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ARTICLE TYPE

Halogenophilic pathway in the reactions of transition metal carbonyl anions with [(η^6-iodobenzene)$Cr(CO)_3$]

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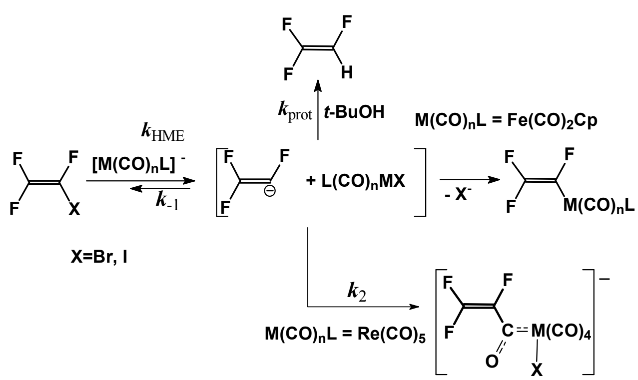
The paper provides a first example of formal nucleophilic substitution by halogenophilic pathway in $Cr(CO)_3$ complexes of haloarenes with metal carbonyl anions. All metal carbonyl anions examined attack [(η^6-iodobenzene)$Cr(CO)_3$] at halogen, which is shown by aryl carbanion scavenging with *t*-BuOH. The reaction with K[$CpFe(CO)_2$] gives only the dehalogenated arene, but the reaction with K[$Cp^*Fe(CO)_2$] (Cp^*=η^5-C_5Me_5) results in nucleophilic substitution to give [(η^6-$C_6H_5FeCp^*(CO)_2$)$Cr(CO)_3$]. Reaction with Na[$Re(CO)_5$] quantitatively gives the iodo(acyl)rhenate anion Na[(η^6-$C_6H_5C(O)ReI(CO)_4$)$Cr(CO)_3$] and in case of K[$Mn(CO)_5$] a mixture of σ-aryl complexes [(η^6-$C_6H_5Mn(CO)_5$)$Cr(CO)_3$] and K[(η^6-$C_6H_5Mn(CO)_4I$)$Cr(CO)_3$]. An analogous rhenium complex Na[(η^6-$C_6H_5Re(CO)_4I$)$Cr(CO)_3$] is formed from the initial iodo(acyl)rhenate upon prolonged standing at 20°C, and its structure (in the form of $[NEt_4]^+$ salt) is established by X-ray diffraction analysis. The reaction of [(η^6-chlorobenzene)$Cr(CO)_3$] with K[$CpFe(CO)_2$], on the contrary, proceeds by common S_N2Ar mechanism.

Introduction

Nucleophilic substitution with a transition-metal centered nucleophile is arguably one of the easiest ways to form a transition-metal carbon σ-bond. For more than five decades metal carbonyl anions, carbonylmetallates, have been widely used for that purpose due to their nucleophilic reactivity, availability and better stability, compared to other transition metal anions. [1-7] Besides aliphatic substitution, carbonylmetallates can be also used to create transition metal – sp^2-carbon bond in nucleophilic vinylic and aromatic substitution reactions. Among the notable examples are the reactions of carbonylmetallates with $Cr(CO)_3$ π-complexes of haloarenes leading to heterobimetallic complexes with bridging σ,π-arene ligand.[8-10] Complexation with $Cr(CO)_3$ activates haloarene towards nucleophilic attack,[11, 12] and these reactions display rather a rich and interesting chemistry of competitive nucleophilic aromatic substitution and haloarene reduction. It was concluded, however, that more detailed studies are required to define both the mechanism of the substitution and the relationship between the substitution and dehalogenation processes.[8]

On the other hand, transition metal carbonyl anions gained significant importance as model systems in organometallic chemistry, and were used by our group to study the mechanisms of nucleophilic vinylic and aromatic substitution by metal-centered nucleophiles. In the reactions with halopentafluorobenzenes[13, 14] and bromtrifluoroethylene[15] we were able to prove a halogenophilic mechanism of nucleophilic substitution. In this pathway carbonylmetallate first attacks not at carbon atom, but at halogen, and the "normal" nucleophilic substitution product is formed on the second step by the coupling of carbanion and metal carbonyl halide intermediates (Scheme 1).



Scheme 1. The halogenophilic mechanism of nucleophilic vinylic substitution

Later it was shown, that the halogenophilic attack is one of the major pathways in the reactions of carbonylmetallates with vinyl halides.[16, 17] However, the scope of the same mechanism in aromatic substitution with carbonylmetallates remained unexplored, the known examples are still limited to the pentafluorophenyl halides. The aim of this work is to study the reaction mechanism of carbonylmetallates with $Cr(CO)_3$ π-complexes of chloro- and iodobenzene, and to seek evidence for or against the halogenophilic pathway in both substitution and competing reduction processes.

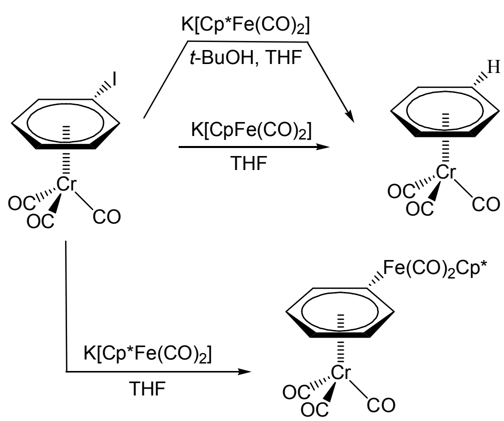
Table 1. Products of the reaction of (η^6-C_6H_5X)$Cr(CO)_3$ (X=Cl, I) with K[(C_5R_5)$Fe(CO)_2$] (R=H, CH_3), THF, 22°C

entry	ArX	Reagent and additive	Product yields, % [a] (Ar = (η^6-C_6H_5)$Cr(CO)_3$) ArFp or ArFp*	ArH	Fp_2 or $(Fp^*)_2$
1	(C_6H_5Cl)$Cr(CO)_3$	KFp, no additive	80	7	16
2	(C_6H_5Cl)$Cr(CO)_3$	KFp, *t*-BuOH	80	11	16
3	(C_6H_5I)$Cr(CO)_3$	KFp, no additive	-	25	~100
4	(C_6H_5I)$Cr(CO)_3$	K[Fp*], no additive	60	15	25
5	(C_6H_5I)$Cr(CO)_3$	K[Fp*], t-BuOH	-	50	~100

[a] Product yields were determined by ^1H NMR spectroscopy using durene as internal standard.

Results and Discussion

The reaction of $Cr(CO)_3$ complexes of chlorobenzenes with K[$CpFe(CO)_2$] (KFp) was studied most extensively by Heppert et. al.[8] The reaction usually gives the nucleophilic substitution products (ArFp) in good yields accompanied by minor amounts of reduced haloarene (ArH) and $[Fp]_2$. To test for aryl carbanion intermediates in this reaction we performed it in the presence of an “anion scavenger” – *t*-BuOH, the test previously used by us[13-16] and others[18-20] to detect the halogenophilic reaction mechanism (Scheme 1). The yield of the ArFp complex, and the substitution/reduction product ratio (ArFp/Fp_2) did not change in the presence of *t*-BuOH (en. 2, Table 1)*, which effectively rules out the halogenophilic pathway for the nucleophilic substitution reaction.



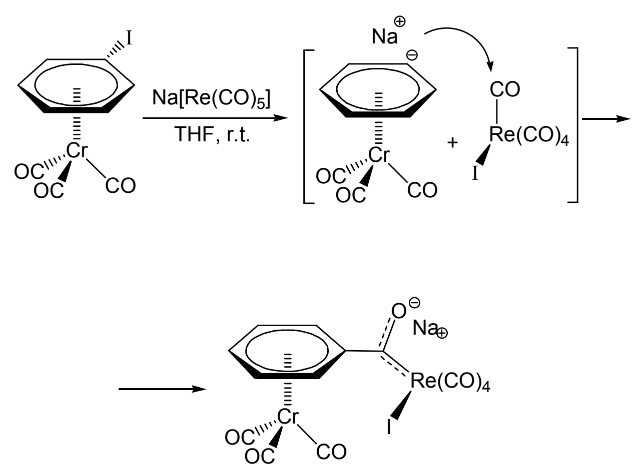
Scheme 2. Reaction of (η^6-C_6H_5I)$Cr(CO)_3$ with K[(C_5R_5)$Fe(CO)_2$] (R=H, CH_3)

Haloarene reduction becomes the only observed process in the reaction of KFp with [(η^6-iodobenzene)$Cr(CO)_3$], with no substitution product detected in the reaction mixture. A considerable amount of ArH formed without an added alcohol may be explained by aryl carbanion proton abstraction from Cp-group of Fp_2 or FpI. If this is indeed the case, one can try to exclude this proton source (and aryl carbanion sink) by replacing KFp with its pentamethylated analog, K[$C_5Me_5Fe(CO)_2$] (K[Fp*]).

We were pleased to find that the reaction of K[Fp*] with [(η^6-C_6H_5I)$Cr(CO)_3$] gave the [(η^6-$C_6H_5Fp^*$)$Cr(CO)_3$] complex with 60% yield (Scheme 2). The addition of *t*-BuOH to the reaction mixture suppressed its formation, completely, proving the halogenophilic pathway for this substitution reaction. The amount of ArH formed in the presence of *t*-BuOH (0.5 mol per mol of K[Fp*]) corresponds to a stoichiometry of halogenophilic reaction when it gives $[Fp^*]_2$ (eqn (1)).

$$\mathrm{ArI} + 2\,\mathrm{K[Fp^*]} \longrightarrow \left|\mathrm{ArK} + \mathrm{Fp^*I}\right| + \mathrm{K[Fp^*]} \longrightarrow \xrightarrow{t\text{-BuOH}} \mathrm{ArH} + [\mathrm{Fp^*}]_2 + \mathrm{KI} \quad (1)$$

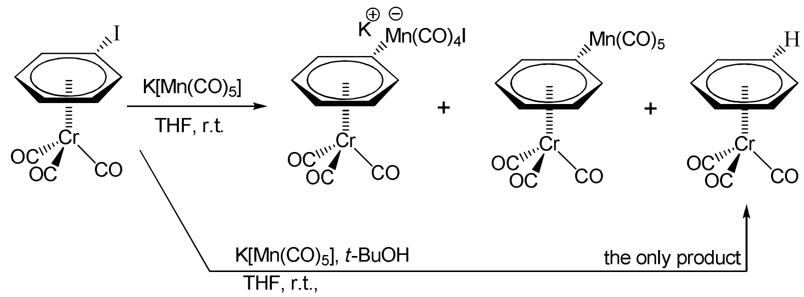
$Cr(CO)_3$ complexes of chlorobenzenes were previously found to be unreactive towards $Na[Re(CO)_5]$ and other less nucleophilic carbonylmetallate anions.[8] Bearing in mind that iodoarenes are much more reactive in halogenophilic processes than chloroarenes (by a factor of ~10^6)[17], we studied the reaction of [(η^6-iodobenzene)$Cr(CO)_3$] with pentacarbonylrhenate anion, $Na[Re(CO)_5]$. The reaction actually gave a single product with a quantitative yield, the iodo(acyl)rhenate anion† expected for the halogenophilic mechanism (Scheme 3). The isolation of the iodo(acyl)rhenate was not attempted, instead it was characterized in solution by IR, ^{13}C NMR (Fig. S1-S2 of the ESI) and HR ESI MS spectra. Halo(acyl)rhenate results from the nucleophilic addition of carbanion to the equatorial CO ligand of $[Re(CO)_5X]$,[14, 15] and thus provides direct evidence of the intermediates generated in the halogenophilic attack.



Scheme 3. Iodo(acyl)rhenate formation in the reaction of $Na[Re(CO)_5]$ with (η^6-C_6H_5I)$Cr(CO)_3$

The reactions of [(η^6-iodobenzene)$Cr(CO)_3$] with K[Fp*] or

Na[Re(CO)$_5$] are instantaneous at room temperature, but its



Scheme 4. The reaction of [(η^6-C_6H_5I)Cr(CO)$_3$] with K[Mn(CO)$_5$]. Effect of the "anion scavenger"

reaction with less nucleophilic K[Mn(CO)$_5$] is not, its progress can be monitored spectroscopically and in this case a more complex picture arises. Its main product is not the iodo(acyl)manganate, by the analogy with Na[Re(CO)$_5$], but the iodo(aryl)manganate anion, K[ArMnI(CO)$_4$] (Ar=(η^6-C_6H_5)Cr(CO)$_3$) (Scheme 4, Table 2). The anionic product is easily identified by its characteristic CO-signal patterns in IR and ^{13}C NMR spectra, closely resembling that of halo(acyl)metallates, but with no bridging acyl carbon signal (δ>250 ppm, Fig. S3 and S4 of the ESI). In contrast to acylate anions, addition of 18-crown-6 has a negligible effect on the IR and NMR spectra of K[ArMnI(CO)$_4$], indicating that it forms solvent-separated ion pairs in THF solution.

Table 2. Yields of the arene products in the reaction of [(η^6-C_6H_5I)Cr(CO)$_3$] with K[Mn(CO)$_5$], THF, 22°C.

		Product yields, % (Ar = (η^6-C_6H_5)Cr(CO)$_3$)		
Entry	Additive	K[ArMnI(CO)$_4$]	[ArMn(CO)$_5$]	ArH
1 [a]	-	40	18	15
2 [b]	18-crown-6	50	-	20
3	*t*-BuOH	-	-	78

[a] Minor amounts of [Mn(CO)$_5$I] and [Mn$_2$(CO)$_{10}$] were also detected by IR spectroscopy. [b]Minor amount of K[Mn(CO)$_4$I$_2$] also detected by IR.

Also present in the mixture is the neutral pentacarbonylmanganese σ-aryl complex, [ArMn(CO)$_5$], together with the iodoarene reduction product, [(η^6-C_6H_6)Cr(CO)$_3$]. However, K[ArMnI(CO)$_4$] and [ArMn(CO)$_5$] are not the initial products, as they are both absent at the early stages of the reaction (10-30 min) whereas the signals of the two intermediates are seen in ^{1}H and ^{13}C NMR spectra (Fig. S5 of the ESI).

The intermediate, appearing first and decaying faster (~1 hr), exhibits signal patterns characteristic for a iodo(acyl)manganate anion: the ^{13}C NMR signal of bridging CO group at 285.6 ppm, the signal of C-para of C_6H_5-group at 95.8 ppm, in lower field than that of *ortho* and *meta* carbons (94.8, 91.7 ppm)**. The IR band at 2073 cm^{-1} observed in the first minutes of reaction presumably also belongs to this intermediate and is replaced towards the end of the reaction (4 hr) by the band at 2060 cm^{-1} belonging to K[ArMnI(CO)$_4$] (Fig. S6 of the ESI).

Upon the addition of 18-crown-6 the band at 2073 cm^{-1} is immediately replaced by the band at 2060 cm^{-1}, which may be explained by the dissociation of contact ion pairs of the iodo(acyl)manganate intermediate (Fig. S7 and S8 of the ESI). Signals presumably belonging to this intermediate are also observed in ^{13}C NMR spectrum of the reaction performed in the presence of 18-crown-6 (93.63, 92.20, and 93.50 ppm). The final products composition in the presence of 18-crown-6 is simpler and contains only K[ArMnI(CO)$_4$] and ArH (en. 2, Table 2) and minor amount of K[Mn(CO)$_4$I$_2$].

These observations lead one to conclude that acylmanganate, K[ArC(O)MnI(CO)$_4$] is the initial product of the reaction, which then transforms into [ArMn(CO)$_5$] and K[ArMnI(CO)$_4$]. Besides, this is in good agreement with the previous data on the facile decomposition of halo(acyl)manganates into *σ*-aryl complexes in the reactions of K[Mn(CO)$_5$] with C_6F_5X (X=Br,I).[14]

Halogenophilic character of the [(η^6-C_6H_5I)Cr(CO)$_3$] reaction with K[Mn(CO)$_5$] was further confirmed by the aryl carbanion intermediate trapping with proton donor. With *t*-BuOH added, no *σ*-aryl manganese complexes were formed, and [(η^6-C_6H_6)Cr(CO)$_3$] became the only arene product (Scheme 4, en.3, Table 2), while [Mn(CO)$_5$I] was mainly trapped in the form of K[*t*-BuOC(O)Mn(CO)$_4$I][14] and [Mn$_2$(CO)$_{10}$] according to IR spectrum.

A rate plot consistent with second-order kinetics is observed for the reaction of [(η^6-C_6H_5I)Cr(CO)$_3$] with K[Mn(CO)$_5$] in the presence of *t*-BuOH (Fig. S9 and S10 of the ESI), allowing for the second order rate constant (k_{obs}=0.031 l/mol·s) to be calculated from this data. However, the same reaction without an added proton donor is definitely slower (k_{obs}=0.010-0.015) and deviates from the second order rate law. The reversible halogen-metal exchange step in the case of relatively weak K[Mn(CO)$_5$] nucleophile may be the cause underlying this kinetic behavior. We will refere here to the general Scheme 1 because it shows the same mechanism; reversible halogen-metal exchange step means that k_{-1}> k_2.When the intermediate carbanion is captured by the proton donor, and provided this step is sufficiently fast (k_{prot}>k_{-1}), the fist step becomes irreversible and the overall rate increases (k_{obs}= k_{HME}).

The transformation of acylmanganate K[ArC(O)MnI(CO)$_4$] into arylmanganate may go through the elimination of KI followed by aryl migration, to give the neutral σ-aryl complex in which the CO-ligand is then substituted by iodide anion (Scheme

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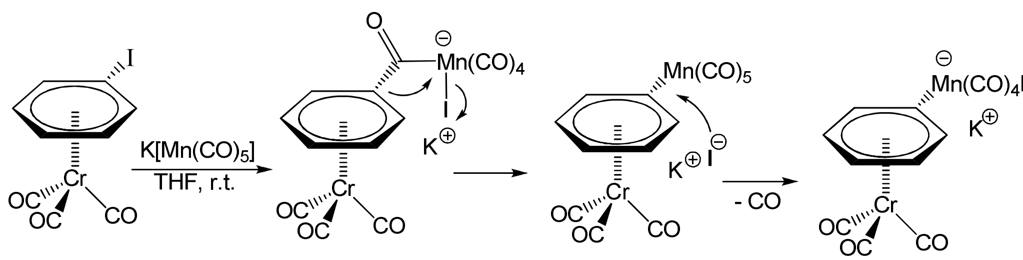

Scheme 5. Pathway for iodo(aryl)maganate formation in the reaction of [(η^6-C_6H_5I)$Cr(CO)_3$] with K[$Mn(CO)_5$]

5). However, [$ArMn(CO)_5$] was not observed as intermediate, i.e. its signals appeared only when the signals of K[$ArMnI(CO)_4$] product were already visible in the spectrum (Fig. S5 of the ESI). Yet, this alternative possibility of direct elimination of CO from K[$ArC(O)MnI(CO)_4$] seems less likely. DFT calculationsshowed that the barrier for the CO elimination from Na[(η^6-$C_6H_5C(O)MnI(CO)_4$)$Cr(CO)_3$] is much higher (32.9 kcal/mol) than the barrier for elimination of NaI (19.8 kcal/mol). ‡ Moreover, the reaction of [$Mn(CO)_5Br$] with [(C_6H_5Li)$Cr(CO)_3$] in the presence of $P(OMe)_3$ was reported to give the product of bromide (not CO) substitution in the intermediate bromo(acyl)manganate, i.e. [*cis*-(($MeO)_3P$)$Mn(CO)_4$(η^6-$C_6H_5C(O)$)$Cr(CO)_3$].[23, 24]

The K[$ArMnI(CO)_4$] complex was not isolated and therefore was characterized in solution with spectroscopic methods (IR, ^{13}C NMR and HR ESI MS). However, it was observed that the iodo(acyl)rhenate, K[$ArC(O)ReI(CO)_4$], on prolonged standing in THF solution was also transformed into analogous iodo(aryl)rhenate. After 6 months, only 17% of iodo(acyl)rhenate was left and iodo(aryl)rhenate, K[$ArReI(CO)_4$], was formed in 58% yield (eqn (2)). It was isolated in solid state as an [Et_4N]$^+$ salt (using the method from [10]) and its structure was unambiguously established by single-crystal X-ray diffraction analysis.

$$\mathrm{Na}[(\eta^6\text{-}\mathrm{C_6H_5C(O)Re(CO)_4I})\mathrm{Cr(CO)_3}] \xrightarrow[\text{- CO}]{\text{THF, 6 month}} \mathrm{Na}[(\eta^6\text{-}\mathrm{C_6H_5Re(CO)_4I})\mathrm{Cr(CO)_3}] \quad (2)$$

It should be pointed out, that the ^1H and ^{13}C NMR signal patterns of the K[$ArMnI(CO)_4$] and of the isolated iodo(aryl)rhenate are quite similar, which confirms the identification of the former.

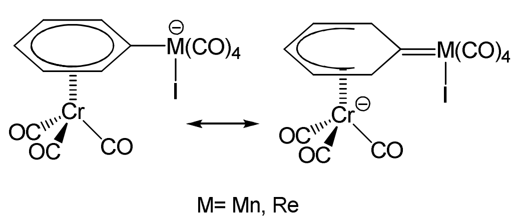

Fig. 1 Resonance with a metal carbene structure for iodo(aryl)metallates

The downfield shift of the signals of *ortho*-protons (~6.05 ppm) and *ortho*-carbons (~113 ppm) is a distinctive spectrum feature and reflects the contribution of the metal carbene resonance structure (Fig. 1) in these complexes.

The structure of the iodo(aryl)rhenate complex is shown in Fig. 2. The coordination around rhenium is approximately octahedral, slightly distorted by an “umbrella” effect, the displacement of the two mutually *trans* carbonyl groups (C12-O6 and C11-O5) towards the aryl ring.[25-27] The octahedral rhenium moiety adopts a “staggered” conformation relative to the plane of the aryl ring (C12-Re-C1-C2 torsion angle 51.7°). Iodine and the aryl group are expectedly in *cis*-position, which is the preferred configuration for [$XYM(CO)_4$] (M=Mn, Re) complexes. The Re1-C13 distance is significantly shorter (1.898 Å) than the other three Re-C_{CO} distances (1.978 – 2.007 Å), reflecting the stronger *trans*-effect of CO and aryl ligands compared to iodide ligand.

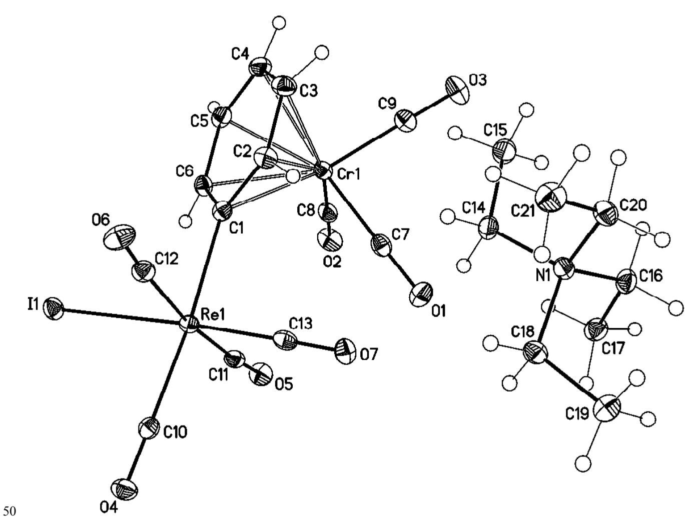

Fig.2. Molecular structure of [Et_4N][(η^6-$C_6H_5ReI(CO)_4$)$Cr(CO)_3$]. Selected bond distances (Å) and angles (°): Re1-I1 2.8321(3), Re1-C1 2.214(3), Re1-C12 2.007(4), Re1-C13 1.899(4), Re1-C10 1.978(5), Cr1-C1 2.321(3), C1-C2 1.436(5), C2-C3 1.401(5), Cr1-C4 2.238(4), Cr1-C7 1.824(4), C11-Re1-C12 172.9(1), C13-Re1-I 177.2(1), C12-Re1-C1-C2 51.7(2)

There is no significant shortening of Re1-$C1_{aryl}$ bond (2.214 Å) in comparison to the known rhenium σ-aryl complexes (2.22-2.23 Å)[28], and it is significantly longer than found in rhenium carbene complexes (2.09-2.13 Å)[29-31]. However, the contribution of metal carbene resonance structure (Fig. 1) can be traced in the slight elongation of C1-C6 (1.435 Å) and C1-C2 (1.424) bonds adjacent to rhenium, compared to 1.409 Å average for the other four C-C bonds in the aromatic ring and a slight slipping of $Cr(CO)_3$ unit away from C1 by 0.08 Å.

Conclusions

The reactions of iodobenzene $Cr(CO)_3$ π-complex with carbonylmetallates show an illustrative example of halogenophilic attack in nucleophilic aromatic substitution. Depending on the carbonylmetallate anion, the final product of the reaction may be the σ-aryl complex (with $K[(C_5Me_5)Fe(CO)_2]$), the iodo(acyl)rhenate anion (with $Na[Re(CO)_5]$) or the iodo(aryl)manganate anion (with $K[Mn(CO)_5]$), but in all these cases the reaction proceeds *via* initial attack of carbonylmetallate anion at halogen in $[(\eta^6$-iodobenzene$)Cr(CO)_3]$. Thus, the halogenophilic pathway of nucleophilic substitution is common for aryl halides with different types of activation – polyfluorinated and π-coordinated.

Experimental

General

^{1}H NMR (400.13 MHz) and ^{13}C NMR (100.61 MHz) spectra were obtained on a Bruker Avance spectrometer at 22°C and referenced to the signals of the solvent. IR spectra were recorded on Thermo Nicolet IR-200 spectrometer in THF in a 0.2 mm CaF_2 cell. High resolution mass spectra (HR MS) were measured on the Bruker micrOTOF II instrument using electrospray ionization (ESI). The measurements were done in a negative ion mode for anionic complexes and in positive ion mode for neutral complexes (3200 V); external or internal calibration was done with Electrospray Calibrant Solution (Fluka).

All operations with metal carbonyl anion salts were performed in "all-fused" glassware using vacuum-line techniques. Break-seal ampoules were used for the transfer of substances. Potassium salts of metal carbonyl anions were obtained quantitatively (95-98%) by reductive cleavage of the corresponding dimers $[M(CO)_nL]_2$ with excess of $NaK_{2.8}$ alloy (0.15 ml per 1 mmol of dimer) in THF. $Na[Re(CO)_5]$ was prepared by the reduction of $Re_2(CO)_{10}$ with 0.5% NaHg (30-50% excess) and purified by the low temperature crystallization from THF. The dicarbonyl(η^5-pentamethylcyclopentadienyl)iron dimer was prepared by the modified literature procedure by the reaction of pentamethylcyclopentadien with $[Fe(CO)_5]$ (1:2 molar ratio) in refluxing xylene.[32]

NMR spectroscopy (^{1}H and ^{13}C) was used as a primary tool for the analysis of the reaction mixtures usually combined with the IR spectra in the metal carbonyl stretching region (1550-2200 cm^{-1}). Samples of the reaction mixture were transferred under vacuum into thin-walled glass tubes (~3.5 mm diameter) which were sealed-off with flame and placed into standard NMR tubes containing acetone-d_6 for the lock signal. Product yields were determined by the integration of the ^{1}H NMR spectra of the reaction solutions containing an internal standard (durene). The signals were referenced to the individual products by comparison to the spectra of the isolated compounds or literature data.

The $[(\eta^6\text{-}C_6H_5I)Cr(CO)_3]$ was prepared according to published procedure[33] by metallation of $[(\eta^6\text{-}C_6H_6)Cr(CO)_3]$ with *n*-BuLi in THF and subsequent quenching of the resulting aryllithium with iodine. ^{1}H NMR (THF, 400.13 MHz), δ: 5.77 (m, 2H), 5.40 (m, 3H). ^{13}C NMR (THF, 100.6 MHz), δ: 233.39 (CO), 94.39 (C_{quat}), 101.41, 95.24, 91.61 (CH). IR (THF), ν/cm^{-1}: 1901 vs (ε=4130), 1973 vs (ε=3830).

Reactions of $[(\eta^6$-haloarene$)Cr(CO)_3]$ with $K[(\eta^5\text{-}C_5R_5)Fe(CO)_2]$ (R=H, CH_3)

Reactions were performed by adding haloarene (0.2 mmol) to a THF solution of carbonylmetallate (0.2 mol in 3 ml THF) prepared *in situ* by the reduction of the dimer with $NaK_{2.8}$. Product yields determined by ^{1}H NMR are given in Table 1. Nucleophilic substitution product was isolated by column chromatography on silica gel (Merck 60) using petroleum ether – CH_2Cl_2, 2:3 as eluent. **$[(\eta^6\text{-}(C_5Me_5)(CO)_2FeC_6H_5)Cr(CO)_3]$**, ^{1}H NMR (THF, 400.13 MHz), δ: 5.27 (m, 4H), 5.14 (m, 1H), 1.71 (s, 15H). ^{13}C NMR (THF, 100.6 MHz), δ: 235.88 (3CO), 216.97 (2CO), 137.30 (*ipso*-Ar), 107.14, 96.79, 90.96 (CH), 97.31 (*ipso*-Cp*), 9.55 (CH_3). IR (THF), ν/cm^{-1}: 1873 vs, 1950 vs, 1959 vs, 2011 vs. HR ESI MS, *m/z* (relative intensity, %): 498.9683 $[M+K]^+$ (50%), 482.9945 $[M+Na]^+$ (100%). Calcd. for $C_{21}H_{20}CrFeKO_5$ 498.9702, for $C_{21}H_{20}CrFeNaO_5$ 482.9963.

Reaction of $[(\eta^6\text{-}C_6H_5I)Cr(CO)_3]$ with $Na[Re(CO)_5]$

Reaction of $[(\eta^6\text{-}C_6H_5I)Cr(CO)_3]$ (24 mg, 0.071 mmol) with $Na[Re(CO)_5]$ (0.311 g of THF solution, 0.0648 mmol) produced a single product, quantitatively formed in solution, **$Na[(\eta^6\text{-}C_6H_5C(O)Re(CO)_4I)Cr(CO)_3]$**. ^{1}H NMR (THF, 400.13 MHz), δ : 5.82 (m, 2H), 5.49 (m, 3H). ^{13}C NMR (THF, 100.6 MHz), δ : 259.58 (1CO), 233.95 (3CO), 189.11 (2CO), 188.45 (1CO), 187.38 (1CO), 122.05 (C_{quat}), 94.74 (1C) , 94.63 (2C), 92.98 (2C) (CH). IR (THF), ν/cm^{-1}: 1894 vs, 1915 s, 1967 sh, 1979 vs, 2084 m. IR (THF+18-crown-6), ν/cm^{-1}: 1890 vs, 1912 s, 1966 vs, 1982 vs, 2082 m. HR ESI MS, *m/z* (relative intensity, %): 554.8174 $[M\text{-}4CO]^-$ (60%), 526.8222 $[M\text{-}5CO]^-$ (80%), 498.8275 $[M\text{-}6CO]^-$ (100%). Calcd. for $C_{10}H_5CrIO_4Re$ 554.8196, for $C_9H_5CrIO_3Re$ 526.8246, for $C_8H_5CrIO_2Re$ 498.8298. When the THF solution of the iodo(acyl)rhenate complex was reanalyzed by NMR after standing for 6 month at room temperature its main component was another complex, **$Na[(\eta^6\text{-}C_6H_5Re(CO)_4I)Cr(CO)_3]$**. ^{1}H NMR (THF, 400.13 MHz), δ: 6.05 (m, 2H), 5.12 (m, 3H). ^{13}C NMR (THF, 100.6 MHz), δ: 237.57 (3CO), 189.95 (2CO), 189.31 (1CO), 188.45 (1CO), 129.81 (C_{quat}), 113.41, 96.37, 92.14 (CH). This iodo(aryl)rhenate was isolated in the form of $[Et_4N]^+$ salt using a modified literature procedure.[10] THF was replaced by equal volume (0.2 ml) of degassed water, the turbid solution obtained was filtered, and the product precipitated by the addition of $[Et_4N]I$ (20 mg in 0.1 ml H_2O) in the form of yellowish oil, which soon solidified and was dried in vacuum. **$[Et_4N][(\eta^6\text{-}C_6H_5Re(CO)_4I)Cr(CO)_3]$,** IR (THF), ν/cm^{-1}: 1861 s, 1942 s ($Cr(CO)_3$), 1913 s, 1965 vs, 1980 vs, 2081 m ($Re(CO)_4$). Crystals suitable for X-ray diffraction analysis were grown by slow diffusion of petroleum ether into the solution of the complex in CH_2Cl_2.

Reaction of $[(\eta^6\text{-}C_6H_5I)Cr(CO)_3]$ with $K[Mn(CO)_5]$

Reactions were performed in THF on the same 0.1 mmol scale as with other carbonylmetallates, the ^{1}H NMR spectroscopic product yields are given in Table 2. The neutral $Mn(CO)_5$ σ-aryl complex was isolated by column chromatography on silica gel (Merck 60) using petroleum ether – CH_2Cl_2, 2:1 (increasing to 1:2) as eluent. **K[(η^6-$C_6H_5Mn(CO)_4I)Cr(CO)_3$]**. ^{1}H NMR (THF, 400.13 MHz), δ: 6.02 (m, 2H), 5.14 (m, 2H), 5.10 (m, 1H). ^{13}C NMR (THF, 100.6 MHz), δ: 237.42 (3CO), 224.9 br (1CO), 217.5 br (2CO), 216.1 br (1CO), 137.86 (C_{quat}), 112.82, 95.50, 91.95 (CH). IR (THF), ν/cm^{-1}: 1865 vs, 1942 vs ($Cr(CO)_3$), 1921 s, 1965 s, 1980 s, 2060 m ($Mn(CO)_4$). **[K·18-crown-6] [(η^6-$C_6H_5Mn(CO)_4I$) $Cr(CO)_3$]**. ^{1}H NMR (THF, 400.13 MHz), δ: 6.00 (m, 2H), 5.13 (m, 2H), 5.08 (m, 1H). ^{13}C NMR (THF, 100.6 MHz), δ : 237.27 (3CO), 224.9 br (1CO), 217.7 br (2CO), 216.2 br (1CO), 137.74 (C_{quat}), 112.64, 95.38, 91.72 (CH). IR (THF), ν/cm^{-1}: 1865 s, 1942 s ($Cr(CO)_3$), 1921 s, 1965 s, 1980 s, 2060 m ($Mn(CO)_4$). HR ESI MS, *m/z* (relative intensity, %): 366.8161 [*M*-5CO]$^-$ (100%). Calcd. for $C_8H_5CrIO_2Mn$ 366.8048. **[(η^6-$C_6H_5Mn(CO)_5)Cr(CO)_3$]**. ^{1}H NMR (THF, 400.13 MHz), δ: 5.49 (m, 2H), 5.33 (m, 3H). ^{13}C NMR (THF, 100.6 MHz), δ: 235.51 (CO), 210.1 br (CO), 130.4 (C_{quat}), 108.87 (2C), 95.95 (2C), 93.24 (1C) (CH). IR (THF), ν/cm^{-1}: 2123 m, 2065 w, 2027 vs, 2009 sh ($Mn(CO)_4$), 1955 vs, 1878 vs ($Cr(CO)_3$). Calc. for $C_{14}H_5CrMnO_8$: C 41.20, H 1.23. Found: C 41.55, H 1.48. ESI MS, *m/z* (relative intensity, %): 388 [*M*-3CO, +CH_3CN, +Na]$^+$ (100%), 338 [*M*-4CO, +CH_3CN, +H]$^+$ (60%), 332 [*M*-5CO, +CH_3CN, +Na]$^+$ (30%).

Crystal structure determination of complex [Et_4N][(η^6-$C_6H_5Re(CO)_4I)Cr(CO)_3$].

The crystal of 0.10×0.12×0.15 mm^3 ($C_{21}H_{25}CrINO_7Re$, M = 768.52) is monoclinic, space group $P2_1$/n, at T = 100 K: a = 7.5063(2) Å, b = 29.7019(8) Å, c = 11.2833(3) Å, β = 95.6170(10)°, V = 2503.55(12) Å^3, Z = 4, d_{calc} = 2.039 g/cm^3, $F(000)$ = 1464, μ = 6.537 mm^{-1}. 32904 total reflections (7288 unique reflections, R_{int} = 0.039) were measured on a three-circle Bruker APEX-II CCD diffractometer (λ(MoK_α)-radiation, graphite monochromator, φ and ω scan mode, $2\theta_{max}$ = 60°) and corrected for absorption using the *SADABS* program (T_{min} = 0.441; T_{max} = 0.561).[34] The structure was determined by direct methods and refined by full-matrix least squares technique on F^2 with anisotropic displacement parameters for non-hydrogen atoms. All hydrogen atoms were placed in calculated positions and refined within riding model with fixed isotropic displacement parameters [U_{iso}(H) = 1.5U_{eq}(C) for the CH_3-groups and U_{iso}(H) = 1.2U_{eq}(C) for the other groups]. The final divergence factors were R_1 = 0.029 for 6493 independent reflections with $I > 2\sigma(I)$ and wR_2 = 0.064 for all independent reflections, S = 1.002. All calculations were carried out using the SHELXTL program.[35]

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC 999498. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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Notes and references

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* An increase of ArH yield from 7 to 11% in the presence of *t*-BuOH shows some aryl carbanions participation in haloarene reduction process.

† Acylrhenate anions (and acylmetallates in general) are often decribed as oxycarbene complexes because of a large contribution of metal carbene resonance structre, as evidenced by the downfield shift of acyl CO resonance in ^{13}C NMR.

** δ(C_{para})> δ(C_{ortho}) is the trend observed for iodo(acyl)rhenate as opposed to σ-aryl metal complexes, in which C-*ortho* signal is shifted downfied because of the contribution of the metal carbene resonance structure (Fig. 1).

‡ Both computational model reactions lead to the intermediate structures with η^2-coordination of the acyl group. The calculations were performed by DFT method with a PBE functional[21] and a triple-ζ all-electron basis set, including polarization functions, TZ2P using PRIRODA program package.[22]

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Graphical abstract

Formal nucleophilic substitution in [(η^6-iodobenzene)Cr(CO)$_3$] begins with the attack of carbonylmetallate [M(CO)$_n$L]$^-$ anion at iodine to form the aryl carbanion and [IM(CO)$_n$L] intermediates, which then give all of the variety of products observed.