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Cyclopentadienyliron-mediated introduction of functionalized alkyl or alkynyl groups to arenes in an addition–demetallation sequence

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Abstract

Nitromethyl, cyanomethyl, and phenylethynyl anions add selectively *ortho* to arenes containing electron-withdrawing groups and complexed with cyclopentadienyliron. Under similar reaction conditions anions such as alkyl, dichloromethyl and trichloromethyl add in a non-selective way. Addition of the trichloromethyl anion is thermodynamically controlled at extended reaction times and, due to the size of the anion, the *meta* addition product is favoured. Demetallation of adducts leads to *ortho*-nitromethylated, cyanomethylated or phenylethynylated arenes, respectively. With symmetrical arene complexes the addition–demetallation sequence leads to the introduction of a trichloromethyl group into the arene ring, yielding a single product. A one-pot procedure for trichloromethylation of dialkylarenes starting from appropriate cyclopentadienyliron complexes gives β-trichloromethylated dialkylarenes in a good yield.

Introduction

Temporary π-complexation of arene to a metal moiety has become an important alternative tool in synthetic organic chemistry [1–3]. Such complexation allows for the completion of reactions which are unknown for free arenes. The most heavily studied protocol involves an addition–demetallation sequence [4] and it is an equivalent to the substitution of an arene ring hydrogen by another group. For complexes of substituted arenes this method shows only restricted selectivity and usually gives a mixture of isomeric products due to the influence of both electronic and steric factors. *meta*-Adducts are predominant isomers for arenes possessing electron-donating substituents complexed with chromium tricarbonyl or manganese tricarbonyl moieties [1–12]. In some cases, due to a combination of electronic and steric factors, full selectivity has been achieved allowing for an incorporation of such step in a total synthesis [3,12].

Chromium tricarbonyl promoted synthesis that involve addition of nucleophile and a subsequent demetallation step requires that hard nucleophiles are used in the addition step [3,10,11]. Recently we have reported that cyclopentadienyliron complexes of arenes bearing electron-withdrawing substituents such as carbonyl, *p*-tolylsulfonyl, chloro, cyano or nitro group undergo selective addition with the *ortho* isomer being the only product of addition of softer nucleophiles such as cyano or enolate anions [13–17]. *ortho*-Selectivity is predominant even if *ortho*-positions are blocked with methyl groups [15].

In the present contribution we report on an important extention of such methodology involving the use of other anions in the addition step.

Results and discussion

Selective ortho-*addition*

Low temperature (−78°C) addition of anions generated from nitromethane, acetonitrile and phenylethyne to iron(Cp) complexes of nitrobenzene, Ia, or *p*-nitrotoluene, Ic, leads to the formation of adducts IIa, IIb and IIc, respectively, in yields of 65–70%. Analytical data of adducts which are given in Tables 1–4 indicate that only a single product of addition of anion *ortho* to the nitro group of starting complex was formed in each case. Structure of the adducts IIa–c have been established on the basis of analysis of NMR data which show similar chemical shifts and splitting patterns to those observed for the enolate and cyano adducts described earlier [13–17].

Addition of the nitromethyl anion to bis(mesitylene)iron dication has been reported by Helling and Cash [18] in 52% yield. Similar reaction of (benzene) iridium(pentamethylcyclopetadienyl) cation with nitromethyl anion has been studied by Grundy et al. [19]. In both cases no conclusion could have been drawn as to the selectivity of addition. In our work this addition has occurred selectively *ortho* to the electron-withdrawing nitro group and it constitutes the first regioselective case of

Table 1

Yields and isomer ratios for the nucleophilic addition reactions

Starting complex [a]	Nu–X [b]	Base [c]	Adduct [a]	Isomer ratio	Yield [d] (%)
Ia	NO_2CH_3	LDA [c]	IIa	–	69
Ia	$CNCH_3$	BuLi	IIb	–	70
Ic	PhC≡CH	BuLi	IIc	–	65
Id	BuLi	–	IId/IIId/IVd	5.0/2.2/1	61
Ie	BuLi	–	IIe	–	75
Ie	Cl_2CH_2	LDA [e]	IIg	–	42
Ih	Cl_3CH	^{t}BuOK	IIh/IIIh/IVh	1/2/1	75
Ib	Cl_3CH	^{t}BuOK	IIi/IIIi	1/1	72
Ij	Cl_3CH	^{t}BuOK	IIIj/IVj	3/2	69
Ie	Cl_3CH	^{t}BuOK	IIk	–	70

[a] The structures for these starting complexes and resulting adducts are given in schemes. [b] Nu = nucleophile, X = H or Li. [c] The anions were all prepared at −78°C. For trichloromethyl anion, reaction mixtures were allowed to warm up to the room temperature after introduction of the complex. [d] Total yield if more than one isomer is formed. [e] Lithium diisopropylamide.

Table 2

Elemental analysis for adducts and demetallation products a–k

Complex of compound	Formula	Found (%)			Calculated (%)		
		C	H	N	C	H	N
IIa	$C_{12}H_{12}FeN_2O_4$	52.65	4.39	10.74	52.97	4.45	10.30
IIb	$C_{13}H_{12}FeN_2O_2$	55.11	4.43	10.03	54.96	4.26	9.86
IIc	$C_{20}H_{17}FeNO_2$	66.58	4.44	4.12	66.87	4.77	3.90
IId/IIId/IVd	$C_{15}H_{19}ClFe$	61.60	6.32	–	61.99	6.59	–
IIe	$C_{15}H_{18}Cl_2Fe$	55.67	5.87	–	55.42	5.58	–
IIg	$C_{12}H_{10}Cl_4Fe$	40.71	3.12	–	40.96	2.86	–
IIh/IIIh/IVh	$C_{19}H_{17}Cl_3FeO_2S$	48.74	3.44	–	48.39	3.63	–
IIi/IIi	$C_{13}H_{12}C_{13}FeNO_2$	41.84	3.13	4.10	41.48	3.21	3.72
IIj/IVj	$C_{16}H_{19}Cl_3Fe$	51.59	5.01	–	51.45	5.13	–
IIk	$C_{12}H_9Cl_5Fe$	36.99	2.72	–	37.31	2.35	–
Va	$C_7H_6N_2O_4$	46.35	3.55	14.97	46.15	3.30	15.38
Vb	$C_{15}H_{11}NO_2$	75.55	4.83	5.67	75.95	4.64	5.91
Ve	$C_{10}H_{12}Cl_2$	59.32	5.68	–	59.41	5.94	–

addition of a nitromethyl group. Similar *ortho* regioselectivity was found when the cyanomethyl and phenylethynyl anions were anions were added to nitrobenzene and *p*-nitrotoluene complexes, respectively. It could be expected that these three anions will add *ortho* selectively to cationic complexes of arenes bearing electron-withdraw-

Table 3

^{1}H NMR data for the nucleophilic addition products a–g

Adduct [b]	δ($CDCl_3$)(ppm for TMS) [a]							
	Cp	H(1)	H(2)	H(3)	H(4)	H(5)	H(6-*endo*)	Others
IIa	4.46	–	5.93	6.34	4.90	3.59	4.26	3.37, 2.97(CH_2NO_2)
	J(2–3) = J(3–4) = J(4–5) = 5.6; J(5–6-*endo*) = 6.5; CH_2: J(H–H) = 11.3; J(H-6-*endo*) = 8.7, 5.2							
IIb	4.45	–	5.90	6.35	4.92	3.71	−3.81	1.55, 1.10(CH_2CN)
	J(2–3) = J(3–4) = 5.4; J(4–5) = 5.6; CH_2: J(H–H) = 11.3; J(H-6-*endo*) = 8.7, 4.4							
IIc	4.33	–	5.90	6.24	–	3.67	4.37	1.95(CH_3), 7.18(Ph)
	J(2–3) = 5.6; J(2-6-*endo*) = 1.4; J(3–5) = 1.6; J(5-6-*endo*) = 7.0							
IId	4.26	–	4.40	5.71	4.01	2.81	2.70	0.03–0.20, 0.53–1.14 [(CH_2)$_3$] [c]; 0.76 (CH_3)
	J(2–3) = J(3–4) = J(4–5) = 5.4; J(5–6-*endo*) = 6.8; J(3–5) = 1.3; CH_3–CH_2: J(H–H) = 7.2							
IIId	4.25	2.88	–	6.08	4.13	2.33 [c]	2.70 [c]	[d] (^{n}Bu)
	J(1–6-*endo*) = 6.6; J(3–4) = 4.7; J(4–5) = 5.1							
IVd	4.24	2.28	4.53	–	4.53	2.28	2.33	[d] (^{n}Bu)
	J(1–6-*endo*) = 6.8; J(1–2) = 6.3							
IIe	4.40	–	4.50	6.03	–	3.33	2.82	0.17, 0.64–1.07 [(CH_2)$_3$]; 1.07 (CH_3)
	J(2–3) = 5.3; J(2–6-*endo*) = 1.6; J(3–5) = 1.8; J(5–6-*endo*) = 7.0; CH_3–CH_2: J(H–H) = 7.0							
IIf	4.44	–	5.99	6.15	4.90	3.75	4.03	3.84 ($CHCl_2$)
	J(2–3) = J(3–4) = 5.2; J(4–5) = 5.6; J(5–6) = 6.0; $CHCl_2$: J(H-6-*endo*) = 7.0							
IIg	4.49	–	4.74	6.03	–	3.53	3.34	4.07 ($CHCl_2$)
	J(2–3) = 5.3; J(2–6-*endo*) = 1.6; J(3–5) = 1.7; J(5–6-*endo*) = 6.8; $CHCl_2$: J(H-6-*endo*) = 8.6							

[a] J values are in Hz. [b] The structure and numbering for each of these adducts are given in Scheme 1. [c] δ values are approximate due to overlapping. [d] Signals cannot be assigned due to overlapping.

Table 4

^{13}C NMR data for the nucleophilic addition products a–g

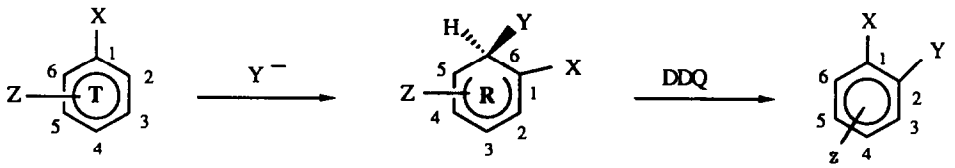
Adduct	$\delta(CDCl_3)$ (ppm from TMS)							
	Cp	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	Others
IIa	76.68	77.19 [a]	78.06	82.10	80.91	30.29	34.29	35.12 (CH_2)
IIb	76.47	80.96 [a]	70.50	81.98	77.81	32.66	36.32	23.89 (CH_2); 116.68 (CN)
IIc	76.95	64.96 [a]	76.42	81.60	96.67 [a]	38.39	28.97	79.62, 89.25 (C≡C); 122.89 [a] (1C), 131.47 (2C), 127.95 (2C), 127.47 (1C, Ph); 22.11 (CH_3)
IId	76.07	66.26 [a]	76.75	77.93	76.80	35.35	47.88	37.81, 27.41, 23.03 [$(CH_2)_3$]; 14.21 (CH_3)
IIId	75.78	33.10	103.83 [a]	79.80	75.64	32.18	40.68	39.13, 26.62, 22.94 [$(CH_2)_3$]; 14.23 (CH_3)
IVd	75.36	28.57	79.36	104.92 [a]	79.36	28.57	46.83	36.03, 27.40, 22.96 [$(CH_2)_3$]; 14.24 (CH_3)
IIe	77.96	64.09 [a]	73.70	77.00	101.24 [a]	36.15	49.80	36.91, 26.65, 22.34 [$(CH_2)_3$]; 13.91 (CH_3)
IIg	78.88	74.91 [a]	78.69	78.76	101.23 [a]	31.74	56.78	73.20 ($CHCl_2$)

[a] Quaternary carbons.

ing substituents and this fact is of significant preparative importance. Addition of the cyanomethyl anion to bis(mesitylene) iron complex has been described earlier by Helling and Cash [18] while for benzene and substituted benzenes complexed by tricarbonylchromium moiety similar additions have been studied by Semmelhack et al. [6,10]. In all these cases no conclusions as to the selectivity could be reached and the yields were poorer [5,7,10].

Non-selective additions

Under conditions similar to those described earlier the n-butyl anion adds indiscriminately to the iron(Cp) complex of the chlorobenzene Id giving all three possible isomers. Analysis of the spectral data leads to the conclusion that the isomer ratio of addition *ortho/meta/para* to the chloro substituent was 5/2.2/1. This ratio has been obtained from the integration of peaks both in proton and in carbon-13 spectra (an inverse gated experiment with a long relaxation delay has been completed) and a good agreement of those values has been found in calculations. When the symmetrical starting cation, iron(Cp) *p*-dichlorobenzene complex Ie was used, formation of a single product IIe was observed. Yields of the products IId/IIId/IVd and IIe are 61 and 75%, respectively, and the analytical data are presented in Tables 1–4. Addition of the dichloromethyl anion to iron(Cp) nitrobenzene complex Ia leads to the formation of an extremely unstable adduct IIf, which, despite many attempts, has not been isolated. Due to the instability of this adduct only proton NMR spectrum has been registered (Table 3). This spectrum indicates the presence of ca. 10% of other isomers (presumably IIIf and IVf) although we were unable to assign their spectra with reasonable certainty. Addition of the dichloromethyl anion to a symmetrical substrate, iron(Cp) *p*-dichlorobenzene cation Ie, leads to the formation of a stable single adduct IIg in a 42% yield. Analytical data for this complex are given in Tables 1–4. Addition of the trichloro-



I II V

T = $FeCpPF_6$ R = FeCp

Ia;	$X=NO_2$ Z=H $Y=CH_2NO_2$	IIa;	$X=NO_2$ Z=H $Y=CH_2NO_2$
Ia;	$X=NO_2$ Z=H $Y=CH_2CN$	IIb;	$X=NO_2$ Z=H $Y=CH_2CN$
Ic;	$X=NO_2$ Z=4-Me $Y=C\equiv CPh$	IIc;	$X=NO_2$ Z=4-Me $Y=C\equiv CPh$

Va;	$X=NO_2$ Z=H $Y=CH_2NO_2$
Vb;	$X=NO_2$ Z=H $Y=CH_2CN$
Vc;	$X=NO_2$ Z=4-Me $Y=C\equiv CPh$

Scheme 1

methyl anion to various starting complexes has been studied in order to establish the influence of the steric hindrance exerted by substituents present on the complexed benzene ring. In each case the isomer ratio was estimated on the basis of analysis of both proton and carbon-13 spectra. Full analytical data of complexes h–k, obtained in yields of 69–75%, are given in Tables 1, 2, 4, 5 and 6. It has been found that reaction of the trichloromethyl anion with iron(Cp) *p*-toluenesulfonylbenzene complex Ih leads to the formation of three isomeric adducts *ortho*-IIh, *meta*-IIIh and *para*-IVh in the ratio 1/2/1, respectively. Addition to the *p*-nitrobenzene complex Ib leads to the formation of adducts *ortho*-IIi and *meta*-IIIi to nitro substituent in a ratio 1/1. This mixture of isomers has been separated on a chromatographic column (5 cm; deactivated Alumina) using carbon tetrachloride for elution of IIIi and chloroform for elution of IIi. Addition of the trichloromethyl anion to t-butylbenzene complex Ij gives a 3/2 mixture of adducts *meta*-IIIj and *para*-IVj to the t-butyl substituent while addition to iron(Cp) *p*-dichlorobenzene complex Ie gives a single adducts IIk.

Addition of alkyl anions to arene complexes have been studied extensively. It should be noted that in the case of tricarbonylchromium complexes this reaction competes with the metallation of the ring [7]. Iron(Cp) complexes undergo addition of the methyl anion in a non-selective manner. Khand et al. [20] found that the *ortho / meta* adducts ratio for chlorobenzene complex was 4/1 and it was similar for the *p*-chlorotoluene complex [21*]. The obvious lack of selectivity of alkyl anion addition leaves symmetrical starting cations as the only worthwhile starting materi-

* Reference number with asterisk indicates a note in the list of references.

Table 5

^{1}H NMR data for the trichloromethyl addition products h–k

Adduct [b]	δ($CDCl_3$) (ppm for TMS) [a]							
	Cp	H(1)	H(2)	H(3)	H(4)	H(5)	H(6-*endo*)	Others
IIh	4.72	–	5.63	6.17	4.83	3.53 [c]	4.09	2.35 (CH_3); 7.17, 7.72 (Ph)
	J(2–3) = 5.5; *J*(3–4) = 5.8; *J*(5–6-*endo*) = 6.7; *J*(2–3 of Ph) = 8.2							
IIIh	4.71	3.59	–	6.51	4.68 [c]	3.10 [c]	3.59	2.38 (CH_3); 7.25, 7.81 (Ph)
	J(1–6-*endo*) = 6.3; *J*(3–4) = 5.3; *J*(2–3 of Ph) = 8.2							
IVh	4.63	3.14	5.26	–	5.26	3.14	3.53 [c]	2.38 (CH_3); 7.27 [c], 7.87 (Ph)
	J(1–6-*endo*) = 6.6; *J*(1–2) = 6.6; *J*(2–3 of Ph) = 8.2							
IIi	4.34	–	6.04	6.13	–	3.82	4.76	2.02 (CH_3)
	J(2–3) = 5.8; *J*(2–6-*endo*) = 1.4; *J*(5–6-*endo*) = 6.8; *J*(3–5) = 1.4							
IIIi	4.40	–	7.16	4.63	–	3.96	4.17	1.80 (CH_3)
	J(2–3) = 5.8; *J*(2–6-*endo*) = 1.3; *J*(3–5) = 1.3; *J*(5–6-*endo*) = 6.7							
IIIj	4.35	–	3.03	5.86	4.52	2.96	3.50	1.20 [$C(CH_3)_3$]
	J(1–6-*endo*) = 6.0; *J*(3–4) = 5.4; *J*(4–5) = 6.0							
IVj	4.35	2.85	4.48	–	4.48	2.85	3.57	1.46 [$C(CH_3)_3$]
IIk	4.52	–	4.91	6.05	–	3.69	4.08	–
	J(2–3) = 5.5; *J*(2–6-*endo*) = 1.6; *J*(5–6-*endo*) = 6.9; *J*(3–5) = 1.8							

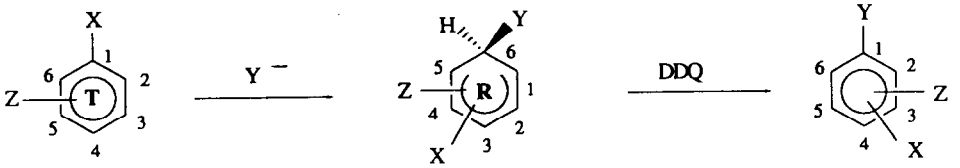
[a] *J* values are in Hz. [b] The structure and numbering for each of these adducts are given in Scheme 2. [c] δ values are approximate due to overlapping.

Table 6

^{13}C NMR data for the trichloromethyl addition products h–k

Adduct	δ($CDCl_3$) (ppm from TMS)							
	Cp	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	Others
IIh	76.53	53.54 [a]	79.47	81.73	81.20	31.72	53.81	21.49 (CH_3); 102.96 (CCl_3); 126.64 (2C), 128.79 (2C). 142.43 [a] (1C), 143.77 [a] (1C, Ph)
IIIh	75.85,	32.93	98.78 [a]	79.35	79.06	28.20	54.63	21.49 (CH_3); 102.55 (CCl_3); 127.42 (2C), 129.10 (2C), 138.54 [a] (1C), 143.70 [a] (1C, Ph)
IVh	74.46	31.30	80.08	98.73 [a]	80.08	31.30	53.51	21.41 (CH_3); 102.28 (CCl_3); 127.26 (2C), 129.59 (2C), 138.79 [a] (1C), 140.72 [a] (1C, Ph)
IIi	77.57	66.57 [a]	75.66	80.78	97.97 [a]	36.63	53.20	21.80 (CH_3); 102.19 (CCl_3)
IIIi	78.22	49.28 [a]	75.52	80.07	105.52 [a]	22.73	61.25	25.81 (CH_3); 101.46 (CCl_3)
IIIj	72.73	31.17	107.66 [a]	77.53	74.66	29.18	55.62	30.39 (CH_3); 33.86 (CCH_3); 104.04 (CCl_3)
IVj	72.85	25.22	75.19	107.66 [a]	75.19	25.22	55.46	30.85 (CH_3); 33.35 (CCH_3); 103.48 (CCl_3)
IIk	78.79	59.91 [a]	77.95	77.01	100.77 [a]	33.47	64.20	102.44 (CCl_3)

[a] Quaternary carbons.



I			II 1-X III 2-X IV 3-X	V
Id;	X=Cl Z=H	Y=n-Bu	**IId;** X=1-Cl Z=H **IIId;** X=2-Cl **IVd;** X=3-Cl	
Ie;	X=Cl Z=4-Cl	Y=nBu	**IIe;** X=1-Cl Z=4-Cl	**Ve;** Y=1-n-Bu X=2-Cl Z=5-Cl
Ia;	$X=NO_2$ Z=H	$Y=CHCl_2$ Z=H	**IIf*;** $X=1-NO_2$	
Ie;	X=Cl Z=4-Cl	$Y=CHCl_2$ Z=4-Cl	**IIg;** X=1-Cl	**Vg;** $Y=1-CHCl_2$ X=2-Cl Z=5-Cl
Ih;	$X=p-TolSO_2$ Z=H	$Y=CCl_3$	**IIh;** $X=1-TolSO_2$ **IIIh;** $X=2-TolSO_2$ **IVh;** $X=3-TolSO_2$	
Ic;	$X=NO_2$ Z=4-Me	$Y=CCl_3$	**IIi;** $X=1-NO_2$ Z=4-Me **IIIi;** $X=2-NO_2$ Z=5-Me	
Ij;	X=t-Bu Z=H	$Y=CCl_3$	**IIIj;** X=2-t-Bu **IVj;** X=3-t-Bu	
Ie;	X=Cl Z=4-Cl	$Y=CCl_3$	**IIk;** X=1-Cl Z=4-Cl	**Vk;** X=2-Cl Z=5-Cl $Y=CCl_3$

Scheme 2. * indicates the presence of minor isomers IIIf and IVf, established from the ^1H NMR spectrum.

als from the synthetic point of view and in the reaction of the *p*-dichlorobenzene complex with n-butyl anion we have isolated a single adduct in 75% yield. More interesting seemed to be the possibility of introduction of chlorinated alkyl groups into the ring. In that area, after an early report by Green et al. [22] on the addition of trichloromethyl to cobaltocene followed by reduction to a dichloromethyl group, there has been no reports on such reactions until recently. Nesmeyanov et al. [23] reported the trichloromethyl adduct to benzene iron(Cp) and Vol'kenau and Petrakova [24] also obtained the same compound starting from the peroxide dimer. These reactions are unsuitable for synthetic purpose due to difficulties with the preparation of starting materials. Recently Zaworotko and coworkers reported on the direct addition of a chloromethyl group to bis(arene)iron complexes [25] and the

Table 7

Analytical data for demetallation products a–k

Compound [a]	Yield (%)	MS (m/z, (%))	^{1}H NMR (δ, $CDCl_3$, ppm from TMS) [b]	^{13}C NMR (δ, $CDCl_3$, ppm from TMS)
Va	70	200, $[M+18]^+$, 100	8.29 (d, 8.0; d, 1.0; 1H); 7.67 (d, 8.0; d, 7.6; d, 1.2; 1H); 7.77 (d, 7.6; d, 7.4; d, 1.0; 1H); 7.52 (d, 7.4; d, 1.2; 1H); 5.84 (s, 2H)	148.20 [d], 134.39, 134.07, 131.50, 125.83 124.29 [d], 76.28
Vb	73	162, M^+, 15	8.23 (d, 11.2; 1H); 7.77–7.70 (m, 2H); 7.61–7.55 (m, 1H); 4.22 (s, 2H)	144.42 [d], 134.44, 131.10, 129.64, 125.82, 125.68 [d], 116.31(CN), 22.75
Vc	77	237, M^+, 10	8.02 (d, 8.5; 1H); 7.61–7.58 (m, 2H); 7.52 (s, 1H); 7.38 (m, 3H); 7.23 (d, 7.0; 2H)	148.30 [d], 145.53 [d], 135.64, 132.56, 130.79, 130.19 129.54, 125.60, 123.26, 118.67 [d], 96.60, 85.73, 21.10
Ve	75	202, M^+, 25	7.25 (d, 8.3, 1H); 7.19 (s, 1H); 7.09 (d, 8.3; 1H); 2.68 (t, 7.7; 2H); 1.58 (sextet, 7.7; 2H); 1.38 (sixtet, 7.7; 2H); 0.95 (t, 7.7; 3H)	142.13 [d], 132.29 [d], 132.15 [d], 130.40, 130.09, 127.05, 33.24, 31.64, 22.43, 13.88
Vg	59	228 [c], M^+, 8	7.90 (s, 1H); 7.40–7.20 (m, 2H); 7.06 (s, 1H)	139.03 [d], 131.65 [d], 131.10, 130.70, 129.81 [d], 128.92, 67.07 ($CHCl_2$)
Vk	78	262 [c], M^+, 5	8.17 (d, 2.4; 1H); 7.46 (d, 8.4, 1H); 7.36 (d, 8.4; d, 2.4; 1H)	140.20 [d], 133.89, 132.43 [d], 131.38, 131.25 [d], 127.88, 94.37 (CCl_3)

[a] The structure for each of these compound is given in the Schemes. [b] J values are in Hz. [c] Relative intensities of isotopic peaks are in agreement with the presence of four or five chlorine atoms for multichloroarenes, respectively. [d] Quarternary carbons.

addition of dichloromethyl anion to bis(mesitylene)iron dication [26]. We have successfully completed direct addition of both the dichloromethyl and trichloromethyl anions to iron(Cp) complexed arenes in the course of this study. The dichloromethyl anion adds non-selectively to the nitrobenzene complex but gives predominantly an *ortho* adduct of very low stability. The adduct with the *p*-dichlorobenzene complex shows high stability and was completely characterized. The addition of the dichloromethyl anion cannot be utilized in synthesis at this point since both its lower selectivity and low yields restrict its applicability.

Direct addition of the trichloromethyl anion is a reaction with enormous synthetic potential. Because of its high reactivity the trichloromethyl group may be converted into a carboxylic group [27], may be utilized directly for the synthesis of heterocyclic compounds [28] or converted into trifluoromethyl group [29]. This synthetic potential prompted us to examine the direct addition to arene iron(Cp) complexes in some detail. Reactions occur with a good yield regardless of the type of the substituents present on the benzene ring [30*] and usually a mixture of isomeric products is formed. Using substituents of various size we have established that the steric hindrance of a substituent is a primary factor determining a ratio of isomers. For the substituents of similar size a mixture with statistical ratio of isomeric products is formed as is observed in an addition of the trichloromethyl anion to the *p*-nitrotoluene complex (ratio 1/1). Use of the *p*-tolylsulfonyl substituent leads to the formation of a mixture *o*/*m*/*p* 1/2/1 as a result of steric and strong electronic interactions. The t-butyl substituent does not allow the formation of *ortho* adduct. The combination of a steric effect and the weakly donating effect of that group leads to the formation of *m*/*p* adducts in the ratio 3/2. Addition of the trichloromethyl anion to the *p*-dichlorobenzene complex leads to the formation of a single adduct, as expected.

Single products of all above addition reactions have been subjected to the demetallation reaction using the DDQ procedure described in earlier reports [27]. Analytical data for isolated substituted arenes are given in Tables 2 and 7. It should be noted that although reasonable good yields of demetallated arenes have been obtained (over 50%) both addition reactions and demetallation of adducts have been completed under standard conditions and the yields have not been optimized.

Addition of trichloromethyl anion to dialkylarenes

This study has been extended to include the addition of the trichloromethyl anion to dialkylarenes such as the isomeric xylenes, indan, tetralin and benzosuberane. Only the *p*-xylene complex, due to its symmetry, gives one adduct; the *m*-xylene complex can give rise to three isomeric products while the others (*o*-xylene, indan, tetralin and benzosuberane) could give rise to two adducts. We have found that on either short or extended reaction times, tetralin and benzosuberane complexes give only one adduct with trichloromethyl group entering the β-position to the alkyl chain. For indan, *o*-xylene and *m*-xylene short reaction times give two isomeric adducts, α- and β- to alkyl substituent. Interestingly, we did not find trace of a third isomeric product for the *m*-xylene complex with trichloromethyl group attached to the carbon between the two methyl substituents. The β-isomer is formed as a sole product of reaction upon extention of reaction time. The time necessary to obtain the β-adduct exclusively is approximately 4 h for *o*- and *m*-xylene while a 24 h period is required in the case of indan complex. These results parallel earlier

reports on regioselectivity of addition of anions to tricarbonylchromium complexes of *N*-methylindole by Ohlsson and Ullenius [32] and naphthalene or 5,8-dimethoxynaphthalene by Kundig et al. [33]. Kinetic studies presented by those authors indicated that the kinetically favoured product will be formed on a shorter reaction time while upon equilibration the thermodynamically stable adduct will predominate. Such argumentation also explains our results and under equilibration conditions thermodynamically favored β-adduct was an exclusive product in each case. Analysis of the structure of the addition complexes seems to indicate that steric factors play a dominant role in equilibration and this could explain the observation that the indan complex, showing the least steric hindrance, requires the longest reaction time. For *m*-xylene, an absence of addition to the carbon between the methyl substituents may be the result of the influence of both electronic factors, deactivating strongly this particular position and the steric hindrance of two methyl groups.

Our study indicates that a high selectivity of addition the trichloromethyl anion to dialkylarene complexes can be achieved. Subsequent demetallation with iodine leads to the development of a one-pot procedure allowing for the introduction of a trichloromethyl substituent selectively β to the alkyl substituents. We have found that addition reactions with iron (Cp) complexes of tetralin Il, benzosuberane, Im, and *p*-xylene, Iq, leads to the formation of a single adduct, IIIl, IIIm and IIIq respectively. In the remaining cases of indan, In; *o*-xylene, Io, and *m*-xylene, Ip complexes, both possible isomers (II and III) are formed in short reaction times but in each case, after an extended reaction time, only β-adducts (IIIn, IIIo, IIIp) remain. Analytical data for these adducts are presented in Tables 8–11. Demetallation of adducts, achieved in one-pot reactions, leads to the synthesis of β-trichloromethyldialkylarenes for which some analytical data have been presented earlier [34].

Demetallation of adducts leads to arenes with unusual substitution patterns. Iodine promoted demetallation of β-adducts to dialkylarenes in a one-pot reaction has been already described [34]. Demetallation of other adducts, effected upon treatment with DDQ according to the procedure published earlier [31] leads to the synthesis of some previously unknown compounds. Using this procedure we have prepared 2-nitromethylnitrobenzene [35], 4-methyl-2-phenylethynylnitrobenzene, 2-

Table 8

Selectivity of trichloromethyl addition to the CpFe complexes of dialkylarenes l–q

Complex	Arene in complex	Reaction time (h)	Ratio of the adducts	Yields of adduct (%)
Il	tetralin	1	IIIl (100%)	76
Im	benzosuberane	1	IIIm (100%)	85
In	indan	1	IIn (50%), IIIn (50%)	77
In	indan	4	IIn (40%), IIIn (60%)	72
In	indan	18	IIn (15%), IIIn (85%)	69
In	indan	24	IIIn (100%)	69
Io	*o*-xylene	1	IIo (25%), IIIo (75%)	73
Io	*o*-xylene	4	IIIo (100%)	71
Ip	*m*-xylene	1	IIp (28%), IIIp (72%)	70
Ip	*m*-xylene	4	IIIp (100%)	70
Iq	*p*-xylene	1	IIIq (100%)	75

Table 9

Elemental analysis for adducts and demetallation products l–q

Complex or compound	Formula	Found (%)		Calculated (%)	
		C	H	C	H
IIIl	$C_{16}H_{17}Cl_3Fe$	51.46	4.43	51.73	4.61
IIIm	$C_{17}H_{19}Cl_3Fe$	52.68	4.92	52.96	4.97
IIn/IIIn	$C_{15}H_{15}Cl_3Fe$	50.33	4.48	50.40	4.23
IIo/IIIo	$C_{14}H_{15}Cl_3Fe$	48.92	4.21	48.67	4.38
IIp/IIIp	$C_{14}H_{15}Cl_3Fe$	48.85	4.12	48.67	4.38
IIIq	$C_{14}H_{15}Cl_3Fe$	48.71	4.50	48.67	4.38
Vl	$C_{11}H_{11}Cl_3$	53.22	4.09	52.94	4.04
Vm	$C_{12}H_{13}Cl_3$	54.36	4.14	54.68	4.18
Vn	$C_{10}H_9Cl_3$	51.12	4.05	50.99	3.85
Vo	$C_9H_9Cl_3$	48.61	4.28	48.36	4.06
Vp	$C_9H_9Cl_3$	48.55	4.31	48.36	4.06

n-butyl-1,4-dichlorobenzene, as well as the earlier reported compounds such as 2-cyanomethylnitrobenzene [36], 1,4-dichloro-2-(dichloromethyl)benzene [37] and 1,4-dichloro-2-(trichloromethyl)benzene [37]. For dialkylarenes, a one-pot sequence

Table 10

^{1}H NMR data for the trichloromethyl adducts p–q

Adduct [b]	δ($CDCl_3$) (ppm for TMS) [a]							
	Cp	H(1)	H(2)	H(3)	H(4)	H(5)	H(6-*endo*)	Others
IIIl	4.21	2.81 [c]	–	–	4.43	2.81 [c]	3.43	1.70–1.98 (m, 4H);
	J(4–5) = 6.5; J(1–6-*endo*) = 6.0; J(5–6-*endo*) = 6.0							1.99–2.03 (m, 2H);
								2.39–2.46 (m, 1H);
								2.86–2.95 (m, 1H)
IIIm	4.11	2.77	–	–	4.34	2.69	3.33	1.48–1.68 (m, 4H);
	J(4–5) = 6.3; J(1–6-*endo*) = 6.1; J(5–6-*endo*) = 6.0							1.86–1.92 (m, 2H);
								1.95–2.10 (m, 2H);
								2.60–2.65 [c] (m, 1H);
								3.16–3.25 (m, 1H)
IIn	4.17	–	–	5.91	4.37	2.88	4.00	1.45–1.89 (m, 4H);
	J(3–4) = 5.0; J(4–5) = 5.3; J(5–6-*endo*) = 6.1							[d] (m, 1H); 3.38–3.47 (m, 1H)
IIIn	4.20	3.01	–	–	4.63	2.76	3.49	2.05–2.28 (m, 4H);
	J(4–5) = 6.2; J(1–6-*endo*) = 5.8; J(5–6-*endo*) = 6.1							2.55–2.63 (m, 1H);
								2.80–2.91 (m, 1H)
IIo	4.17	–	–	5.67	4.35	3.41 [c]	3.59	1.89, 1.96 (two s, CH_3)
	J(3–4) = 5.2; J(4–5) = 5.7; J(5–6-*endo*) = 6.3							
IIIo	4.18	2.86	–	–	4.42	2.78	3.40 [c]	1.91, 2.40 (two s, CH_3)
	J(4–5) = 6.2; J(1–6-*endo*) = 5.9; J(5–6-*endo*) = 6.2							
IIp	4.17	–	4.30 [c]	–	4.31 [c]	2.73	3.61	1.81, 2.17 (two s, CH_3)
	J(5–6) = 6.3							
IIIp	4.18	2.89	–	5.71	–	2.89	3.45	1.90 (s, CH_3)
	J(1–6-*endo*) = 6.0							
IIIq	4.17	–	4.32	5.66	–	2.87	3.63	1.80, 1.86 (two s, CH_3)
	J(2–3) = 5.2; J(5–6-*endo*) = 6.2							

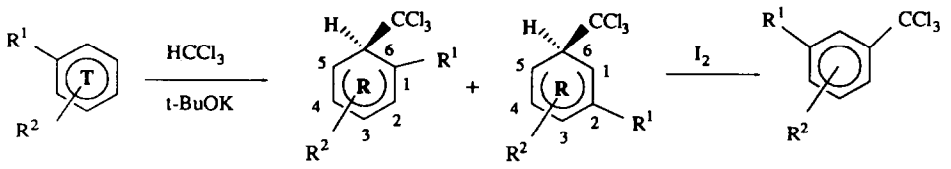
[a] J values are in Hz. [b] The structure and numbering for each of these adducts are given in Scheme 3. [c] δ values are approximate because of overlapping. [d] signal cannot be assigned due to overlapping.

Table 11

^{13}C NMR data for the trichloromethyl adducts IIIl–q

Adduct [b]	$\delta(CDCl_3)$ (ppm from TMS) [a]								
	Cp	CCl_3	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	Others
IIIl	74.22	103.72	30.04	93.30 [a]	94.07 [a]	76.67	29.25	56.41	23.15, 23.66, 28.51, 28.69 [$(CH_2)_4$]
IIIm	73.35	103.78	35.00	96.93 [a]	97.27 [a]	79.54	28.13	55.83	27.81, 27.82, 32.74, 32.75, 36.78 [$(CH_2)_5$]
IIIn	73.42	103.33	28.23	98.03 [a]	99.51 [a]	73.48	25.33	56.51	23.56, 31.65, 32.36 [$(CH_2)_3$]
IIIo	73.87	103.60	32.09	91.59 [a]	91.79 [a]	79.40	28.80	56.32	18.60, 20.00 (CH_3)
IIIp	73.76	104.46	31.85	92.63 [a]	79.67	92.63 [a]	31.85	56.57	22.04 (CH_3)
IIIq	74.25	103.67	43.85 [a]	77.69	79.50	91.24 [a]	29.61	61.58	21.83, 26.10 (CH_3)

[a] Quaternary carbons. [b] ^{13}C NMR spectra of adducts IIn, IIo and IIP have not been taken.



I	IIa	IIIb	Vc
Arene in I			
Il- tetralin	----	**IIIl**	**Vl**
Im-benzosuberane	----	**IIIm**	**Vm**
In- indan	**IIn**	**IIIn**	**Vn**
Io- o-xylene	**IIo**	**IIIo**	**Vo**
Ip- m-xylene	**IIp**	**IIIp**	**Vp**
Iq- p-xylene	----	**IIIq**	**Vq**

Scheme 3. [a] Adduct α to alkyl substituents. [b] Adduct β to alkyl substituents. [c] Only products of β addition have been demetallated. [d] Due to the symmetry of Iq, IIIq = IIq but description IIIq has been arbitrarily chosen.

of reactions has been devised and this leads to the synthesis of other previously unknown compounds, i.e. 3,4-dimethyltrichloromethylbenzene, 3,5-dimethyltrichloromethylbenzene, 5-trichloromethylindan, 6-trichloromethyltetralin and 7-trichloromethylbenzosuberane.

In summary we would note out that our results expands further applicability of the nucleophilic addition-demetallation procedure in synthetic organic chemistry. The list of the anions which add in a regioselective *ortho* fashion to an electron-withdrawing substituent in a (CpE) arene, containing so far 2-oxoalkyl and cyano functions has been extended by the nitromethyl, cyanomethyl and phenylethynyl anions. Of the anions which show no regioselectivity under similar conditions, the introduction of a trichloromethyl group either to symmetrical arenes or to unsymmetrical arenes under controlled conditions, might have synthetic utility.

Experimental

^{1}H NMR spectra (300.133 MHz) and ^{13}C NMR spectra (75.469 MHz) were recorded on a Bruker 300AM spectrometer using ca. 1% solutions for ^{1}H NMR and saturated solutions for ^{13}C NMR. Chemical shifts are referred to internal tetramethylsilane (TMS, ^{1}H NMR) or to solvent signals (^{13}C NMR). The inverse gated decoupling ^{13}C NMR spectra were registered using pulse width of 5.0 μs and long relaxation delay time (25 s) at 64 K memory capacity for Fourier Transform (FT). Mass spectra were obtained using an AEI MS 12 instrument. Elemental analyses were performed in the Department of Chemistry, University of Saskatchewan.

Commercially available reagents including n-butyllithium, lithium diisopropylamide, potassium t-butoxide, 2,3-dichloro-5,6-dicyanobenzoquinone, iodine (Aldrich Chemical Co.), were used directly in the reactions. Liquid chemicals such as arenes, phenylacetylene, nitromethane, acetone and acetonitrile were distilled before use.

All solvents such as chloroform, methylene chloride, tetrahydrofuran and diethyl ether of reagent grade were purified by standard procedures. Alumina F20 (Alcoa Chemica) was deactivated by exposure to air for 48 h before being used in the column chromatography.

Preparation of arene iron(Cp) complexes I

Arene iron(Cp) hexafluorophosphates (I) have been prepared using procedures described in the literature: nitrobenzene, Ia, and *p*-nitrotoluene, Ic [38]; chlorobenzene, Id, and *p*-dichlorobenzene, Ie [39]; *p*-toluenesulfonylbenzene, In [40]; t-butylbenzene, Ij [41]; tetralin, Il [42]; indan, In [43]; *o,m,p*-xylene, Io,p,q [44]. Benzosuberane which was used in the ligand exchange reaction was prepared from commercially available 1-benzosuberone (Aldrich Co.) following a reported procedure [45].

In the ligand exchange reaction, a mixture of 4.6 g (25 mmol) of ferrocene, 6.7 g (50 mmol) of $AlCl_3$, 0.7 g (25 mmol) of Al and 3.7 g (25 mmol) of benzosuberane in 50 mL of n-nonane was heated under reflux at 130–135 °C for 5 h. The reaction mixture was decomposed with water, the water layer washed with n-hexane and then treated with 2 g of solid NH_4PF_6 giving 4.7 g (46%) of the CpFe complexed benzosuberane Im, as a yellow powder. Analysis. Found: C, 46.42; H, 4.71. $C_{16}H_{19}F_6FeP$ calc.: C, 46.60; H, 4.61%. ^1H NMR (δ, ppm from TMS, acetone-d_6): 1.21–1.33 (m, 2H); 1.73–2.13 (m, 4H); 2.88–2.99 (m, 2H); 3.30–3.39 (m, 2H); 5.07 (s, 5H); 6.27 (br. s, 4H). ^{13}C NMR (δ, ppm from TMS, acetone-d_6): 28.10 (2C); 32.03 (1C); 35.21 (2C); 77.65 (Cp); 86.77 (2C); 89.31 (2C); 108.79 (2C).

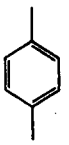
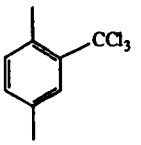
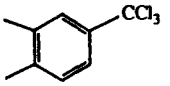
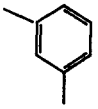
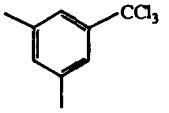
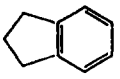
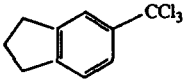
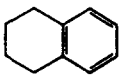
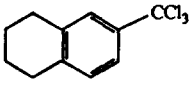
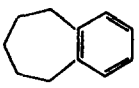
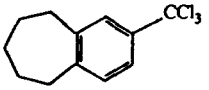
Addition reaction–general procedure

A solution of 2–5 mL of the base precursor in 10 mL of THF was deaerated by bubbling N_2 through it for 10 min. After the solution was cooled to −78 °C, an appropriate base was added (4 mL of a 1.5 *M* solution of LDA in hexane; 2.0 mL of a 1.5 *M* solution of BuLi in hexane or 0.896 g or 8.0 mmol of ^{t}BuOK, See Table 1) and the mixture was stirred for 2–3 min. To the resulting mixture, 1.0 mmol of cation I was introduced and stirring was continued at −78 °C under N_2 for 1.5 h. The reaction mixture was then poured into 150 mL of ether–chloroform (1/1), and then filtered through a sintered glass filter. The resulting solution was washed with H_2O (3 × 50 mL), dried over $MgSO_4$, and the solvent was removed on a rotary evaporator. The residual crude product was redissolved in a small volume of chloroform, filtered and evaporated giving the product. Yields and analytical data for products II–IV are given in Tables 1–4, 10, and 11.

DDQ Demetallation—general procedure

To a stirred solution of 0.5 mmol of adduct II in 10 mL of acetonitrile, 170 mg (0.75 mmol) of DDQ was added rapidly. The mixture was stirred at room temperature for 30 min. The resulting material was filtered through a sintered glass filter and then evaporated to dryness. The residue was then redissolved in chloroform and passed through a short column (5 cm) packed with deactivated F-20 alumina. The n-pentane and ether eluates were discarded and the combined chloroform and methylene chloride fraction gave the product V. Analytical data for products V are presented in Tables 2 and 7.

Table 12

Starting Complex	Arene in complex	Addition time (h)	Product		Yield of V %
Iq		1		Vq	53
Io		4		Vo	55
Ip		4		Vp	50
In		24		Vn	45
Il		1		Vl	65
Im		1		Vm	52

One-pot trichloromethylation of dialkylarenes

In a general procedure for the one-pot trichloromethylation reaction, 2.0 mmol of a CpFe complexed dialkylarene was introduced to a solution prepared by stirring 896 mg (8.0 mmol) of ^{t}BuOK and 5.0 mL of $CHCl_3$ in 20 mL of THF at −78°C. The mixture was allowed to warm up to the room temperature and stirring was continued at room temperature under N_2 over a period of time as indicated in Table 12. A solution of 40 mg of iodine in 10 mL of THF was then introduced and the mixture was stirred further for 10–12 h. The resulting mixture was diluted with ether and any solid material was removed by filtration. The ethereal solution was washed with a saturated solution of $NaHSO_3$ in H_2O (4 × 50 mL) and then with H_2O (2 × 50 mL). After drying over $MgSO_4$, the ether was removed using a rotary evaporator. The residual oil was distilled using a microdistillation apparatus (Büchi GKR-50) to give the trichloromethylated arene. Analytical data for trichloromethylated arenes are presented in Tables 2 and 7.

Acknowledgements

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