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Effect of $M(CO)_3$ ($M = Cr, Mn^+$) on Aromatic C−Cl BDE in (η^6-ArCl)$M(CO)_3$ Complexes

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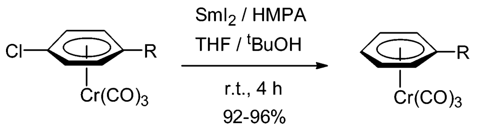

Relative reactivities toward SmI_2/HMPA at 0 °C:

PhI : PhCl-$Cr(CO)_3$: PhBr : PhCl = 50 : 1 : 0.3 : <0.001

The coordination of $Cr(CO)_3$ to chlorobenzenes significantly reduces the C−Cl bond dissociation energy. Treatment of chloroarene−$Cr(CO)_3$ complexes with SmI_2/HMPA at room temperature led to complete dechlorination. Reaction of *o*-allyloxychlorobenzene−$Cr(CO)_3$ complexes with SmI_2 at room temperature resulted in the corresponding dechlorinative cyclization products in good to excellent yields. Competition experiments indicated the following relative reactivities of dehalogenation by SmI_2: PhI/PhCl−$Cr(CO)_3$/PhBr/PhCl = 50:1:0.3:<0.001. On the other hand, the coordination of $Mn(CO)_3^+$ to chlorobenzene showed a much smaller activation effect. Density functional theory calculations revealed that the spin delocalization effect of the metal center plays an important role in the C−Cl bond activation.

Aromatic halides are important materials in synthetic organic chemistry. Chloroarenes are among the most attractive aryl halides for synthetic purposes on an industrial scale. However, the high stability of the aromatic C−Cl bond makes aryl chlorides inert in many cases.[1]

It is well documented that the complexation of a $Cr(CO)_3$ or $Mn(CO)_3^+$ moiety on an arene ring significantly reduces the electron density of the arene ring and facilitates nucleophilic[2] and radical[3−5] additions. The coordination of $Cr(CO)_3$ or $Mn(CO)_3^+$ also activates aryl C−Cl bonds toward oxidative addition to Pd^0 complexes, allowing a number of subsequent reactions such as the Heck reaction or carbonylation to proceed smoothly.[6−8] Moreover, Carpentier and co-workers demonstrated that the activating effect of $Mn(CO)_3^+$, which is a more powerful electron-withdrawing group, is at least comparable to that of $Cr(CO)_3$ toward Pd^0 insertion.[9] Therefore, it is interesting to see if $Cr(CO)_3$ or $Mn(CO)_3^+$ has any significant effect on the homocleavage of the aryl C−Cl bond or on the bond dissociation energy (BDE) of the aromatic C−Cl bond. Recently, Kündig et al. reported the first examples of the $Cr(CO)_3$-bound aryl radicals generated from the interaction of an iodoarene−$Cr(CO)_3$ complex with SmI_2 at room temperature (rt) or from the treatment of a bromoarene−$Cr(CO)_3$ complex with Bu_3SnH/AIBN at 80 °C.[8] On the other hand, the corresponding chloroarene−$Cr(CO)_3$ complex failed to react with Bu_3SnH/AIBN at 80 °C,[8] which seems to imply that the coordination of $Cr(CO)_3$ does not impose a significant activating effect on the homocleavage of the aryl C−Cl bond. We report here that the complexation of $Cr(CO)_3$ on a chloroarene ring indeed significantly reduces the C−Cl BDE and the effect of $Cr(CO)_3$ is much greater than that of $Mn(CO)_3^+$. Density functional calculations at B3LYP/BSII level reveal that the spin delocalization effect of the metal center plays an important role in the activation.

During our recent investigation of aromatic radical substitution reactions of chloroarene−$Cr(CO)_3$ complexes with SmI_2 and a carbonyl compound, we observed that dechlorination occurred as a side reaction even at a very low reaction temperature (−40 °C).[4b] This observation was surprising compared to Kundig's results and prompted us to look into the

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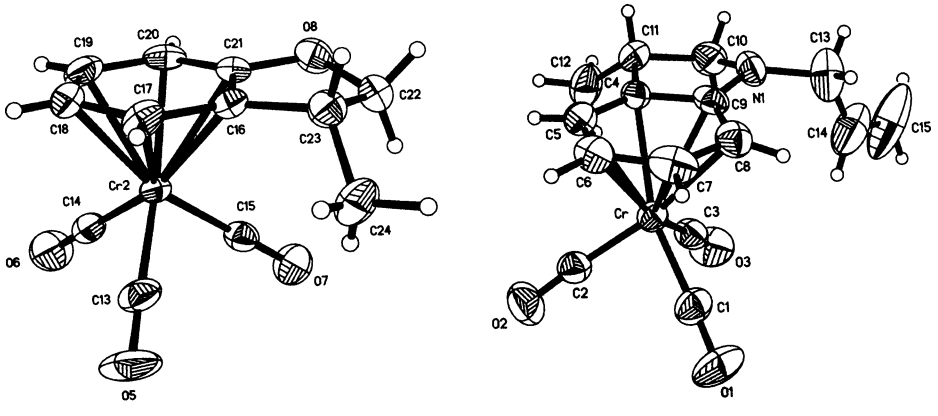
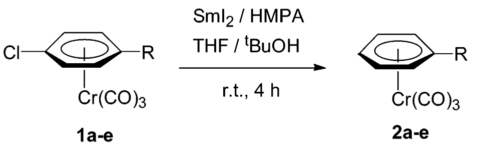


syn-**4a** *syn*-**4d**

FIGURE 1. ORTEP Drawings of Compounds *syn*-**4a** and *syn*-**4d**.

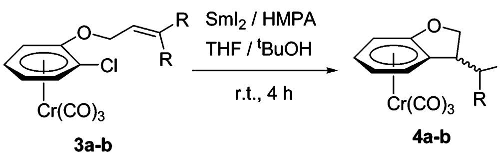
reactions in detail. Thus, treatment of chloroarene−$Cr(CO)_3$ complexes **1a**−**e** with SmI_2/HMPA at rt for 4 h resulted in the complete dechlorination of **1**, and the corresponding products **2a**−**e** were isolated in almost quantitative yield (eq 1). On the contrary, no dechlorination was observed under the above experimental conditions with the uncomplexed chloroarenes.



(1)

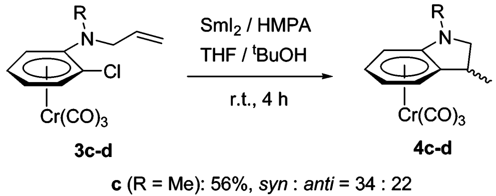
a R = H (96%); **b** R = Me (96%); **c** R = OMe (92%)
d R = CF3 (92%); **e** R = F (94%)

We then prepared *o*-allyloxychlorobenzene−$Cr(CO)_3$ complexes **3a**,**b** and *o*-allylaminochlorobenzene−$Cr(CO)_3$ derivatives **3c**,**d**[10] and subjected them to the same treatment described above. The corresponding dechlorinative cyclization products **4a**−**d** were obtained in good to excellent yields (eqs 2 and 3), indicating the radical nature of the dechlorination step. The stereochemistry of **4** was based on the X-ray crystal structures of *syn*-**4a** and *syn*-**4d**, as shown in Figure 1. On the other hand, the corresponding uncomplexed *o*-allyloxychlorobenzene derivatives remained unchanged under the same experimental conditions.[11]



(2)

a (R = H): 68%, *syn* : *anti* = 42 : 26
b (R = Me): 86%, *syn* : *anti* = 36 : 50

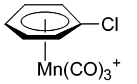


(3)

c (R = Me): 56%, *syn* : *anti* = 34 : 22
d (R =allyl): 92%, *syn* : *anti* = 57 : 35

The above results clearly demonstrated a remarkable activation effect of the $Cr(CO)_3$ coordination on the homocleavage of the aryl C−Cl bonds. To understand further the extent of the activation effect, we measured the relative activities of **1a** and halobenzenes in dehalogenation reactions with SmI_2/HMPA at 0 °C by competition experiments (monitored by HPLC). The results (the average of two runs) were as follows: PhI/**1a**/PhBr/PhCl = 50:1:0.3:<0.001. These results revealed that the C−Cl bond in **1a** is even more reactive than the C−Br bond in bromobenzene in reactions with SmI_2. Competition experiments among **1a**−**d** on their relative dechlorination rates at 0 °C showed that these rates were roughly at the same level.

In light of the above results, we were motivated to find if $Mn(CO)_3^+$ shared similar behaviors. Therefore, we tested (η^6-PhCl)$Mn(CO)_3^+PF_6^-$ (**5**) under the same experimental conditions as in eq 1. (η^5-C_6H_6Cl)$Mn(CO)_3$ (**6**) was isolated in 24% yield as the reduction product,[12] while PhCl was recovered in 67% yield, indicating little if any dechlorination product (η^6-C_6H_6)$Mn(CO)_3^+$ could be detected (see the Supporting Information). Moreover, competition experiments between **5** and **1a** at 0 °C showed that the major product was **2a** along with a small amount of **6**, indicating a much more powerful activation effect of $Cr(CO)_3$ over $Mn(CO)_3^+$. This is in sharp contrast to the relative activation effect of $M(CO)_3$ (M = Cr or Mn^+) toward oxidative addition described above.



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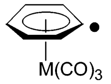
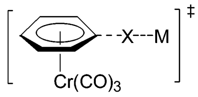


7a (M = Cr)
7b (M = Mn$^+$)



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To understand further the effect of $M(CO)_3$ complexation on the aryl C−Cl BDE, density functional theory (B3LYP) calculations have been carried out on the C−Cl BDEs of chlorobenzene−$M(CO)_3$ complexes, which have been demon-

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TABLE 1. Calculation Results of 1a and 5 at the B3LYP/BSII Level

compd	M	C−Cl length (Å)	C−Cl BDE (kcal/mol)	ΔBDE (kcal/mol)	spin density distribution in **7**	
					C-1	M
PhCl		1.761	89.7	0.0	0.855	
1a	Cr	1.748	85.2	−4.5	0.775	0.116
5	Mn^+	1.723	86.9	−2.8	0.823	0.005

strated to be an accurate tool in the theoretical study of arene−$Cr(CO)_3$ systems.[5,13] Vibrational frequency calculation was done for each structure, and the calculated BDEs were enthalpy corrected. The geometries were optimized with basis set I (BSI), 6-31G* for C, H, O, and Cl and LANL2DZ for metals, and the energies were estimated with basis set II (BSII), 6-311+G* for C, H, O, Cl and SDDALL for metals. The results are summarized in Table 1 (see the Supporting Information for details).

The calculations reveal that $Cr(CO)_3$ significantly reduces the C−Cl BDE by about 4.5 kcal/mol. The positively charged $Mn^+(CO)_3$ has a reduced effect of 2.8 kcal/mol. These are in good agreement with the above experimental observations.

As shown in Table 1, the calculated C−Cl bond length is shortened upon complexation by $M(CO)_3$. This is because the benzene ring donates electron density to the metal center and enhances the C−Cl bonding in these complexes. Thus, the reduced C−Cl BDE should be mainly attributed to the stabilization of the radical by the $M(CO)_3$ moiety.

There is an increased interaction between the carbon radical and metal centers, as indicated by the reduced C_1−M distance from the reactants to the radicals **7**. The C_1−Cr distance is shortened from 2.27 Å in **1a** to 2.17 Å in the corresponding radical **7a** (M = Cr). A reduction of about 0.1 Å in the C_1−M distance is also calculated in the case of the Mn^+-complexed radical **7b**.

It is well-known that a carbon radical is stabilized by spin delocalization and polar effects.[14] The spin density at the C_1 is about 0.855 in the parent phenyl radical (σ radical), but it is reduced significantly upon Cr complexation. On the other hand, less delocalization is computed for $Mn^+(CO)_3$. In terms of the polar effect, the carbon radical, which is electron-deficient, is more destabilized by the more electron-withdrawing $Mn^+(CO)_3$. These expectations correlate well with the calculated reduction in the C−Cl BDE by the two metal centers.

The above experimental and theoretical results clearly demonstrate the remarkable activation effect of $Cr(CO)_3$ on the C−Cl bond homocleavage. Then how to account for Kündig's observation with Bu_3SnH?[8] To gain more understanding on this matter, we conducted the following experiments. The reaction of **1a** with Bu_3SnH/AIBN at 80 °C for 7 h gave the dechlorination product **2a** in only about 12% yield, while the rest of **1a** remained unchanged. With substrate **1c** bearing an electron-donating methoxy group, only a trace amount if any dechlorination product **2c** was observed, which was consistent with Kündig's results. We also tried $(TMS)_3SiH$, which is another popular radical initiator. However, no reaction occurred in the reaction of **1a** with $(TMS)_3SiH$/AIBN at 80 °C for 7 h. These experiments indicated the reactivity trend toward **1a** was $SmI_2 \gg Bu_3SnH > (TMS)_3SiH$.

The relative reactivities of **1a** and halobenzenes toward Bu_3SnH/AIBN at 80 °C were also measured by competition experiments. The results were as follows: PhI/PhBr/**1a** = 20:1:0.001. Complex **1a** was now much less reactive than PhBr, which was in sharp contrast to the situation in the reaction with SmI_2.

An obvious difference between SmI_2 and Bu_3SnH is that SmI_2 is a reducing agent while Bu_3SnH is not. However, it is unlikely that the reactions of SmI_2 with chromium complexes **1** proceed via a single-electron-transfer process. The oxidation potential of SmI_2 in water is −1.55 V,[15] while the reduction potential of toluene−$Cr(CO)_3$ complex **2b** is about 2.25 V (vs SCE)[16] and the halide substitution on the phenyl ring does not alter the reduction potential much.[17] In fact, the above phenomena could be well rationalized by the transition states of the dehalogenation process. In transition state **8**, the metal approaches the halogen atom to form a partial metal−halogen bond, while the carbon−halogen bond was weakened. Based on this model, it is clear that the rates of dehalogenation not only depend on the strength of the C−X bond but also depend on the strength of the M−X bond.

The reactivity trend toward **1a** could be rationalized by the relative bond strength of the M−Cl bonds. The ΔH_f at 298 K is −168.6 kJ/mol for $SiCl_2$ (g) and −197.9 kJ/mol for $SnCl_2$ (g), while the ΔH_f is −815.5 kJ/mol for $SmCl_2$ (s) and −328.0 kJ/mol for $SnCl_2$ (s).[18] These data illustrate that the relative bond strength is as follows: Si−Cl < Sn−Cl ≪ Sm−Cl. Therefore, the reactivities toward **1a** are on the order of $SmI_2 \gg Bu_3SnH > (TMS)_3SiH$.

The two different results on the competition between **1a** and bromobenzene in reaction with SmI_2 and Bu_3SnH could also be rationalized on the basis of the transition structures **8**. With the powerful SmI_2 as the reducing agent, the BDE difference between the C−Cl bond in **1a** and the C−Br bond in bromobenzene was compensated by the formation of the stronger Sm−Cl bond in **1a** and the weaker Sm−Br bond in bromobenzene. As a result, the activities of **1a** and bromobenzene toward SmI_2 are of same level. On the other hand, with Bu_3SnH as a much weaker reducing agent, the BDE difference between C−Cl bond in **1a** and C−Br bond in bromobenzene predominated. Thus, bromobenzene is more reactive than **1a** toward Bu_3SnH.

As an extension, we also studied the effect of $Cr(CO)_3$ complexation on the activation of aromatic C−Br and C−I BDEs experimentally and computationally (see the Supporting Information for details). The competition experiments showed that the relative reactivities of PhBr−$Cr(CO)_3$ complex and bromobenzene toward Bu_3SnH/AIBN(cat.) at 80 °C were 100:<1. The relative reactivities of PhI−$Cr(CO)_3$ complex and

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iodobenzene toward Bu_3SnH/BEt_3(cat.) at 0 °C were also measured by competition experiments to be larger than 100:1 within the experimental error. DFT calculations at the B3LYP/BSII level indicate a reduction of 4.6 kcal/mol in C−Br BDE and a reduction of 3.9 kcal/mol in C−I BDE upon complexation with $Cr(CO)_3$. These results are in line with the C−Cl BDE activation.

In summary, we have experimentally demonstrated a remarkable activation effect of $Cr(CO)_3$ complexation on the aromatic C−Cl bond homolytic cleavage. Theoretical calculations indicate that the spin delocalization effect of the metal center may play an important role in reducing the C−Cl BDE. Moreover, the different reactivity patterns between SmI_2 and Bu_3SnH toward dehalogenation have also been elucidated. The current findings should have important implications in the further development of the chemistry of arene−metal complexes, and we are currently exploring possible C−Cl bond activation in other metal-complex systems.

Experimental Section

Typical Procedure for the Dechlorination Reactions of 1a−e. HMPA (0.6 mL) was degassed with nitrogen purge for 30 min. The solution of SmI_2 (9 mL, 0.9 mmol, 0.1 M in THF) was added, resulting in a color change from blue to violet. Then a THF (2 mL) solution of (η^6-chlorobenzene)$Cr(CO)_3$ (**1a**) (74.8 mg, 0.3 mmol) and *t*-BuOH (44.5 mg, 0.6 mmol) was added via cannula. The solution was stirred at rt for 4 h. Water (2 mL) was added, and the mixture was stirred for another 2 h. The resulting solution was then extracted with ether (3 × 30 mL). The combined organic phase was washed with $NaHSO_3$ (3 × 30 mL) and dried over anhydrous Na_2SO_4. After removal of solvent under reduced pressure, the crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1/15, v/v) as the eluent to give pure **2a** as a yellowish solid. Yield: 61 mg (96%).

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Supporting Information Available: Experimental procedures for the competition experiments of dehalogenation; characterization of **4a**−**d**; computational details for halobenzenes **1a**, **5**, and **7** and PhX-$Cr(CO)_3$, and X-ray crystal structures of *syn*-**4a** and *syn*-**4d** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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