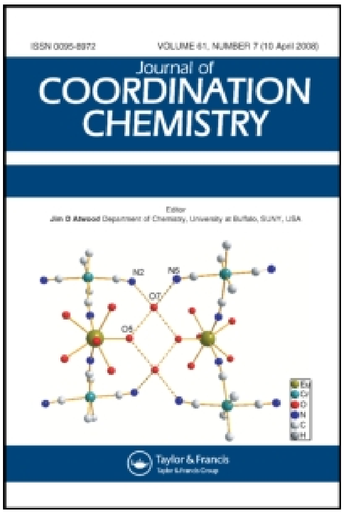

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

MONO-η^6-ARENE COMPLEXES OF CHROMIUM (II) AND CHROMIUM (0). ARENE EXCHANGE AND ARENE DISPLACEMENT REACTIONS OF η^6-FLUOROARENE-DICARBONYLBIS (TRICHLOROSILYL) AND -TRICARBONYLCHROMIUM DERIVATIVES

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To cite this Article Jagirdar, Balaji R. and Klabunde, Kenneth J.(1995) 'MONO-η^6-ARENE COMPLEXES OF CHROMIUM (II) AND CHROMIUM (0). ARENE EXCHANGE AND ARENE DISPLACEMENT REACTIONS OF η^6-FLUOROARENE-DICARBONYLBIS (TRICHLOROSILYL) AND -TRICARBONYLCHROMIUM DERIVATIVES', Journal of Coordination Chemistry, 34: 1, 31 — 43

To link to this Article: DOI: 10.1080/00958979508024301
URL: http://dx.doi.org/10.1080/00958979508024301

J. Coord. Chem., 1995, Vol 34, pp. 31–43
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MONO-η^6-ARENE COMPLEXES OF CHROMIUM (II) AND CHROMIUM (0). ARENE EXCHANGE AND ARENE DISPLACEMENT REACTIONS OF η^6-FLUOROARENE-DICARBONYLBIS (TRICHLOROSILYL) AND -TRICARBONYLCHROMIUM DERIVATIVES

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(Received; June 2, 1994; in final form August 26, 1994)

In an attempt to obtain chromium-arene derivatives possessing high arene lability, $(C_6H_5F)Cr(CO)_2(SiCl_3)_2$, $(C_6H_4F_2)Cr(CO)_2(SiCl_3)_2$, $(C_6H_5F)Cr(CO)_3$, and $(C_6H_4F_2)Cr(CO)_3$ have been investigated. Kinetics of arene exchange have been studied showing that the Cr(II) derivatives exhibit ten-fold higher rates than the Cr(O) derivatives. Both electronic and steric effects appear to be important, although electronic effects dominate. Arene displacement by phosphine and phosphite ligands has also been studied. Although arene displacement took place, unexpected rearrangement and disproportionation reactions occurred yielding seven-coordinate $(CO)_4Cr(PR_3)(SiCl_3)_2$ species.

KEYWORDS: arene exchange, ring slippage, chromium, kinetics and mechanism

INTRODUCTION

The sequential formation, functionalization, and cleavage of transition metal π-bonds, for example M-arene bonds, is of fundamental importance in catalytic processes and stoichiometric organometallic synthesis.[1–3] Basolo and Pidcock and their co-workers proposed stepwise displacement of arene by phosphines and phosphites from $(arene)Mo(CO)_3$ complexes (eq. 1).[4,5]

A focus of recent interest has been the phenomenon of arene exchange in $(arene)Cr(CO)_3$ complexes (eq. 2).[6–8]

This reaction proceeds in the displacing aromatic reagent as solvent with a half-life of several hours at 170°C.[9–11] Mahaffy and Pauson[11] reported on the equilibria of reaction (2) with a variety of arenes and arene complexes; they found that the labilities of (arene)tricarbonyl chromium complexes are in the order:

$$C_6(CH_3)_6 < C_6H_3(CH_3)_3 < \text{N,N-dimethyl aniline} \leq \text{xylene} < C_6H_5CH_3 \sim C_6H_6 < C_6H_5Cl << \text{Naphthalene}$$

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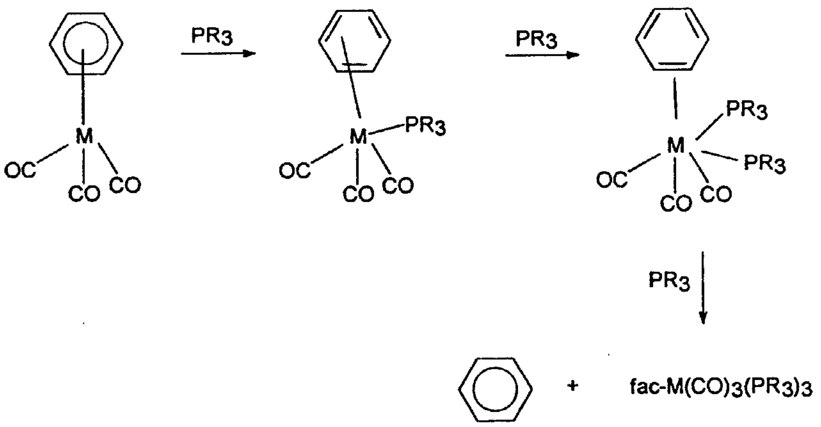

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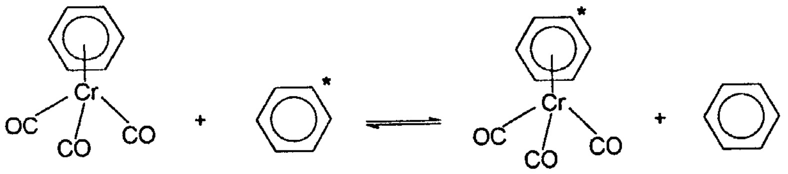

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Strohmeier *et al.*[10] reported on kinetic studies of uncatalyzed/self exchange in hydrocarbon solvents for arene complexes of Cr, Mo, and W using ^{14}C-labeled reagent arene and, on the basis of their initial rate measurements, gave a rate law (eq. 3):

$$-d[S]/dt = k_I[S] + k_{II}[S]^2 + k_{III}[S][L] \qquad (3)$$

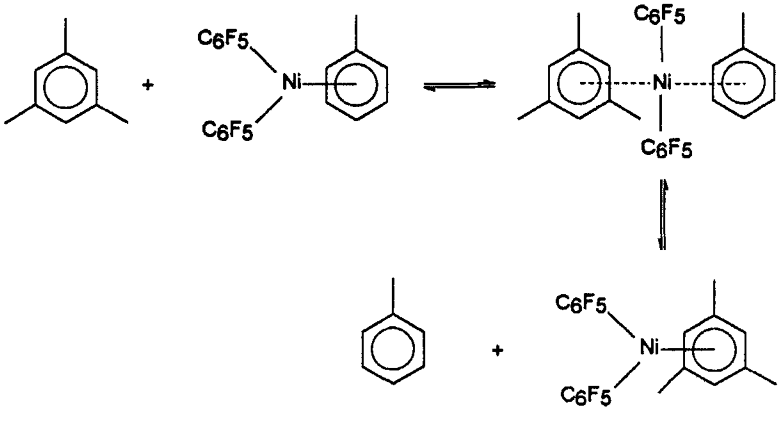
where S is the initial (arene)Cr(CO)$_3$ complex and L is the incoming arene.

For relatively labile substrates like (naphthalene)Cr(CO)$_3$ or (cycloheptatriene) Cr(CO)$_3$, the second term in eq. (3) is absent, whereas, for less labile systems such as (toluene)Cr(CO)$_3$, (benzene)Cr(CO)$_3$, or (chlorobenzene)Cr(CO)$_3$, the first term is absent.

Some scientists have criticized[3,8] the mechanism proposed by Strohmeier and co-workers which involves the dissociation of (arene)Cr(CO)$_3$ to arene and $-$Cr(CO)$_3$ as the rate-limiting step. The work carried out by Traylor *et al.*[7] clarified aspects of the exchange process, especially the possible self-catalysis of exchange inherent in the $k_{II}[S]^2$ term of Strohmeier.

Youngerman[12] studied the mechanism of ketone, ether or nitrile catalyzed exchange reactions of arene tricarbonyl chromium complexes. It was found that the catalyst moiety was covalently bound to the arene bearing the tricarbonyl chromium group and the rate showed first order dependence on concentration of the catalyst.

Klabunde and co-workers[13,14] studied the kinetics of toluene exchange with mesitylene and *vice versa* in the (π-toluene)Ni(C$_6$F$_5$)$_2$ complex. They found that the exchange in both cases was first order in complex and first order in incoming arene, indicating a transition state involving both the displacing arene as well as complex as shown below (eq. 4):



(4)

Arene displacement in π-arene complexes of Cr is an area which has received much attention in recent years not only because it leads to new complexes but also because of its potential catalytic applications. Displacement of arene in (η^6-arene)$Cr(CO)_3$ has been carried out in presence of certain amines,[15,16] phosphines,[15] and phosphites.[17] For example, the reaction with refluxing pyridine yielded $[(py)_3Cr(CO)_3]$,[16] however the products were not easily converted back to arene complex such that M could be reused.[15] With strong donor ligands such as MeCN the reactions proceeded to completion, but with weaker donors (*e.g.* ethers) equilibria were involved.

Klabunde and co-workers [18] found that the arene ligand in (η^6-toluene)$Ni(SiX_3)_2$ (X = F, Cl) undergoes facile displacement in the presence of phosphines, phosphites, or amines to yield $L_2Ni(SiX_3)_2$ or $L_3Ni(SiX_3)_2$ complexes. They found that steric factors govern the formation of disubstituted (square planar) or trisubstituted (trigonal bipyramidal) systems.

Lability of the π-arene ligand controls the rich chemistry of these types of complexes. The stepwise loss of the π-arene opens up 1,2 or 3 potential coordination sites and exposes the metal center without change in oxidation state. We have been attempting to control this feature by introducing electronically and sterically demanding ligands. Thus, we have prepared and structurally characterized a series of (η^6-arene)Cr(II) and (η^6-arene)Cr(0) derivatives,[19,20] which include (η^6-C_6H_5F)$Cr(CO)_2(SiCl_3)_2$, (η^6-*p*-$C_6H_4F_2$)$Cr(CO)_2(SiCl_3)_2$, (η^6-C_6H_5F)$Cr(CO)_3$, and (η^6-*p*-$C_6H_4F_2$)$Cr(CO)_3$. Herein we report kinetic studies of arene exchange as well as arene displacement reactions by phosphine and phosphite ligands.

EXPERIMENTAL

General Procedures

All reactions were carried out under Ar using standard Schlenk[21] and inert atmosphere techniques unless otherwise stated. Tetrahydrofuran (THF) was distilled under Ar from Na/benzophenone. Methylene chloride (CH_2Cl_2) and pentane were distilled from CaH_2 under Ar. Fluorobenzene and *p*-difluorobenzene were refluxed over CaH_2 for several days before distilling and storing over molecular sieves. Mesitylene was refluxed over Na for several days before distilling and storing over molecular sieves. Decahydronaphthalene (decalin) was purchased from Aldrich and used without further purification. Acetonitrile was stored over molecular sieves for several days before distillation under Ar. The phosphines and phosphites were purchased from Aldrich and used without further purification.

Infrared spectra were obtained using a Perkin Elmer 1330 spectrophotometer and reference to the 1601 cm^{-1} band in polystyrene film. The ^1H and ^{13}C NMR data were obtained using a WM-400 Bruker 400-MHz instrument. All shifts are reported on the δ scale. The resonance of the deuterated solvent was used as an internal reference. Mass spectra were recorded on a Hewlett-Packard MS-Engine instrument. Elemental analyses were obtained from Galbraith Laboratories, Inc. The starting arene tricarbonyl $(C_6H_5F)Cr(CO)_3$, $(p\text{-}C_6H_4F_2)Cr(CO)_3$, and the disilyl complexes $(C_6H_5F)Cr(CO)_2(SiCl_3)_2$, and $(p\text{-}C_6H_4F_2)Cr(CO)_2(SiCl_3)_2$ were prepared and purified as described earlier.[19]

Kinetic Studies of Arene Exchange

In decalin solvent and with mesitylene as the displacing arene, the reagents were taken in a 50 mL 3-neck round bottomed flask equipped with a condensor, an Argon inlet and a magnetic stir bar. The reactions were carried out at 170°, 150°, 130°, and 110°C in a constant temperature bath. Progress of the reactions was monitored by taking aliquots and recording the infrared spectra in the ν_{co} region at various times during the exchange. All the reactions exhibited normal first-order kinetics. First-order rate constants were calculated as the slope of the first-order kinetic plots for disappearance of starting complex and/or appearance of product complex using a least squares fit program. All the reactions were followed up to three half-lives.

Triethylphosphine Reaction: Synthesis of $(CO)_4Cr(P(C_2H_5)_3)(SiCl_3)_2$

$(C_6H_5F)Cr(CO)_2(SiCl_3)_2$ (0.2 g, 0.4 mmol) was dissolved in 20 mL of CH_2Cl_2 and cooled to −78°C in a dry ice — acetone bath. To this solution, 0.5 mL (3.3 mmol) of PEt_3 was added dropwise. After the addition was complete, the solution was stirred at −78°C for *ca.* 1 h and then slowly warmed to room termperature and stirred for an additional 2 h. During this period, the color of the solution changed from yellow to green with an intermediate brown-red/orange. When the reaction mixture was worked up a yellow green oil was obtained. Attempts to recrystallize the product failed. See Table 1.

In a separate experiment, the solvent was quickly removed in *vacuo* when the color changed from yellow to brownish-red/orange. The brownish red/orange residue which resulted was highly unstable and immediately changed to green in color. See Table 1.

Trimethylphosphite Reaction: Synthesis of $(CO)_4Cr(P(OCH_3)_3)(SiCl_3)_2$

To a cold solution (−30° C) of $(C_6H_5F)Cr(CO)_2(SiCl_3)_2$ (0.1 g, 0.2 mmol) in fluorobenzene (15 mL) was added a solution of $P(OMe)_3$ (0.4 mL, 3.3 mmol) in 5 mL of fluorobenzene dropwise from an addition funnel. The addition was

Table 1 Spectral data and analyses for new compounds

Compound	
$(CO)_4Cr(PEt_3)(SiCl_3)_2$	IR(CH_2Cl_2, cm^{-1})$\nu_{C=O}$ = 1880 s, 1845 vs, 1808 *vs.* ^{1}H NMR(C_6D_6,δ), 1.24(q-overlap, 6 H, due to CH_2), 0.98 (pent-overlap, 9H, due to CH_3). MS(El, 70eV) 551[M^+], 516[M^+-Cl], 460[M^+ – (2 CO + Cl)], 439[$Cr(SiCl_3)_2(PEt_3)]^+$, 432[M^+ – (3 CO+Cl)], 404[M^+ – 4 CO+Cl], 304[M^+ – (4 CO+$SiCl_3$)], 170 [$Cr(PEt_3)]^+$, 90 [$PEt_2]^+$, 60[$PEt]^+$
$(CO)_4Cr(P(OMe)_3)(SiCl_3)_2$	IR(CH_2Cl_2, cm^{-1}) $\nu_{C=O}$ = 1960 m, 1905 vs, 1798 m. ^{1}H NMR (C_6D_6, δ), 3.42 (4 peaks with 12 Hz spacing — possibly due to two isomers. MS(El, 70eV), 554[M^+], 519[M^+ – Cl), 463[M^+ – (2CO + Cl)], 442 [$Cr(SiCl_3]_2P(OMe)_3]^+$, 309 [M^+ – (4 CO+$SiCl_3$)], 124 ($P(OMe)_3]^+$, 93 [$P(OMe)_2]^+$, 62 [$P(OMe)]^+$
$(CO)_4Cr(P(O^1Pr)_3(SiCl_3)_2$	IR(CH_2Cl_2, cm^{-1}), $\nu_{C=O}$ = 1930 m, 1830 *vs.* ^{1}H NMR (C_6D_6, δ), 4.75 (q, 1 H), 1.18 (dd, 6 H). ^{13}C NMR (C_6D_6, δ), 228.06 (s, CO), 207.93 (s, CO), 73.64 (C-H of O^iPr), 23.56 (CH_3 of O ^iPr). Anal. Calc. C, 24.79; H, 3.33; P, 4.93; found C, 25.37, H, 2.99, P, 4.96

continued over a period of 10 min. The resulting solution was slowly warmed to room temperature and stored at room temperature for a week. A brown residue and an orange yellow supernatant solution were obtained. The supernatant was carefully separated from the residue and the residue was discarded. Solvent from the supernatant solution was removed in *vacuo* to obtain an orange yellow oil which was recrystallized from CH_2Cl_2:pentane (8:50 v/v) mixture at –3° C for several days. The $(CO)_4Cr(P(OCH_3)_3)(SiCl_3)_2$ complex was obtained as a yellow brown powder in a yield of 33% (0.02 g). See Table 1.

Tri-isopropylphosphite Reaction: Synthesis of $(CO)_4Cr(P(O^iC_3H_7)_3)(SiCl_3)_2$

To a solution of $(C_6H_5F)Cr(CO)_2(SiCl_3)_2$ (0.23 g, 0.5 mmol) in CH_2Cl_2 (20 mL) held at – 78° C, $P(O^iPr)_3$ (0.7 mL, 2.8 mmol) was added dropwise. The reaction mixture was allowed to stir at – 78° C for 4 h. Then it was slowly warmed up to room temperature and stirred overnight. An orange yellow solution resulted which was concentrated to *ca.* 8 mL and then a large excess of pentane (*ca.* 100 mL) was layered on top and stored in the freezer for a week. A crystalline product of $(CO)_4Cr(P(O^iC_3H_7)_3)(SiCl_3)_2$ was obtained in 32% (0.05 g) yield. See Table 1.

Attempt to prepare (2,4,6-trimethylpyridine)$Cr(CO)_2(SiCl_3)_2$/Synthesis of (2,4,6-trimethylpyridine)$_2CrCl_2$

Irradiation of a mixture of $(C_6H_5F)Cr(CO)_3$(0.3 g, 1.3 mmol), 2,4,6-trimethylpyridine (= 2,4,6-collidine) (0.5 mL, 3.8 mmol), and $HSiCl_3$ (3.4 mL, 33.7 mmol) in CH_2Cl_2 (45 mL) with 450-W UV lamp for *ca.* 4 h in a quartz tube equipped with a water-cooled probe afforded a reddish brown solution. Upon workup of the reaction mixture and recrystalliztion from CH_2Cl_2:pentane (15:100 v/v) mixture, a purple powder mixed with a white material was obtained. Manual separation in a glove box yielded a purple powder (0.35 g, 74%), still contaminated with small amounts of the white material. Therefore, no satisfactory elemental analysis could be achieved as is evident from the results.[22a] From the elemental analysis mass spectral data, and melting point determination we identified the product as the square planar (2,4,6-collidine)$_2$CrCl$_2$ which is in agreement with our earlier results.[22a,b]

In a separate experiment, we attempted to prepare (2,4,6-trimethyl- pyridine) Cr(CO)$_2$(SiCl$_3$)$_2$ *via* arene exchange by treating (C$_6$H$_5$F)Cr(CO)$_2$(SiCl$_3$)$_2$ (0.1 g, 0.2 mmol) and 2,4,6-collidine (0.5 mL, 3.8 mmol) in CH$_2$Cl$_2$ (15 mL) at room temperature. This reaction yielded only green oxidized products but not the desired complex.

RESULTS

Arene Exchange

Arene exchange kinetics have been studied for (C$_6$H$_5$F)Cr(CO)$_3$, (*p*-C$_6$H$_4$F$_2$) Cr(CO)$_3$, (C$_6$H$_5$F)Cr(CO)$_2$(SiCl$_3$)$_2$, and (*p*-C$_6$H$_4$F$_2$)Cr(CO)$_2$(SiCl$_3$)$_2$ with mesitylene at eight different concentrations of mesitylene and a fixed concentration of the arene complex. First order rate constants were calculated from the slope of the first order plots for the disappearance of starting (arene)Cr(CO)$_3$ or (arene) Cr(CO)$_2$(SiCl$_3$)$_2$ and/or appearance of (mesitylene)Cr(CO)$_3$ or (mesitylene)Cr(CO)$_2$(SiCl$_3$)$_2$, respectively, using a least squares fit program. As a representative example, Figure 1 shows the IR spectra of a solution of (reaction carried out at 170° C) 5.92×10^{-3} M (C$_6$H$_5$F)Cr(CO)$_2$(SiCl$_3$)$_2$ complex and mesitylene (decalin solvent) at various intervals of time. These spectra demonstrate the disappearance of (C$_6$H$_5$F)Cr(CO)$_2$ (SiCl$_3$)$_2$ and the appearance of (C$_6$H$_3$(CH$_3$)$_3$)Cr(CO)$_2$(SiCl$_3$)$_2$ as the reaction progresses.

Table 2 summarizes all the rate data for (C$_6$H$_5$F)Cr(CO)$_3$, (*p*-C$_6$H$_4$F$_2$)Cr(CO)$_3$, and (C$_6$H$_5$F)Cr(CO)$_2$(SiCl$_3$)$_2$. It should be noted that k_{obs} is dependent on [mesitylene] in the case of tricarbonyl complexes, but is *much less* dependent in the dicarbonyldisilyl compound.

In the case of (η^6-*p*-C$_6$H$_4$F$_2$)Cr(CO)$_2$(SiCl$_3$)$_2$ no rate data were obtained since a rapid equilibrium was established (K_{eq} independent of [mesitylene]).

Table 3 collects k_{obs} values for comparison with literature values for an analogous compound, and kinetic data at different reaction temperatures for these three compounds are shown in Table 4. Note that direct comparisons of literature k_{obs} values were possible since exchange reactions were carried out at the same temperature and in alkane solvents.

Ligand Displacement of Arene

Reactions between (η^6-arene)Cr(CO)$_3$ and neutral Lewis bases generally lead to arene ring displacement, for example with L = NH$_3$,[23] pyridine,[15,16] PPh$_3$,[15] and P(OPh)$_3$[17](eq. 5):

$$\text{(arene)Cr(CO)}_3 + 3\ \text{L} \rightarrow \text{fac} - \text{L}_3\text{Cr(CO)}_3 + \text{arene} \qquad (5)$$

Such arene displacement reactions are thought to take place stepwise such that the arene goes from $\eta^6 \rightarrow \eta^4 \rightarrow \eta^2 \rightarrow \eta^0$ as L moieties attack.

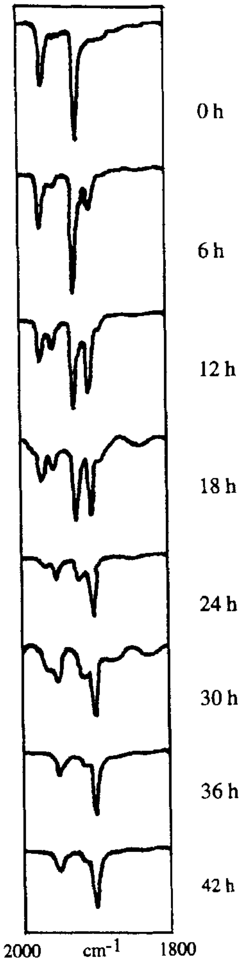


Figure 1 Infrared spectra of the ν_{C-O} region of a solution of 5.92×10^{-3} M $(C_6H_5F)Cr(CO)_2(SiCl_3)_2$ during exchange with mesitylene at 170°C in decalin.

We have carried out similar studies with one of our new compounds $(\eta^6\text{-}C_6H_5F)Cr(CO)_2(SiCl_3)_2$ and expected a straightforward arene displacement. The ligands studied were PMe_3, PEt_3, PPh_3, $P(OMe)_3$, and $P(O^iPr)_3$. Only in the cases of PEt_3, $P(OMe)_3$, and $P(O^iPr)_3$ were we able to isolate and characterize the products. To our surprise, seven-coordinate tetracarbonyl complexes were formed, apparently due to substitution and disproportionation processes (eq. **6**).

$$2(\eta^6\text{-}C_6H_5F)Cr(CO)_2(SiCl_3)_2 \xrightarrow{L} (CO)_4Cr(SiCl_3)_2(L) + \text{“}Cr(SiCl_3)_2\text{”} + 2C_6H_5F \quad (6)$$

This reaction is independent of the concentration of L; that is equimolar, 3-fold excess, and 6-fold excess of L yielded the same product.

Table 2 Rate constants for arene exchange in $(C_6H_5F)Cr(CO)_3$, $(p\text{-}C_6H_4F_2)Cr(CO)_3$, and $(C_6H_5F)Cr(CO)_2(SiCl_3)_2$ with mesitylene at 170°C in decalin

Complex	Complex Conc. × 10^{-3}, M	Mesitylene Conc. × 10^{-3}, M	Rate Constant^{a,b,c} × 10^{-6} k_{obs}, s^{-1}
$(C_6H_5F)Cr(CO)_3$	12.1	6.1	5.23
	12.1	12.1	6.93
	12.1	18.2	7.86
	12.1	24.2	8.39
	12.1	48.4	16.6
	12.1	194	17.8
	12.1	1210	25.0
	12.1	6050	27.0
$(p\text{-}C_6H_4F_2)Cr(CO)_3$	11.2	5.6	12.4
	11.2	11.2	21.0
	11.2	16.8	28.5
	11.2	22.4	29.2
	11.2	44.8	29.5
	11.2	179	30.1
	11.2	1120	38.2
	11.2	5600	39.5
$(C_6H_5F)Cr(CO)_2(SiCl_3)_2$	5.92	2.96	23.7 (21.1)
	5.92	5.92	24.9 (21.4)
	5.92	8.88	25.6 (22.1)
	5.92	11.8	25.9 (22.5)
	5.92	47.0	26.5 (22.9)
	5.92	95.0	28.1 (23.1)
	5.92	592	28.9 (23.4)
	5.92	2960	30.3 (24.0)

[a] From the rate of disappearance of complex. [b] Numbers in parentheses are from rate of appearance of the (η^6-mesitylene) Cr complex. [c] Error estimates are 5%.

Table 3 Rate constants for $(\eta_6\text{-Arene})Cr(CO)_3$ and $(\eta^6\text{-Arene})Cr(CO)_2(SiCl_3)_2$

Complex	mesitylene conc. × 10^{-3}, M	k_{obs},s^{-1} × 10^{-6}
$(C_6H_6)Cr(CO)_3{}^a$	7.2	1.8(±0.6)
$(C_6H_5F)Cr(CO)_3{}^b$	6.1	5.23^c
$(p\text{-}C_6H_4F_2)Cr(CO)_3{}^b$	5.6	12.4^c
$(C_6H_5F)Cr(CO)_2(SiCl_3)_2{}^b$	5.9	24.9^c

[a] From reference 7, exchange carried out in cyclohexane-d_{12} at 170°C. [b] This work, in decalin at 170°C. [c] Error estimates are 5%.

Table 4 Observed rate constants at different temperatures

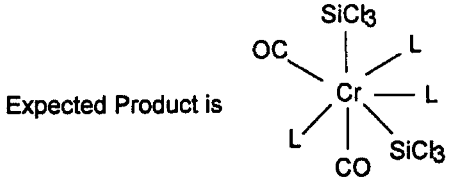
Temp. (°C)	$k_{obs}(s^{-1})^a$		
	$(C_6H_5F)Cr(CO)_2(SiCl_3)_2$	$(C_6H_4F_2)Cr(CO)_3$	$(C_6H_5F)Cr(CO)_3$
170	2.49 × 10^{-5}	2.10 × 10^{-5}	0.693 × 10^{-5}
150	5.80 × 10^{-8}	2.50 × 10^{-8}	0.280 × 10^{-8}
130	3.80 × 10^{-10}	2.20 × 10^{-10}	—
110	2.80 × 10^{-12}	2.30 × 10^{-12}	—

[a] Error estimates are 5%.

DISCUSSION

Ligand Displacements of Arene

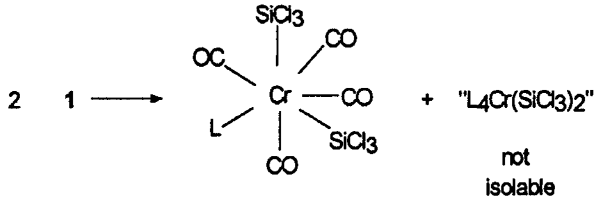
To account for the unexpected result that a simple arene substitution by L_3 did not take place it is illustrative to consider the structure of the expected product:



1

L = PEt_3, $P(OMe)_3$, $P(O^iPr)_3$

This 7-coordinate compound with large PR_3 and $SiCl_3$ ligands would be very sterically conjested. In order to maintain the 18-electron configuration with two $SiCl_3$ groups, however, a 7-coordinate complex is necessary. In order to relieve the steric strain, ligand disproportionation takes place, eventually yielding the observed tetracarbonyl complex (**2**) perhaps through the intermediacy of **1**, (eq. 7).



2 **3**

(7)

In such a sequence a structure like **3** might be predicted to form; however, steric problems in **3** would be tremendous, and so **3** or fragments of **3** were not isolable.

The stereochemistry of **2** is currently not known but we assume that the L and $SiCl_3$ groups will be as far away from each other as possible, as we have tried to indicate in **2**.

Coordination number 7, although well known, cannot be considered very common. The relative instability of such species can be attributed to the fact that additional bond energy of the seventh bond is offset by: (a) increased L-L repulsion, (b) weaker bonds, and (c) generally reduced crystal field stabilization energy (CFSE) as a result of non-octahedral geometry.[24] There are three distinct geometries known: (1) pentagonal bipyramid, (2) capped octahedron in which a seventh ligand has been added to a triangular face, and (3) a capped trigonal prism in which a seventh ligand has been added to a rectangular face. In addition, there are many intermediate cases, and the situation is reminiscent of 5-coordinate geometries.[25] The results from our studies show that the η^6-C_6H_5F ligand is readily displaced, and there is a very strong tendency to restore the 18-electron configuration even to the point of ligand interchanges to remove steric strain. An important point is that $SiCl_3$ groups were not reductively elminated.

Arene Exchange

One of our goals in this work was to develop labile η^6-arene chromium complexes through the use of the Cr(II) oxidation state coupled with steric strain from the presence of $SiCl_3$ groups, and the use of fluorinated arenes. The kinetic data show that we were successful in labilizing the η^6-arene such that k_{obs} was increased by more than 10-fold (Table 3). This labilization should ensure a rich chemistry at the Cr(II) center and this is currently being explored.

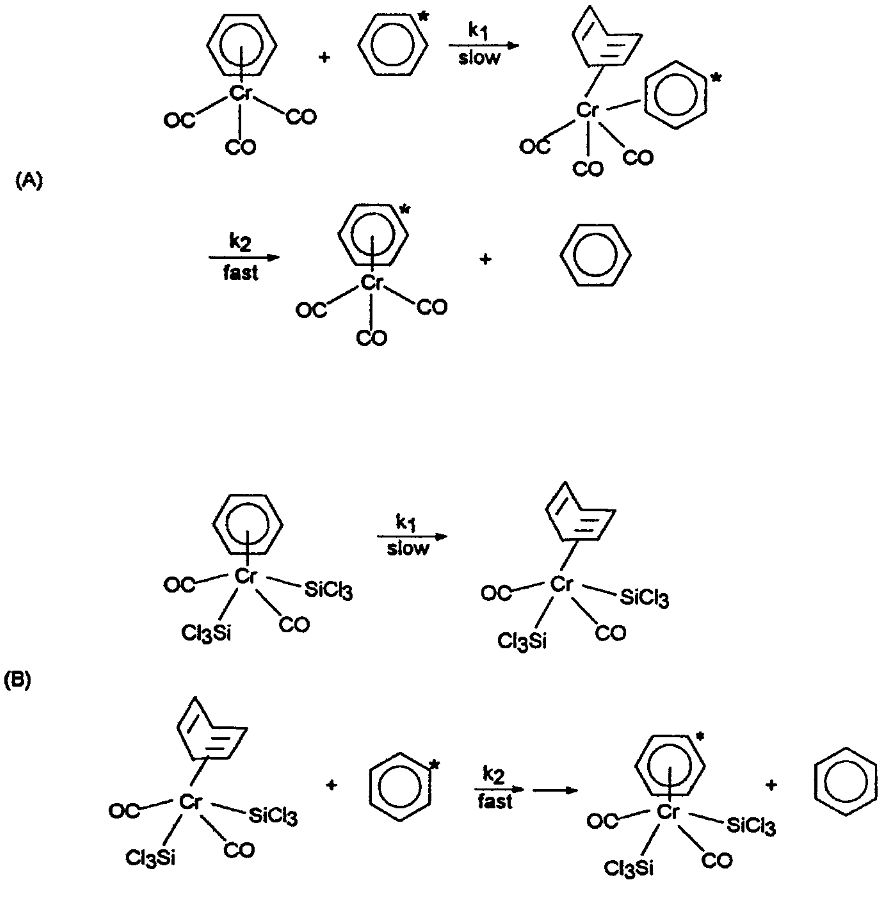
An additional interesting finding was that the mechanism of arene exchange was modified by the Cr(II) oxidation state and the presence of the large $SiCl_3$ groups. Thus, in the case of $(C_6H_5F)Cr(CO)_2(SiCl_3)_2$ the rate of exchange of fluorobenzene with mesitylene *was only slightly dependent on mesitylene concentration*, while in the (arene)$Cr(CO)_3$ cases the rate was very dependent on attacking arene.

Hence our results for the tricarbonyl derivatives are in agreement with Traylor and coworkers[7] and the mechansim of exchange must involve a displacement of bound arene by attack of incoming arene, forcing an η^6-n^4 conversion and eventual $\eta^6 \rightarrow \eta^4 \rightarrow \eta^0$ removal of the intial arene ligand. Therefore, the reaction is dependent on attacking arene concentration (Scheme 1(A)). In these cases, arene exchange is purely governed by electronic effects, that is, the electron rich arene, namely mesitylene displaces a relatively weak π-donor, namely fluorobenzene and *p*-difluorobenzene, respectively, in simple stepwise displacement reactions involving ring-slipped intermediates.

However, in the case of the (η^6-arene)$Cr(CO)_2(SiCl_3)_2$ derivatives, apparently the rate determining step involves as slow $\eta^6 \rightarrow \eta^4$ slipppage followed by attack of displacing arene (Scheme 1(B). An alternative explanation might be an $\eta^6 \rightleftarrows \eta^4$ prequilibrium followed by attack of incoming arene. In either case, the reaction would not be as strictly dependent on arene concentration (Figure 2).

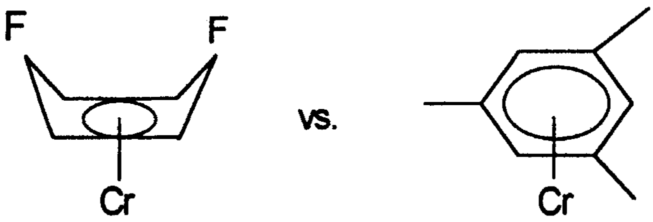
These results are not unreasonable since the bulky $SiCl_{33}$ groups would serve to discourage direct attack of incoming arene. Even though this is apprently true, the arene exchange does proceed faster in the (η^6-C_6H_5F)$Cr(CO)_2(SiCl_3)_2$ case. Thus, electronic demands of the Cr(II) center apparently allow k_2 in Scheme 1(B) to be rapid, and the electronic effects somewhat overwhelm steric effects (although steric effects change the mechanism).

Finally, the (η^6-*p*-$C_6H_4F_2$)$Cr(CO)_2(SiCl_3)_2$ complex should be considered. To our surprise, the *p*-$C_6H_4F_2$ ligand could not be completely displaced by mesitylene over time and an equilibrium was established. Apparently the *p*-$C_6H_4F_2$ ligand competes very well with the more electron rich mesitylene. This unusual result is hard to explain. However, we do know from the crystal structure of this complex that the η^6-$C_6H_4F_2$ ligand is distorted such that the four carbons not bearing the F substituents are closer to the Cr center forming a boat structure. Possibly this slight



Scheme 1 Sequences for arene exchange in (A) (η^6-arene)Cr(CO)$_3$ and (B) (η^6-arene)Cr(CO)$_2$(SiCl$_3$)$_2$

"folding" allows a stronger interaction with the Cr, as discussed earlier,[19] and this coupled with less steric crowding *vs* mesitylene allows enhanced resistance toward displacement.



We are currently attempting to build even more labile (η^6-arene)Cr(II) analogs and hope to report on chemical and catalytic properties in the future.

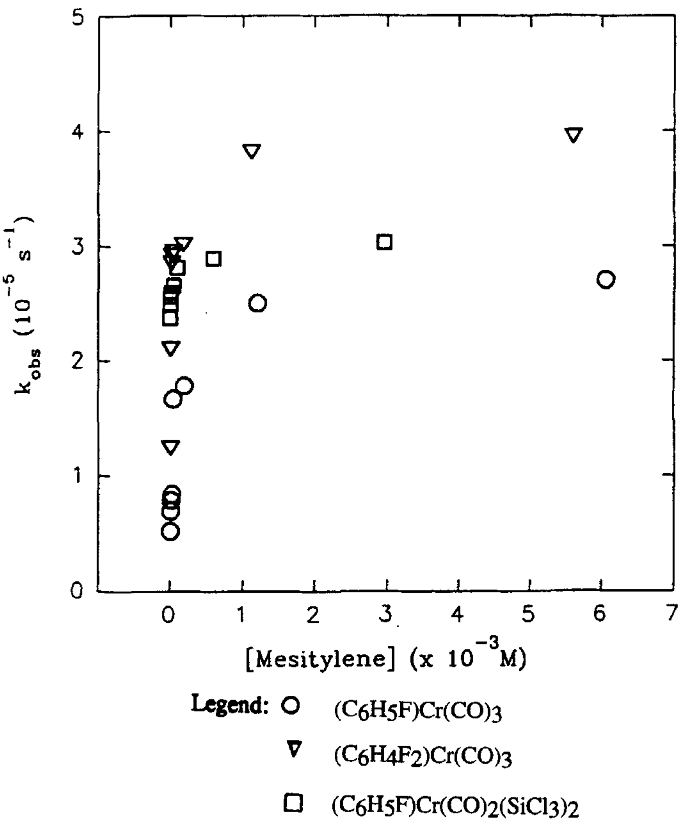


Figure 2 A plot of attacking arene (mesitylene) concentration *vs* k_{obs}. Note the lessened effect of [mesitylene] on the dicarbonyl derivative.

Acknowledgements

The support of the National Science Foundation is acknowledged with gratitude.

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