814(3)
C(4)–C(11)	1.462(4)	Si-C(12)	1.866(3)
Cr-C(4)	2.234(3)	Cr-C(5)	2.239(3)
Cr-C(6)	2.222(4)	Cr-C(7)	2.204(4)
Cr-C(8)	2.220(3)	Cr-C(9)	2.189(3)
C(5)–C(10)	1.495(4)		
Co(2)-Co(1)-C(11)	51.7(1)	Co(2)-Co(1)-C(12)	51.7(1)
Co(1)-Co(2)-C(11)	50.5(1)	Co(1)-Co(2)-C(12)	51.6(1)
Co(1)-C(11)-Co(2)	77.7(1)	Co(1)-C(12)-Co(2)	76.7(1)
Co(1)-C(11)-C(12)	71.7(2)	Co(1)-C(12)-C(11)	68.5(2)
Co(2)–C(11)–C(12)	70.6(2)	Co(2)-C(12)-C(11)	70.0(1)
C(11)-Co(1)-C(12)	39.7(1)	C(11)-Co(2)-C(12)	39.4(1)
Co(1)-C(12)-Si	127.6(2)	Co(2)-C(12)-Si	129.9(1)
Co(1)-C(11)-C(4)	135.5(2)	Co(2)-C(11)-C(4)	125.9(2)

electron-withdrawing group, $Cr(CO)_3$ fragment. The reaction of (12) with $Co_2(CO)_8$ was carried out at room temperature (Scheme 8). A two-dicobalt-fragment coordinated di-enyl complex, $(Co_2(CO)_6)_2 \{\mu-HC \equiv C-C_6H_4 -$ C≡C–(benzene)Cr(CO)₃) { (15), was obtained in a reasonable yield. The results seem to indicate that two triple bond characters of di-enyls are similar. The Cr(CO)₃ metal fragment decomplexed product, $(Co_2(CO)_6)_2$ { μ -HC≡C−C₆H₄−C≡CPh)}(16), was observed in the above reaction. This repeatedly observed phenomenon indicates that the bonding between the arene and Cr(CO)₃ fragment is not as strong as that of Co₂(CO)₆ fragment to an alkyne.

 $(Co_2(CO)_6)_2\{\mu$ -HC=C- C_6H_4 -C=C-(benzene)Cr(CO)_3) $\}$ (15) was characterized by mass, infrared, ¹H, ¹³C NMR spectra as well as X-ray diffraction studies. The basic Co₂C₂ core structure of (15) is not much different from (10). Substituents of the coordinated acetylenes all bend away from the metal center (Fig. 4). The bond length of the two bridged acetylene, C(22)–C(23) and C(30)– C(31) are 1.354 and 1.328 Å, respectively, and these are typical double bonds (Table 5). The bond length of C22– C23 is longer than that of C30–C31. This is probably due to a better backbonding effect caused by the electronwithdrawing group, arene Cr(CO)₃. It is slightly longer than that of Co₂(CO)₅(PPh₃){ μ -PhC=CH}, Co₂(CO)₄ (PPh₃)₂{ μ -PhC=CH}. They are 1.329 and 1.325 Å, respectively.

The reaction between 1,3-diethynylbenzene with



Scheme 8.



Fig. 4. ORTEP drawing with the numbering scheme of (15). Hydrogen atoms are omitted for clarity.

Table 5 Selected bond distances (Å) and angles (°) of (15)

Co(1)-Co(2)	2.472(1)	Co(1)–C(4)	1.827(3)
Co(1)-C(22)	1.954(2)	Co(1)-C(23)	1.977(2)
Co(2) - C(7)	1.825(3)	Co(2)-C(22)	1.990(3)
Co(2)-C(23)	1.965(3)	Co(3) - Co(4)	2.484(1)
Co(3)-C(10)	1.801(4)	Co(3)-C(30)	1.958(3)
Co(3)-C(31)	1.955(3)	Co(4)-C(13)	1.810(4)
Co(4)-C(30)	1.987(3)	Co(4)-C(31)	1.961(3)
Cr(1) - C(1)	1.861(4)	Cr(1)–C(16)	2.219(3)
O(1) - C(1)	1.139(5)	C(21)-C(22)	1.461(4)
C(22)-C(23)	1.354(3)	C(23)-C(24)	1.467(3)
C(27)-C(30)	1.460(4)	C(30)-C(31)	1.328(4)
Co(2)–Co(1)–C(22)	51.8(1)	Co(2)-Co(1)-C(23)	50.9(1)
Co(1)-Co(2)-C(22)	50.6(1)	Co(1)-Co(2)-C(23)	51.4(1)
C(22)-Co(2)-C(23)	40.0(1)	Co(1)-C(22)-Co(2)	77.6(1)
Co(2)-C(22)-C(23)	69.0(2)	Co(1)-C(23)-Co(2)	77.7(1)
Co(2)-C(23)-C(22)	71.0(2)	C(22)-Co(1)-C(23)	40.3(1)
Co(4)-Co(3)-C(30)	51.5(1)	Co(4)-Co(3)-C(31)	50.7(1)
C(30)-Co(3)-C(31)	39.7(1)	Cr(1)-C(1)-O(1)	177.8(3)
Cr(1)-C(2)-O(2)	179.3(3)	Cr(1)-C(3)-O(3)	179.6(4)
Co(1)-C(5)-O(5)	176.9(3)	C(5)-Co(1)-C(6)	98.9(2)
C(7)-Co(2)-C(8)	105.0(2)	Co(1)-C(4)-O(4)	177.2(3)
Co(1) - C(6) - O(6)	178.3(3)	Co(2) - C(8) - O(8)	177.4(3)
Co(3)-C(10)-O(10)	176.5(3)	Co(3)-C(12)-O(12)	178.2(4)
Co(4)-C(14)-O(14)	178.6(4)	Cr(1)-C(16)-C(17)	72.1(2)
C(16)-C(21)-C(22)	121.8(2)	C(23)-C(24)-C(25)	120.6(2)
C(20)-C(21)-C(22)	120.6(2)	C(21)-C(22)-C(23)	144.6(2)
C(22)-C(23)-C(24)	144.9(3)	C(23)-C(24)-C(29)	121.9(2)
C(27)-C(30)-C(31)	143.6(3)		

 $Co_2(CO)_8$ was carried out (Scheme 9). It does not take place until 55°C, presumably, due to the steric hindrance of two neighboring Co(CO)₃ fragments [35]. A two- $Co_2(CO)_6$ coordinated di-envl complex, $(Co_2(CO)_6)_2$ {µ- $HC \equiv C - C_6 H_4 - C \equiv C - H$ (17), was obtained. Complex (17) was characterized by spectroscopic means as well as X-ray diffraction studies. Two dicobalt fragments lie on the same side of the molecule and bend away from each other. The bond lengths of C6-C7 and C30-C26 are 1.318 and 1.320 A, respectively. They are shorter than that of the corresponding bond lengths of (15). Obviously, the electronwithdrawing $Cr(CO)_3$ fragment in (15) plays a significant role on this. By examining the crystal structures of (10), (15) and (17), we observed that the Co-C bond lengths are in the order of $Co-C_H < Co-C_{Ph} < Co-C_{TMS}$ (Fig. 5, Table 6).

The orientation of the Cr(CO)₃ unit in (arene)Cr(CO)₃ complexes is the subject of extensive study. An *anti*eclipsed form is observed for (arene)Cr(CO)₃ with an electron withdrawing substituent. On the other hand, a *syn*-eclipsed form is observed for (arene)Cr(CO)₃ with an electron donating substituent [36,37]. The orientation of Cr(CO)₃ in (arene)Cr(CO)₃ is about *syn*-eclipsed, with respect to the –OMe group, for (**8b**) and (**8c**). It seems that the strong π electron-donating substituent, –OMe group, is the major factor dominated by the orientation of Cr(CO)₃ in (**8b**) and (**8c**). The phenylacetylide substituent as well as the –Me group does not play a significant role here (Fig. 6).

An anti-eclipsed form, with respect to the



Fig. 5. ORTEP drawing with the numbering scheme of (17).



Scheme 9.

Table 6 Selected bond distances (Å) and angles (°) of (**17**)

Co(1)-Co(2)	2.469(1)	Co(1)-C(1)	1.807(4)
Co(1)-C(13)	1.950(3)	Co(1)-C(14)	1.972(3)
Co(2)–C(4)	1.820(4)	Co(2)–C(13)	1.937(3)
Co(2)–C(14)	1.953(3)	Co(3)-Co(4)	2.471(1)
Co(3) - C(7)	1.807(4)	Co(3)–C(21)	1.952(3)
Co(3)–C(22)	1.958(3)	Co(4) - C(10)	1.817(4)
Co(4)–C(21)	1.972(3)	Co(4)–C(22)	1.945(3)
O(1) - C(1)	1.136(5)	C(13)-C(14)	1.317(5)
C(14)–C(15)	1.466(4)		
$C_0(2) - C_0(1) - C(1)$	100.5(1)	C(1)-Co(1)-C(2)	101.6(2)
Co(2)-Co(1)-C(13)	50.3(1)	Co(2)-Co(1)-C(14)	50.7(1)
C(13)-Co(1)-C(14)	39.2(1)	Co(1)-Co(2)-C(13)	50.8(1)
C(4)-Co(2)-C(13)	101.9(2)	Co(1)-Co(2)-C(14)	51.4(1)
C(13)-Co(2)-C(14)	39.6(1)	Co(4)-Co(3)-C(21)	51.3(1)
Co(4)-Co(3)-C(22)	50.5(1)	C(21)-Co(3)-C(22)	39.4(1)
Co(3)-Co(4)-C(21)	50.6(1)	Co(1)-C(1)-O(1)	174.4(4)
Co(1)-C(13)-Co(2)	78.9(1)	Co(1)-C(13)-C(14)	71.3(2)
Co(2)–C(13)–C(14)	70.9(2)	Co(1)-C(14)-Co(2)	77.9(1)
Co(1)-C(14)-C(13)	69.5(2)	Co(2)-C(14)-C(13)	69.5(2)
Co(1)-C(14)-C(15)	128.8(2)	Co(2)-C(14)-C(15)	137.5(2)
C(13)-C(14)-C(15)	144.7(3)	Co(3)-C(21)-Co(4)	78.1(1)
Co(3)-C(21)-C(19)	136.4(2)	Co(4)-C(21)-C(19)	132.1(2)
Co(3)-C(21)-C(22)	70.5(2)	Co(4)-C(21)-C(22)	69.2(2)
C(19)-C(21)-C(22)	142.2(3)	Co(3)-C(22)-C(21)	70.0(2)
$C_0(4) - C(22) - C(21)$	71.4(2)		



Fig. 6. Top view of $(\operatorname{arene})Cr(CO)_3$ of (8b) and (8c).

 $Co_2(CO)_6$ (alkyne) fragment, was observed for both (10) and (15). It might be due to its bulky substituent, alkyne bridged dicobalt fragment [38,39] (Fig. 7).



Fig. 7. Top view of $(arene)Cr(CO)_3$ of (10) and (15).

In summary, acetylides are quite unique nucleophiles that cause the nucleophilic substitution reactions on (fluoroarene)Cr(CO)₃ and undergo unconventional mechanism. In addition, we were able to synthesize μ -alkyne bridged bimetallic compounds, (10) and (15). It is obvious that the distinct spectroscopic and structural changes of (10) and (15) are partially due to the strong electron-withdrawing ability of the Cr(CO)₃ fragment.

3. Experimental

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 ¹³C 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 CHCl₃ were recorded on a Hitachi 270-30 spectrometer. Mass spectra were recorded on JOEL JMS-SX/SX 102A GC/MS/MS spectrometer. Elementary analysis were recorded on Heraeus CHN-O-S-Rapid.

3.1. General procedure for preparations of (5*a*), (6*a*), (6*b*), (8*a*), (8*b*), (8*c*), (9*a*), (12), (13) [1,2]

Into a 50-cm³ flask was placed 4-ethynyltoluene, $CH_3C_6H_4C\equiv CH$, (0.12 cm³, 0.95 mmol) and 20 cm³ of anhydrous tetrahydrofuran. The solution was cooled to $-94^{\circ}C$ (acetone $-N_2(1)$ bath). Next, n-BuLi (1.6 M, 0.4 ml, 0.64 mmol) 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 added HMPA (0.56 cm³, 3.2 mmol); 30 min later, a solution of tricarbonyl(η^{6} -4fluorotoluene)chromium (**1b**) (0.13 g, 0.53 mmol) in 1.0 cm³ of anhydrous THF was added slowly to the cold reaction mixture. The reaction was well stirred at $-94^{\circ}C$ for another 3 h and gently warmed to room temperature 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 the crude product. Purification with centrifugal thin-layer chromatography (eluent: hexane), a yellow band of tricarbonyl[η^{6} -(2-(4-methyl-phenylethynyl))toluene]chromium (**5a**) and trace amount of (**5b**) were obtained. Complex (**5a**) was isolated (0.14 g, 0.41 mmol). The yield of (**5a**) is 77.4%.

3.1.1. Characterization of (5a)

¹H NMR (CDCl₃): δ 2.40 (s, 3H, Me), 2.38 (s, 3H, Me), 5.69 (d, J=6.2 Hz, 1H,), 5.36 (d, J=6.2 Hz, 1H), 5.22 (m, 2H), 7.17 (d, J=8.2 Hz, 2H), 7.41 (d, J=8.2 Hz, 2H). ¹³C NMR (CDCl₃): δ 20.02 (1C, Me), 21.47 (1C, Me), 83.68,

89.11, 90.50, 92.11, 92.52, 96.47, 110.52, 118.93, 129.21, 131.74, 139.34 (12C, Ph), 232.76 (3C, 3CO). IR(CH₂Cl₂): $\nu_{\rm (CO)}$ 1904, 1976 cm⁻¹. MS *m/z* 342 (M⁺).

3.1.2. Characterization of (6a)

¹H NMR (CDCl₃): δ 2.37 (s, 3H, Me), 3.85 (s, 3H, OMe), 4.94 (dd, J=6.2, 6.2 Hz, 1H), 5.12 (d, J=6.6 Hz, 1H), 5.52 (m, 1H), 5.85 (dd, J=1.4, 6.3 Hz, 1H), 7.15 (d, J=8.4 Hz, 2H), 7.43 (d, J=8.4 Hz, 2H). ¹³C NMR (CDCl₃): δ 21.50 (1C, Me), 56.24 (1C, OMe), 73.55, 80.47, 81.46, 84.65, 92.57, 98.18, 119.29, 129.12, 131.87, 139.09, 142.77 (12C, Ph), 232.59 (3C, 3CO). IR(CH₂Cl₂): $\nu_{\rm (CO)}$ 1905, 1977 cm⁻¹. MS m/z 358 (M⁺).

3.1.3. Characterization of (6b)

¹H NMR (CDCl₃): δ 2.37 (s, 3H, Me), 3.74 (s, 3H, OMe), 5.07 (m, 2H), 5.30 (s, 1H), 5.56 (dd, J=6.6, 6.6 Hz, 1H), 7.16 (d, J=7.8 Hz, 2H), 7.42 (d, J=7.8 Hz, 2H). ¹³C NMR (CDCl₃): δ 21.52 (1C, Me), 55.66 (1C, OMe), 76.71, 79.99, 84.61, 88.05, 90.82, 93.08, 93.70, 118.60, 129.25, 131.92, 139.61, 142.35 (12C, Ph), 233.02 (3C, 3CO). IR(CH₂Cl₂): $\nu_{(CO)}$ 1902, 1976 cm⁻¹. MS m/z 358 (M⁺).

3.1.4. Characterization of (8b)

¹H NMR(CDCl₃): δ 2.49 (s, 3H, Me), 3.85 (s, 3H, OMe), 4.88 (d, J = 6 Hz, 1H, areneCr(CO)₃), 5.03 (d, J = 7 Hz, 1H, areneCr(CO)₃), 7.25–7.6 (m, 5H, arene). ¹³C NMR(CDCl₃): δ 20.47 (1C, Me), 56.30 (1C, OMe), 81.28, 95.53 (2C, -C=C-), 81.72, 112.52, 122.64 (3C, ipso of areneCr(CO)₃), 71.70, 86.34, 92.29 (3C, areneCr(CO)₃), 128.36, 128.76, 131.87 (5C, arene), 143.27 (1C, ipso of arene), 232.83 (3C, Cr(CO)₃). IR(CH₂Cl₂): $\nu_{(CO)}$ 1964 (s), 1886 (s) cm⁻¹. MS m/z 358 (M⁺). Anal.: Calcd.: C, 63.69; H, 3.94. Found: C, 62.27; H, 4.29.

3.1.5. Characterization of (8c)

¹H NMR(CDCl₃): δ 2.29 (s, 3H, Me), 3.74 (s, 3H, OMe), 4.99, 5.20 (3H, areneCr(CO)₃), 7.25–7.6 (m, 5H, arene). ¹³C NMR(CDCl₃): δ 20.86 (1C, Me), 55.66 (1C, OMe), 79.05, 89.41 (2C, -C=C-), 92.54, 121.69, 124.99 (3C, ipso of areneCr(CO)₃), 109.26, 113.31, 115.90 (3C, areneCr(CO)₃), 128.43, 129.17, 131.98 (5C, arene), 142.68 (1C, ipso of arene), 233.25 (3C, Cr(CO)₃). IR(CH₂Cl₂): ν_{CO} 1967 (s), 1890 (s) cm⁻¹. MS *m*/*z* 358 (M⁺).

3.1.6. Characterization of (9a)

¹H NMR(CDCl₃): δ 5.58 (d, J = 6.2 Hz, 1H), 5.32 (dd, J = 5.6, 5.6 Hz, 1H), 5.16 (m, 2H), 2.31 (s, 3H, Me), 0.24 (s, 9H, SiMe₃). ¹³C NMR(CDCl₃): δ -0.20 (s, 3C, SiMe₃), 19.95 (s, 1C, Me), 88.92, 91.90, 92.34, 96.47 (4C, areneCr(CO)₃), 89.64, 98.36 (2C, -C=CSiMe₃), 99.65 (1C, ipso of areneCr(CO)₃), 110.63 (1C, ipso of

areneCr(CO)₃), 232.36 (3C,Cr(CO)₃). IR(CH₂Cl₂): $\nu_{(CO)}$ 1968 (s), 1896 (s) cm⁻¹. MS m/z 432 (M⁺).

3.2. General procedure for preparations of (10), (15), (17)

Into a 50-cm³ flask was placed dicobalt octacarbonyl, $Co_2(CO)_8$, (0.2 g, 0.585 mmol) and tricarbonyl[η^6 -(2-trimethylsilylethynyl)toluene] chromium (**9**) (0.12 g, 0.370 mmol) with 20 cm³ of toluene. The solution was stirred under room temperature during the next 16 h.

Subsequently, the resulting dark purple solution was filtered through a small amount of silica gel. The filtrate was evaporated under reduced pressure to yield the crude product. Purification with centrifugal thin-layer chromatography (eluent: hexane), a purple band of $\text{Co}_2(\text{CO})_6$ { μ -Me₃SiC=C-(*o*-tolueneCr(CO)₃)} (10) was obtained. (10) was isolated (0.08 g, 0.131 mmol). The yield of (10) is 35.4%.

Similar procedures were taken. The yield of (15) is 48.3%. The reaction temperature was maintained at 55°C in the synthesis of (17). The yield of (17) is 58.7%.

3.2.1. Characterization of (10)

¹H NMR(CDCl₃): δ 0.47 (s, 9H, SiMe₃), 2.44 (s, 3H, Me), 5.12 (m, 2H, areneCr(CO)₃), 5.60 (t, 1H, areneCr(CO)₃), 5.92 (d, *J*=6.2, 1H, areneCr(CO)₃). ¹³C NMR(CDCl₃): δ 1.83 (s, 3C, SiMe₃), 21.12 (s, 1C, Me), 82.99, 100.27 (2C, -C=C-) 87.88, 90.44, 95.15, 98.85 (4C, areneCr(CO)₃), 105.25, 110.35 (2C, ipso of areneCr(CO)₃), 199.24 (6C, Co₂(CO)₆), 232.49 (3C, Cr(CO)₃). IR(CH₂Cl₂): $\nu_{(CO)}$ 2091 (m), 2056 (s), 2027 (m), 1965 (m), 1894 (m) cm⁻¹. MS *m*/*z* 610 (M⁺). Anal.: Calcd.: C, 41.33; H, 2.64. Found: C, 41.48; H, 2.87.

3.2.2. Characterization of (11)

¹H NMR(CDCl₃): δ 0.42 (s, 9H, SiMe₃), 2.47 (s, 3H, -Me), 7.16–7.24 (m, 3H, Ph), 7.59–7.63 (t, 1H, Ph). ¹³C NMR(CDCl₃): δ 1.62 (3C, SiMe₃), 21.91 (1C, -Me), 82.78, 103.94 (2C, -C=C-), 117.23 (1C, ipso of arene), 126.49, 127.89, 130.51, 133.00 (4C, arene), 136.18 (1C, ipso of arene), 200.32 (6C, Co₂(CO)₆). IR(CH₂Cl₂): ν_{CO} 2086 (m), 2050 (s), 2020 (s) cm⁻¹. MS *m/z* 474 (M⁺).

3.2.3. Characterization of (12)

¹H NMR (CDCl₃): δ 3.19 (s, 1H, $-C\equiv$ CH), 5.28 (t, 1H, J=6.8 Hz, areneCr(CO)₃), 5.36 (t, 2H, J=6.4 Hz, areneCr(CO)₃), 5.53 (d, J=6.4 Hz, areneCr(CO)₃), 7.46 (dd, 4H, -Ph-) ¹³C NMR (CDCl₃): δ 79.40 (s, 1C, CH), 83.02 (1C, $-C\equiv$ CH), 87.07, 89.00 (2C, $-C\equiv$ C-), 89.83 (1C, ipso of areneCr(CO)₃), 90.69, 91.41, 94.76 (5C, areneCr(CO)₃), 131.79, 132.10 (4C, -Ph-), 122.18, 122.75 (2C, ipso of Ph), 232.00 (3C, Cr(CO)₃). IR (CH₂Cl₂): $\nu_{(CO)}=1974$ (s), 1903 (s) cm⁻¹. MS *m/z* 338 (M⁺).

3.2.4. Characterization of (13)

¹H NMR (CDCl₃): δ 2.40 (s, 3H, -CH₃ of areneCr(CO)₃), 3.20 (s, 1H, -C=CH), 5.20 (t, 1H, areneCr(CO)₃), 5.24 (d, J=6.0 Hz, 1H, areneCr(CO)₃), 5.39 (t, 1H, areneCr(CO)₃), 5.69 (d, J=6.4 Hz, 1H, areneCr(CO)₃), 7.47 (dd, 4H, -Ph-). ¹³C NMR (CDCl₂): δ 20.13 (s, 1C, CH₃ of areneCr(CO)₃), 79.33 (s, 1C, \equiv CH), 83.05 (1C, -C=CH), 86.31, 89.21 (2C, -C=C-), 91.49 (1C, ipso of areneCr(CO)₃), 88.80, 91.80, 92.62, 96.45 $(4C, areneCr(CO)_3)$, 110.48 (1C, ipso of areneCr(CO)_3, -CH₃), 122.43, 122.65 (2C, ipso of Ph), 131.66, 132.08 (4H, -Ph-), 232.27 (3C, Cr(CO)₃). IR (CH₂Cl₂): $\nu_{(CO)} =$ 1970 (s), 1896 (s) cm⁻¹. MS m/z 352 (M⁺).

3.3. Preparation of (14)

Into a 100-cm³ flask was placed (13), (390 mg, 1.11 mmol) and 5 cm^3 of anhydrous tetrahydrofuran. The solution was cooled to -40° C (acetonitrile $-N_2(1)$ bath). Next, n-BuLi (0.55 ml, 1.38 mmol) was added drop by drop to the cold reaction flask. The deprotonation process was carried out at that temperature for 1.0 h and then added HMPA (0.8 cm³, 4.6 mmol); 30 min later, a solution of tricarbonyl(η^6 -4-fluorotoluene)chromium (1b) (228 mg,

Table 7

Crystal	data	of	(8b).	(8c).	(10).	(15)	and	(17)
Crystur	autu	01	(00),	(00),	(10),	(10)	una	(1)

0.92 mmol) in 2.0 cm³ of anhydrous THF was added slowly to the cold reaction mixture. The reaction was well stirred and gently warmed to room temperature 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 the crude product. Purification with centrifugal thin-layer chromatography (eluent: hexane), a yellow band of (14) was isolated. The yield of (14) is 37.2%.

3.3.1. Characterization of (14)

¹H NMR (CDCl₃): δ 2.41 (s, 6H, two CH₃ of areneCr(CO)₃), 5.20 (t, J=6.2 Hz, 2H, areneCr(CO)₃), 5.25 (d, J=6.2 Hz, 2H, areneCr(CO)₂), 5.40 (t, 2H, J=6.2 Hz, areneCr(CO)₂), 5.70 (d, J=6.4 Hz, 2H, areneCr(CO)₃), 7.49 (dd, 4H, -Ph-). ¹³C NMR (CDCl₃): δ 20.16 (s, 2C, two CH₃ of each areneCr(CO)₃), 86.67, (4C, −C=C−), 91.57 (2C, ipso of each 89.22 areneCr(CO)₃), 88.80, 91.81, 92.66, 96.48 (8C, two areneCr(CO)₃), 110.52 (2C, ipso of each areneCr(CO)₃, -CH₃), 122.57 (s, 2C, ipso of Ph), 131.49, 131.77 (4C, -Ph-), 232.28 (6C, Cr(CO)₃). IR (CH₂Cl₂): $\nu_{(CO)} = 1970$ (s), 1896 (s) cm⁻¹. MS m/z 578 (M⁺).

Formula	C ₁₉ H ₁₄ CrO ₄	$C_{19}H_{14}CrO_4 \cdot \frac{1}{2}H_2O$	C ₂₁ H ₁₆ Co ₂ CrO ₉ Si	$C_{13}H_{10}Co_4CrO_{15}H_{16}$	C ₂₂ H ₆ Co ₄ O ₁₂
Formula weight	358.3	367.3	610.3	910.1	698.0
Crystal system	Orthorhombic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$Pca2_1$	ΡĪ	ΡĪ	ΡĪ	$P2_1/n$
a (Å)	9.0616(3)	9.0463(1)	8.376(2)	7.5655(1)	9.2780(2)
<i>b</i> (Å)	12.7028(4)	9.2980(1)	8.699(2)	14.5406(1)	12.6522(1)
c (Å)	14.6355(4)	21.1307(3)	17.616(2)	15.8095(2)	22.5876(4)
α (°)		85.074(1)	87.70(2)	95.024(1)	
β (°)		85.877(1)	80.31(2)	97.055(0)	100.178(1)
γ (°)		86.931(1)	74.14(2)	91.599(1)	
$V(\text{\AA}^3)$	1684.7(5)	1764.2(6)	1216.9(4)	1718.0(6)	2609.8(7)
Ζ	4	2	2	2	4
$D_{\rm c} ~({\rm g~cm^{-3}})$	1.413	1.383	1.665	1.759	1.776
λ (Mo K α), Å	0.71073	0.71073	0.71073	0.71073	0.71073
$\mu (\mathrm{mm}^{-1})$	0.697	0.670	1.882	2.267	2.558
Range (°)	2.5-55.9	2.5-55.8	4.0 - 48.0	2.5-56.9	2.5 - 55.8
Scan speed	10.00 s/frame	10.00 s/frame	Variable	10.00 s/frame	10.00 s/frame
Scan range	0.30°/frame	0.30°/frame	0.40°/frame	0.30°/frame	0.30°/frame
No. of reflections	9603	17 269	4063	16 208	14 581
collected	$(8251 \ge 3.0\sigma(I))$	$(12398 \ge 3.0\sigma(I))$		$(13338 \ge 3.0\sigma(I))$	$(11969 \ge 3.0\sigma(I))$
No. of independent	3442	7541	3774	7355	5550
reflections	$(R_{\rm int} = 3.29\%)$	$(R_{\rm int} = 3.69\%)$	$(R_{\rm int} = 1.01\%)$	$(R_{\rm int} = 3.56\%)$	$(R_{int} = 4.11\%)$
No. observed reflections	$(2531 \ge 3.0\sigma(I))$	$(4181 \ge 3.0\sigma(I))$	$(3284 \ge 4.0\sigma(F))$	$(5140 \ge 3.0\sigma(I))$	$(3411 \ge 3.0\sigma(I))$
No. of refined parameters	218	442	307	461	344
R_f for significant	0.0315	0.0715	0.0281	0.0296	0.0294
reflections ^a					
R_w for significant	0.0328	0.0903	0.0447	0.0315	0.0309
reflections ^b					
GoF ^c	1.34	1.24	1.16	1.01	1.19

^a $R_f = [\Sigma(F_o - F_c) / \Sigma F_o].$ ^b $R_w = \Sigma w^{1/2} (F_o - F_c) / \Sigma w^{1/2} F_o.$

^c GoF = $[\Sigma w(F_o - F_c)^2 / (N_{\text{rfins}} - N_{\text{params}})]^{1/2}$. $w^{-1} = \sigma^2(F) + 0.0010F^2$.

3.3.2. Characterization of (15)

¹H NMR (CDCl₃): δ 6.42 (s, 1H, $-C\equiv$ CH), 5.27 (t, 2H, J=5.6 Hz, areneCr(CO)₃), 5.59 (t, 1H, J=6.0 Hz, areneCr(CO)₃), 5.90 (dd, J=5.6 Hz, 2H, areneCr(CO)₃), 7.46 (dd, J=6.4 Hz, 4H, -Ph-). ¹³C NMR (CDCl₃): δ 72.91 (s, 1C, CH), 88.02 (1C, $-C\equiv$ CH), 91.81, 95.12 (2C, $-C\equiv$ C-), 88.82, 94.57, 96.42 (5C, areneCr(CO)₃), 106.73 (1C, ipso of areneCr(CO)₃), 129.62, 130.83 (4C, -Ph-), 137.44, 137.88 (2C, ipso of -Ph-), 198.37, 199.18 (12C, 2 Co₂(CO)₆), 231.19 (3C, Cr(CO)₃). IR (CH₂Cl₂): $\nu_{(CO)}=$ 2091 (m), 2061 (s), 2030 (m), 1968 (m), 1897 (m) cm⁻¹. MS m/z 910 (M⁺). Anal.: Calcd.: C, 40.91; H, 1.11. Found: C, 40.48; H, 1.24.

3.3.3. Characterization of (17)

¹H NMR (CDCl₃): δ 6.38 (s, 2H, -C=CH), 7.28 (t, J=7.2 Hz, 1H, -Ph-), 7.45 (dd, J=7.8 Hz, 2H, -Ph-), 7.68 (m, 1H, -Ph-). ¹³C NMR (CDCl₃): δ 72.62 (s, 2C, C1), 89.18 (s, 2C, C2), 129.19 (s, 1C, C6), 129.33 (s, 2C, C4), 132.20 (s, 1C, C5), 138.42 (s, 2C, C3), 199.08 (m, 12C, 2 Co₂(CO)₆). IR (CH₂Cl₂): $\nu_{(CO)}$ =2092 (s), 2060 (s), 2027 (s) cm⁻¹. MS *m*/*z* 698 (M⁺) Anal.: Calcd.: C, 37.86; H, 0.87. Found: C, 38.14; H, 1.00.

3.4. X-ray crystallographic studies

Suitable crystals of (8b), (8c), (15), (17) and (10) were sealed in thin-walled glass capillaries under nitrogen atmosphere. The first four crystals were mounted on a Siemens Smart CCD diffractometer; the fifth crystal was mounted on a Siemens P4 diffractometer. The crystallographic data were collected using a θ -2 θ scan mode with Mo K α radiation. The space group determination was based on a check of the Laue symmetry and systematic absences, and was confirmed by the structure solution. The structure was solved by direct methods using Siemens SHELXTL PLUS package [40]. All non-H atoms were located from successive Fourier maps. Anisotropic thermal parameters were used for all non-H atoms and fixed isotropic for H atoms that were refined using the riding model [41].

Crystallographic data of (8b), (8c), (10), (15) and (17) are summarized in Table 7.

Supplementary data

Supplementary data are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number CCDC 114041–CCDC 114045.

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References

- [1] F.-E. Hong, S.-C. Lo, M.-W. Liou, L.-F. Chou, C.-C. Lin, J. Organomet. Chem. 516 (1996) 123.
- [2] F.-E. Hong, S.-C. Lo, M.-W. Liou, Y.-T. Chang, C.-C. Lin, J. Organomet. Chem. 506 (1996) 101.
- [3] S.G. Davies (Ed.), Organotransition Metal Chemistry Applications to Organic Synthesis, Vol. vol. 2, Pergamon Press, Oxford, 1982, p. 170, and references therein.
- [4] W. Lamanna, M. Brookhart, J. Am. Chem. Soc. 102 (1980) 3490.
- [5] G.A.M. Munro, P.L. Pauson, J. Chem. Soc., Chem. Commun. (1976) 134.
- [6] R. Khourzom, J.P. Djukic, E. Rose, J. Organomet. Chem. 195 (1994) 467.
- [7] J.C. Boutonnet, F. Rose-Munch, E. Rose, Tetrahedron Lett. 26 (1985) 3989.
- [8] J. C. Boutonnet, F. Rose-Munch, E. Rose, A. Semra, Bull. Soc. Chim. Fr. (1987) 640.
- [9] V. Gagliardini, V. Onnikian, F. Rose-Munch, E. Rose, Inorg. Chim. Acta 259 (1997) 265.
- [10] F. Rose-Munch, E. Rose, A. Semra, J. Chem. Soc., Chem. Commun. (1986) 1108.
- [11] F. Rose-Munch, E. Rose, A. Semra, J. Chem. Soc., Chem. Commun. (1986) 1551.
- [12] H.-G. Schmalz, K. Schellhaas, Tetrahedron Lett. 36 (1995) 5511.
- [13] H.-G. Schmalz, K. Schellhaas, Angew. Chem., Int. Ed. Engl. 35 (1996) 2146.
- [14] A.J.M. Caffyn, K.M. Nicholas, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, Vol. vol. 12, Elsevier, New York, 1995, p. 685.
- [15] M.J. Chetcuti, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, Vol. vol. 10, Elsevier, New York, 1995, p. 23.
- [16] N.E. Schore, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, Vol. vol. 12, Elsevier, New York, 1995, p. 703.
- [17] J.L. Templeton, Adv. Organomet. Chem. 29 (1989).
- [18] C.M. Lukehart, Fundamental Transition Metal Organometallic Chemistry, Brools/Cole, Monterey, CA, 1985.
- [19] R.S. Dickson, Adv. Organomet. Chem. 12 (1974) 323.
- [20] R.S. Dickson, G.R. Tailby, Aust. J. Chem. 23 (1971) 229.
- [21] U. Krüerke, W. Hübel, Chem. Ber. 94 (1961) 2829.
- [22] I.U. Khand, G.R. Knox, P.L. Pauson, W.E. Watts, J. Chem. Soc., Chem. Commun. (1971) 36.
- [23] I.U. Khand, G.R. Knox, P.L. Pauson, W.E. Watts, J. Chem. Soc., Perkin I, (1973) 975.
- [24] I.U. Khand, G.R. Knox, P.L. Pauson, W.E. Watts, M.I. Foreman, J. Chem. Soc., Perkin I (1973) 977.
- [25] D.C. Billington, P.L. Pauson, Organometallics 1 (1982) 1560.
- [26] P.L. Pauson, Tetrahedron 41 (1985) 585.
- [27] R.H. Crabtree, The Organometallic Chemistry of the Transition Metals, 2nd ed, Wiley, New York, 1994, Ch. 14.
- [28] J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1987.
- [29] The electron-withdrawing ability of the $Cr(CO)_3$ fragment is similar to NO₂ group. The fact that the NO₂ group deactivates the reactivity of the benzene ring is well known.
- [30] M.G. Bodner, L.J. Todd, Inorg. Chem. 13 (1974) 360.
- [31] F.-E. Hong, J.-W. Liaw. C.-C. Lin, Unpublished results.
- [32] J.S. Miller, Adv. Mater. 5 (1993) 587.
- [33] J.S. Miller, Adv. Mater. 5 (1993) 671.
- [34] O. Lavastre, J. Plass, P. Bachmann, S. Guesmi, G. Moinet, P.H. Dixneuf, Organometallics 16 (1997) 184.
- [35] C.E. Housecroft, B.F.G. Johnson, M.S. Khan, J. Lewis, P.R. Raithby, M.E. Robson, D.A. Wilkinson, J. Chem. Soc., Dalton Trans. (1992) 3171.

- [36] T.A. Albright, B.K. Carpenter, Inorg. Chem. 19 (1980) 3092.
- [37] T.A. Albright, P. Hofmann, R. Hoffmann, J. Am. Chem. Soc. 99 (1977) 7546.
- [38] F. van Meurs, H. van Konigsveld, J. Organomet. Chem. 78 (1974) 229.
- [39] F. van Meurs, H. van Konigsveld, J. Organomet. Chem. 118 (1976) 295.
- [40] G.M. Sheldrick, SHELXTL PLUS User's Manual. Revision 4.1, Nicolet XRD Corporation, Madison, Wisconsin, 1991.
- [41] Hydrogen atoms were ride on carbons or oxygens in their idealized positions and held fixed with the C-H distances of 0.96 Å.