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Kinetics and Mechanism of Arene Displacement in (η-Arene)dicarbonyl(chalcocarbonyl)chromium(0) Complexes, (η-arene)$Cr(CO)_2(CX)$ (X = S, Se), by Tertiary Phosphites[1]

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The kinetics and mechanism of the arene substitution reactions of the chalcocarbonyl complexes (η-arene)$Cr(CO)_2(CX)$ [X = S, arene = C_6H_6, PhMe, $PhNMe_2$, $PhCO_2Me$, *o*-$C_6H_4Me_2$, *p*-$C_6H_4Me_2$, *m*-$C_6H_4(CO_2Me)Me$, *p*-$C_6H_4(CO_2Me)_2$, *p*-$C_6H_4(OMe)_2$, 1,3,5-$C_6H_3Me_3$; X = Se, arene = C_6H_6] by tertiary phosphites [L = $(MeO)_3P$, $(PhO)_3P$, (*n*-$BuO)_3P$, $(C_6H_{11}O)_3P$] in methylcyclohexane to form *mer*-$Cr(CO)_2(CX)L_3$ have been investigated. The reactions are significantly faster than those for the corresponding tricarbonyl complexes and are first-order in both substrate and entering ligand L. Activation parameters for arene = C_6H_6 and L = $(MeO)_3P$: X = S, $\Delta H^* = 74.1$ kJ mol^{-1}, $\Delta S^* = -117$ J mol^{-1} deg^{-1}; X = Se, $\Delta H^* = 74.9$ kJ mol^{-1}, $\Delta S^* = -100$ J mol^{-1} deg^{-1}. A mechanism involving the slight slippage of the arene ring from η^6- to η^x-coordination ($6 > x > 4$) prior to entry of the first L ligand in the rate-determining step is proposed. The greater reactivity of the thio- and selenocarbonyl derivatives compared to that of the tricarbonyl analogues is attributed to the better π-acceptor capacities of CS and CSe compared to that of CO, resulting in weaker bonding between the Cr metal and the arene. Also, on the basis of this kinetic study, it appears likely that the thio- and selenocarbonyl complexes will not be as good catalysts as the (η-arene)chromium tricarbonyl complexes for the hydrogenation of dienes.

Introduction

The study of arene labilization in group 6[3] metal tricarbonyl complexes has been of considerable interest for many years,[4–8] and the mechanism of arene displacement is still under active investigation.[9–15] This interest stems from the importance of these complexes in catalytic hydrogenation,[6,16] as well as the potential utility of arene-exchange processes in the liberation of functionalized arenes from the metal center.[16–18]

In this paper, we report the results of an investigation of the kinetics and mechanism of arene displacement in analogous thio- and selenocarbonyl derivatives, (η-arene)$Cr(CO)_2(CX)$ (X = S, Se), by tertiary phosphites. This study includes the first ever kinetic investigation of an organometallic selenocarbonyl complex. This is particularly important because the free CSe molecule has never been isolated, even at liquid-helium temperatures, and so studies of the coordinated ligand provide the only way of probing the physicochemical properties of this interesting diatomic analogue of CO. It was our aim to obtain a quantitative measure of the influence of the thio- and selenocarbonyl ligands on arene lability in these complexes. We knew already from our work on the reactions of (η-arene)$Cr(CO)_2(CX)$ with CO gas under moderate pressure to give $Cr(CO)_5(CX)$ that arene displacement is much easier in these cases than for the related (η-arene)$Cr(CO)_3$ derivatives, presumably because of the better electron-withdrawing capabilities of CS and CSe compared to that of CO.[19]

Experimental Section

Materials. The (η-arene)$Cr(CO)_2(CX)$ (X = O, S, Se) complexes were prepared by the literature methods indicated.[20–22] Their purity was established by the absence of any superfluous peaks in the ν(CO) region of their FT-IR spectra. $(MeO)_3P$, $(PhO)_3P$, and trimethyl phosphate (Gold Label, purity 99+%) and $(EtO)_3P$ (99% purity) were purchased from Aldrich Chemical Co. and were used as received. (*n*-$BuO)_3P$ and $(C_6H_{11}O)_3P$ were obtained from Strem Chemicals. The tertiary phosphites were always handled under an atmosphere of prepurified N_2. ^{31}P NMR spectra of the ligands were measured periodically over a full spectral window (40 000 Hz) on a Varian Associates XL-200 NMR spectrometer to verify the absence of any phosphorus-containing impurities. Fresh bottles of tertiary phosphite (100 mL) were used every third run or within 4 days of opening a new bottle. The methylcyclohexane and dichloroethane solvents (99%) were distilled under N_2 over Na strips and $CaCl_2$, respectively.

Preparation of Samples. All manipulations were performed under a N_2 atmosphere in a stainless steel glovebox that was periodically evacuated and purged with N_2. This purge was maintained throughout the entire sample preparation procedure. Typically, two samples of (η-arene)$Cr(CO)_2(CX)$ (X = O, S, Se) (1.40 mg) were weighed out on a Cahn electrobalance (±0.01 mg) and then placed in two 25-mL volumetric flasks fitted with hollow Teflon plugs capped with rubber septa. The flasks were flushed with N_2 prior to transferring the solvent. A third flask was filled with distilled solvent under N_2. The three flasks were

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(3) In this paper, the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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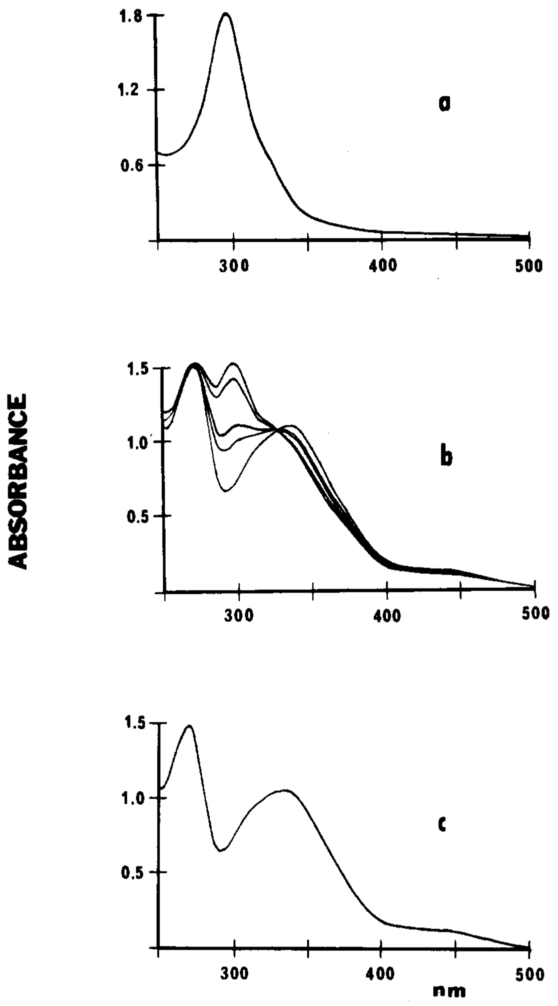

Figure 1. Typical UV–visible spectra obtained in kinetic investigations of (η-arene)Cr(CO)$_2$(CX) (X = S, Se): (a) (η^6-C$_6$H$_6$)Cr(CO)$_2$(CSe); (b) reaction of (η^6-C$_6$H$_6$)Cr(CO)$_2$(CSe) with (MeO)$_3$P at 53 °C, showing isosbestic point; (c) Cr(CO)$_2$(CSe)[(MeO)$_3$P]$_3$.

next transferred to the glovebox together with at least four, matched 1-cm quartz cuvettes fitted with Viton O-rings, the bottle containing the tertiary phosphite ligand, and two 1-mL (±1%) Hamilton syringes with Teflon barrels. A measured volume of the solution was then syringed out and replaced by an equal volume of tertiary phosphite [providing [L] 800–3000 times in excess of [(η-arene)Cr(CO)$_2$(CX)]]. The flask was capped and shaken vigorously. One cuvette was filled with the solution containing only (η-arene)Cr(CO)$_2$(CX), while another was filled with the solution containing both the complex and the ligand. Two other cuvettes were filled with pure solvent.

The cuvettes were mounted in a Varian Associates Cary 210 UV–vis spectrophotometer equipped with a thermostated multisample support assembly. Because of the elevated temperatures used (>45 °C), two water-cooled jackets (supplied by Varian Associates) were placed on either side of the heating assembly to protect the instrument optics. The time allowed for equilibration of the cuvettes to the designated kinetic run temperature was 17 min. The actual temperature was determined by placing a calibrated thermocouple wire into a cuvette containing methylcyclohexane under the same conditions as for the kinetic run. No solvent loss was observed up to 72 h at 85 °C. The UV–vis instrument was equipped with a cell programmer accessory and was interfaced to an Apple II+ computer (64K). The programs Master Scan Storage and Master Kinetic Storage, both supplied by Varian Associates, were used to collect and store wavelength scans (500–280 nm) and absorbances at three selected wavelengths at programmed time intervals. Usually, a run was between 10 and 48 h in duration and the data acquisition was triggered every 10 or 15 min. The data acquired for the disappearance of the substrate were analyzed, yielding k_{obsd}, by using the Advanced Order Kinetic Program supplied by Varian Associates, which is based on the multiple-linear-regression program described in ref 23.

Table I. Pseudo-First-Order Rate Constants for Arene Ring Displacement in (η^6-C$_6$H$_6$)Cr(CO)$_2$(CX) (X = S, Se) by (MeO)$_3$P in Methylcyclohexane[a]

X = S[b]		X = Se[c]	
10[(MeO)$_3$P], M	10^5k_{obsd}, s^{-1}	10[(MeO)$_3$P], M	10^5k_{obsd}, s^{-1}
2.37	1.48	2.71	4.06
4.07	2.22	3.39	4.67
5.10	3.22	4.06	5.87
6.10	3.39	5.08	6.99
6.78	3.85	6.10	8.70

[a] Averages of several runs at the same concentrations; standard deviation <2.5%. [b] At 83.3 °C. A least-squares fit of the kinetic data to the equation $k_{obsd} = k_1 + k_2[(\mathrm{MeO})_3\mathrm{P}]$ yields $k_1 = (1.4 \pm 1.7) \times 10^{-6}$ s^{-1} and $k_2 = (5.46 \pm 0.34) \times 10^{-5}$ M^{-1} s^{-1}; $r = 0.98$. Similar variable-temperature kinetics studies afforded the following data for 10^5k_2 (M^{-1} s^{-1}): 59.9 °C, 0.92 ± 0.06; 67.0 °C, 1.69 ± 0.05; 72.4 °C, 2.42 ± 0.12; 76.6 °C, 3.27 ± 0.09; 83.3 °C, 5.46 ± 0.34. [c] At 72.6 °C. $k_1 = (1.2 \pm 1.8) \times 10^{-6}$ s^{-1}, $k_2 = (1.39 \pm 0.04) \times 10^{-4}$ M^{-1} s^{-1}; $r = 0.99$. Variable-temperature studies gave 10^5k_2 values as follows (M^{-1} s^{-1}): 53.0 °C, 2.72 ± 0.07; 57.9 °C, 4.31 ± 0.13; 63.2 °C, 5.92 ± 0.04; 72.6 °C, 13.9 ± 0.4.

Least-squares analyses for the calculation of k_1, k_2, and the activation parameters were performed with no data smoothing or averaging using a Curve Fitter program written by P. K. Warm (Interactive Microware, 1980).

Results and Discussion

The kinetics of arene displacement in the (η-arene)Cr(CO)$_2$(CX) (X = S, Se) complexes were conveniently monitored by UV–vis spectroscopy. All the kinetic runs exhibited a single isosbestic point (Figure 1), confirming that only one reaction was taking place with no significant side reactions. The pseudo-first-order reaction rates (k_{obsd}) were determined from the decreases in absorbance of the substrate with time. The reaction products in the kinetic runs were identified by the similarity of their spectral properties (UV–vis, FT-IR, ^{31}P NMR) to those of the products isolated from preparative-scale reactions, viz., *mer*-Cr(CO)$_2$(CX)[(MeO)$_3$P]$_3$ (X = S, Se) with a phosphite trans to the CX ligand (denoted as the *mer* I isomer). The stereochemistry of these two reaction products has been established by spectroscopic and X-ray diffraction studies.[24,25] The overall reaction being examined in the kinetic studies is therefore given by eq 1.

$$(\eta\text{-arene})\mathrm{Cr(CO)_2(CX)} + 3\mathrm{L} \rightarrow \mathrm{Cr(CO)_2(CX)L_3} + \text{arene} \quad (1)$$

The dependencies of the reaction rates on [L] were investigated for the reactions of BzCr(CO)$_2$(CX) (Bz = η-C$_6$H$_6$; X = S, Se) with (MeO)$_3$P (Table I). Plots of k_{obsd} vs. [(MeO)$_3$P] were linear for the concentration range examined. Least-squares procedures were used to fit the data to the equation $k_{obsd} = k_1 + k_2[(\mathrm{MeO})_3\mathrm{P}]$. For both complexes, the intercepts were zero within the standard deviation, and so there is no contribution from a first-order dissociative term. The k_2 values were obtained from the slopes of the graphs. The rates of reaction can therefore best be represented by the pure second-order rate expression

$$-d[(\eta\text{-arene})\mathrm{Cr(CO)_2(CX)}]/dt = k_2[(\eta\text{-arene})\mathrm{Cr(CO)_2(CX)}][\mathrm{L}] \quad (2)$$

where $k_2 = k_{obsd}/[\mathrm{L}]$.

The activation parameters derived from the kinetic data for eq 1 are given in Table II. The enthalpies of activation are small and positive, while the associated entropies of activation are large and negative for both the thio- and selenocarbonyl derivatives. Therefore, the rate-determining step appears to involve purely a bimolecular associative process. Similar activation parameters were obtained in previous kinetic studies of the reactions of (η-arene)M(CO)$_3$ (M = Mo, W) with various monodentate ligands

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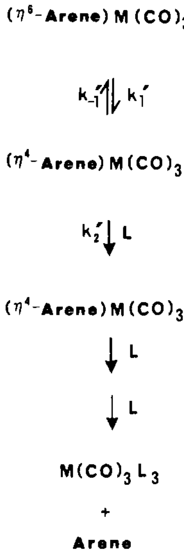
Table II. Activation Parameters for Ring Displacement Reactions of (η^6-C_7H_8)Cr(CO)$_3$ and (η^6-arene)Cr(CO)$_2$(CX) (X = O, S, Se) Complexes

complex	entering ligand	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J mol^{-1} deg^{-1}
(η^6-C_7H_8)Cr(CO)$_3$[a]	(MeO)$_3$P	69.0	−105
(η^6-C_7H_8)Cr(CO)$_3$[b]	PhCN	74.1	−109
(η^6-C_7H_8)Cr(CO$_3$[b]	MeCN	90.4	−63
(η^6-naphth)Cr(CO)$_3$[c]	MeCN	70.3	−84
(η^6-naphth)Cr(CO)$_3$[d]	PhMe	132	−1.4
(η^6-naphth)Cr(CO)$_3$[d]	(MeO)$_3$P	60.5	−100
(η^6-naphth)Cr(CO)$_3$[e]	C_6D_6	91.5	−99
(η^6-C_6H_6)Cr(CO)$_3$[f]	C_6Me_6	124	−17
(η^6-*p*-xylene)Cr(CO)$_3$[f]	C_6Me_6	125	−50
(η^6-mesityl)Cr(CO)$_3$[f]	C_6Me_6	108	−75
(η^6-C_6H_6)Cr(CO)$_2$(CS)[g]	(MeO)$_3$P	74.1	−117
(η^6-C_6H_6)Cr(CO)$_2$(CSe)[g]	(MeO)$_3$P	74.9	−100

[a] Reference 26; methylcyclohexane solution. [b] Reference 7; dichloroethane solution. [c] Reference 26; dichloroethane solution. [d] Reference 15; *n*-nonane solution. [e] Reference 14; neat C_6D_6. [f] Reference 9; cyclohexanone solution. [g] This work; methylcyclohexane solution.

Scheme I



[L = (MeO)$_3$P, R$_n$Cl$_{3-n}$P][4,5] and of (cht)M(CO)$_3$ (M = Cr, Mo, W; cht = η-C_7H_8) with (MeO)$_3$P.[26] The earlier data were rationalized in terms of the mechanism proposed by Zingales et al.[4] involving a stepwise displacement of the η^6-coordinated arene or triene by the entering ligand. For (η-arene)Cr(CO)$_3$ complexes, it is considered likely that the first step in this process is partial slippage of the coordinated arene since nucleophilic attack at the metal in the fully coordinated complex would be highly unfavorable energetically.[27] Accordingly, the mechanism in Scheme I has been proposed for arene displacement from (η-arene)Cr(CO)$_3$ by a ligand L.[12] A steady-state treatment of this mechanism yields

$$-d[(\eta\text{-arene})Cr(CO)_3]/dt = k_1'k_2'[(\eta\text{-arene})Cr(CO)_3][L]/(k_{-1}' + k_2'[L])$$

which reduces to a second-order rate equation for $k_{-1}' >> k_2'[L]$. The kinetic data obtained in the present study are consistent with this limiting case:

$$-d[(\eta\text{-arene})Cr(CO)_2(CX)]/dt = (k_1'k_2'/k_{-1}')[(\eta\text{-arene})Cr(CO)_2(CX)][L]$$

In terms of this postulated mechanism, the k_2 values reported here correspond to $K_{eq}k_2'$, where $K_{eq} = k_1'/k_{-1}'$.

Table III. Pseudo-First-Order Rate Constants for Arene Ring Displacement in (η^6-arene)Cr(CO)$_2$(CS) Complexes by (MeO)$_3$P in Methylcyclohexane at 83.3 °C[a]

complex	arene	10^5k_{obsd},[b] s^{-1}
I	1,3,5-$C_6H_3Me_3$	0.99[c]
II	*p*-$C_6H_4Me_2$	*d*
III	*o*-$C_6H_4Me_2$	2.06
IV	PhMe	1.99
V	C_6H_6	2.91
VI	*m*-$C_6H_4(CO_2Me)Me$	4.15
VII	$PhCO_2Me$	7.33
VIII	*p*-$C_6H_4(CO_2Me)_2$	10.2
IX	*p*-$C_6H_4(OMe)_2$	20.2
X	$C_6H_5NMe_2$	24.8

[a] [(MeO)$_3$P] = 0.508 M. [b] Averages of at least three runs; standard deviations <6%. [c] Rate constant for (*n*-BuO)$_3$P; cf. value for reaction of (η^6-C_6H_6)Cr(CO)$_2$(CS) with (*n*-BuO)$_3$P in Table IV. [d] Reaction too slow to yield an accurate rate constant.

Table IV. Pseudo-First-Order Rate Constants for Arene Ring Displacement from (η^6-arene)Cr(CO)$_2$(CS) Complexes by Tertiary Phosphites in Methylcyclohexane at 83.3 °C[a]

arene	tertiary phosphite	cone angle,[b] deg	k_{obsd},[c] s^{-1}
C_6H_6	(*n*-BuO)$_3$P		14.4
C_6H_6	(EtO)$_3$P	109	7.16
C_6H_6	(MeO)$_3$P	109	2.91
p-$C_6H_4(OCH_3)_2$	(MeO)$_3$P	107	20.2
$C_6H_5N(CH_3)_2$	(MeO)$_3$P	107	24.8
p-$C_6H_4(OCH_3)_2$	(PhO)$_3$P	128	4.82
$C_6H_5N(CH_3)_2$	(PhO)$_3$P	128	5.68
C_6H_6	$(C_6H_{11}O)_3P$	135[d]	no reacn

[a] [(RO)$_3$P] = 0.508 M. [b] Reference 39. [c] Averages of at least three runs; standard deviations <7%. [d] Reference 40.

A closer examination of the activation parameters in Table II reveals that the entropy of activation is the factor governing the difference in reactivity between BzCr(CO)$_2$(CS) and BzCr(CO)$_2$(CSe) since the enthalpies of activation are quite similar. That $\Delta S^{\ddagger}$ is more negative for the thiocarbonyl complex may imply a closer proximity of the arene and the incoming ligand to the chromium in the transition state, leading to greater steric interactions. This suggestion is supported by the longer Cr-arene bond in (η-PhCO$_2$Me)Cr(CO)$_2$(CSe) compared to that in (η-PhCO$_2$Me)Cr(CO)$_2$(CS) from X-ray diffraction studies.[28] Furthermore, the Cr–P bond lengths in *mer*-Cr(CO)$_2$(CSe)[(MeO)$_3$P]$_3$ (especially for the Cr–P bond trans to CSe) are longer than the corresponding bond lengths in the thiocarbonyl analogue.[24,25] These longer Cr–P bond distances suggest a less significant steric effect due to the incoming ligand in the activated state during bond formation for the selenocarbonyl derivative.

A second factor that should be considered in accounting for the observed difference in $\Delta S^{\ddagger}$ is the ease of distortion of the arene ring. [η-1,2,3-(MeO)$_3$C$_6$H$_3$]Cr(CO)$_3$ and (η-PhNEt$_2$)Cr(CO)$_3$ exhibit greater arene lability than would be anticipated on the basis of their Cr–arene bond strengths.[29] Recent crystal structures of these complexes have revealed significant distortions of the arene ring from planarity.[30] It has been postulated that these distortions allow an incoming nucleophile greater accessibility to the metal center and so enhance the ring lability. However, X-ray data for the (η-PhCO$_2$Me)Cr(CO)$_2$(CX) (X = O, S, Se) triad indicate only minor variations in the Cr–C(ring) distances.[28] No evidence was found for arene distortions of magnitude comparable to those observed for [η-1,2,3-(MeO)$_3$C$_6$H$_3$]Cr(CO)$_3$ or (η-PhNEt$_2$)Cr(CO)$_3$. However, the absence of ring distortion in the solid-state structures does not preclude the possibility that the lower entropy

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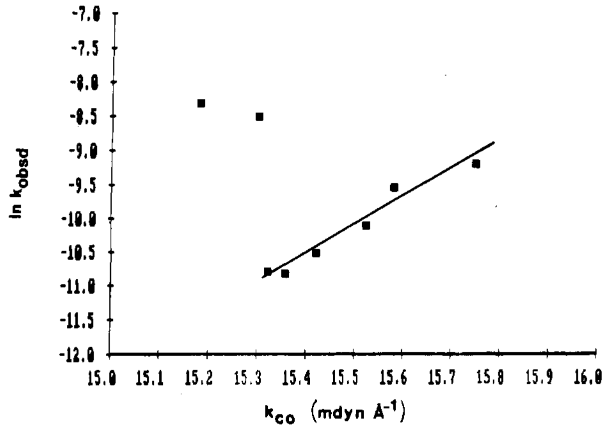

Figure 2. Plot of ln k_{obsd} values for the reactions of (η-arene)$Cr(CO)_2(CS)$ complexes with $(MeO)_3P$ vs. the carbonyl stretching force constants (k_{CO}) of the arene complexes. The following k_{CO} values for the complexes given in Table III were calculated from eq 3 (mdyn Å^{-1}): III, 15.32; IV, 15.36; V, 15.42; VI, 15.52; VII, 15.58; VIII, 15.75; IX, 15.30; X, 15.18.

of activation for arene displacement in $BzCr(CO)_2(CSe)$ compared to that for the thiocarbonyl analogue may be due to a more facile distortion of the arene ring in the activated state.

Subsequent to establishing the rate expression for arene displacement, we examined the effect of substituents on the arene ring. Increasing the number of methyl groups on the ring generally decreases the rate of reaction (Table III). The reaction of (η-mesitylene)$Cr(CO)_2(CS)$ with $(MeO)_3P$ was too slow to measure accurately so that only the rate of reaction with the much more nucleophilic (n-BuO)$_3$P (Table IV) is given in Table III. No attempts were made to investigate reactions of arenes with more than three electron-donating substituents because these would be far too slow to monitor with any degree of accuracy. The results in Table III, including the anomalously fast rate of o-xylene displacement, are in line with the kinetic studies for the related arene displacement reactions of (η-arene)$M(CO)_3$ (M = Mo, W).[4,5,7] The decrease in reaction rate upon addition of electron-donating substituents on the arene ring may be attributed to the strengthening of the metal–arene bond resulting from increased electron density at the ring. Steric effects may also contribute to the observed trend since substituents on the ring may hinder nucleophilic attack at the metal center.

The presence of electron-withdrawing groups on the ring enhances ring lability (Table III) in accord with these groups decreasing the electron density available at the ring for bonding to the metal. The presence of both an electron-donating and an electron-withdrawing group on the ring gives an intermediate rate for the ring displacement reaction, while the presence of a second electron-withdrawing group in the para position has a cooperative effect in enhancing the rate of displacement.

In order to probe further the relationship between the rate of arene displacement and metal–arene bond strength, approximate CO force constants (k_{CO}) were calculated. These force constants are known to reflect quite well the electron density at the metal in such complexes and can be correlated with the electron-donating/electron-withdrawing properties of the substituents on the arene ring. Figure 2 is a plot of ln k_{obsd} for arene displacement for a series of (η-arene)$Cr(CO)_2(CS)$ complexes as a function of k_{CO}. The k_{CO} values were calculated from the positions (ν_1, ν_2) of the two ν(CO) peaks in the IR spectra according to the energy-factored force field approximation

$$k_{CO} = (\lambda_1 + \lambda_2)/2\mu \qquad (3)$$

where $\lambda_i = 1/(4\pi^2c^2\nu_i^2)$, c is the speed of light, and μ is the reduced mass of CO. Least-squares analysis of the data in Figure 2 yields a linear relationship between k_{CO} and ln k_{obsd} ($r = 0.98$), provided the points corresponding to $PhNMe_2$ and p-$(MeO)_2C_6H_4$ are ignored. The same discrepancy has been observed by Pidcock et al. in their studies of arene displacement from (η-arene)$M(CO)_3$ (M = Mo, W).[5] This may be proposed to result from distortion of the arene from planar geometry, as observed for the $PhNEt_2$ and 1,2,3-$(MeO)_3C_6H_3$ derivatives discussed above. Therefore, in the thiocarbonyl complexes examined in the present work, a similar distortion in conjunction with the labilizing effect of the CS ligand can explain the anomalously fast rate of arene displacement from (η-$PhNMe_2$)$Cr(CO)_2(CS)$ and [η-p-$(MeO)_2C_6H_4$]$Cr(CO)_2(CS)$.

Table V. Pseudo-First-Order Rate Constants for Arene Ring Displacement from (η^6-C_6H_6)$Cr(CO)_2(CSe)$ by $(MeO)_3P$ in the Presence of Varying Concentrations of Me_3PO at 42.6 °C[a]

$[(MeO)_3P]$, M	$[(Me)_3PO]$, M	10^5k_{obsd}, s^{-1}
0.510		0.61
0.510	0.171	2.60
0.510	0.343	10.2
	0.510	1.43[b]

[a] In methylcyclohexane solution. [b] Rate of decomposition.

The rate of ring displacement can also be affected if the CO groups are replaced by weaker π-acceptors or stronger σ-donors. The reactivity of (η-$PhCO_2Me$)$Cr(CO)_2(CS)$ can be compared with that of (η-$PhCO_2Me$)$Cr(CO)(CS)[(PhO)_3P]$. The monocarbonyl complex is quite unreactive over a period of 24 h at 87 °C, while the dicarbonyl one reacts at 60 °C in half the time. The lack of reactivity may be attributed to two factors. First, the weaker acceptor and stronger σ-donor properties of the tertiary phosphite relative to CO increase the electron density at the metal available for π-back-bonding to the arene, thus strengthening the metal–arene bond. Second, a steric effect may also contribute in that the phosphite may block access of the entering ligand to the metal. The decreased catalytic activity of (η-arene)$Cr(CO)_2(R_3P)$ (R = Ph, OPh) compared to that of (η-arene)$Cr(CO)_3$ has been attributed to the above factors.[31]

Table IV shows the effect observed on varying the steric and nucleophilic character of the attacking ligand. The reaction rate increases with increasing nucleophilicity for ligands of comparable size (similar cone angles) and decreases with increasing ligand size. This trend has also been reported in the study of arene displacement from (η-arene)$Mo(CO)_3$ complexes.[5a] Thus, the rate of arene displacement by tertiary phosphite decreases in the order (n-BuO)$_3$P > $(EtO)_3P$ > $(MeO)_3P$ > $(PhO)_3P$ > $(C_6H_{11}O)_3P$ [no reaction observed for $(C_6H_{11}O)_3P$].

Catalytic enhancement of ring displacement from $BzCr(CO)_2(CSe)$ occurs in the presence of Me_3PO (Table V). However, decomposition is observed in the absence of tertiary phosphite. The strong labilizing effect of O-donor bases has been noted before.[32] Trialkylphosphine oxides have been used in various systems to catalyze CO substitution[33] and have been reported to enhance ring lability in (η-arene)$Mo(CO)_3$.[5a] In the present work, the catalytic enhancement can be postulated to involve nucleophilic attack on the Cr by the O atom of Me_3PO, possibly forming (η^4-Bz)$Cr(CO)_2(CSe)(OPMe_3)$.

A kinetic study of arene displacement (in (η-arene)$Cr(CO)_2(CSe)$ was also performed in dichloroethane ($k_2 = 3.56 \times 10^{-5}$ M^{-1} s^{-1} at 53 °C). This reaction rate is slightly higher than that observed in methylcyclohexane ($k_2 = 2.72 \times 10^{-5}$ M^{-1} s^{-1} at 53 °C), suggesting that the activated complex may be slightly polar and possibly solvent-stabilized.

A striking feature of the arene displacement reactions of (η-arene)$Cr(CO)_2(CX)$ (X = S, Se) complexes is the predominant formation of the *mer* I product rather than the *fac* isomer, as is the case for cht displacement from $(cht)Cr(CO)_3$.[26] In the temperature range at which the reactivity of the arene chalcocarbonyl

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complexes with $(MeO)_3P$ has been studied, the *fac* and *mer* I isomers of $Cr(CO)_2(CS)[(MeO)_3P]_3$ are in equilibrium in favor of the *mer* I isomer ($K_{eq} = 5$).[34] Furthermore, comparison of the rates measured for *fac* → *mer* I isomerization with the results from the kinetic studies reveals that the isomerization of *fac*-$Cr(CO)_2(CX)[(MeO)_3P]_3$ is at least an order of magnitude faster than the rate of arene displacement at all the temperatures investigated.[35] It is therefore likely that *fac*-$Cr(CO)_2(CX)[(MeO)_3P]_3$ is formed first in the reactions of (η-arene)$Cr(CO)_2(CX)$ with $(MeO)_3P$ and then isomerizes to the *mer* I isomer. However, the possibility that isomerization also takes place in the intermediate steps of the reaction prior to formation of the final product cannot be ruled out. Some evidence against this possibility is obtained by monitoring the ^{31}P NMR spectra of the reaction mixture containing $BzCr(CO)_2(CSe)$ and $(PhO)_3P$. In the preliminary stages of the reaction *fac*-$Cr(CO)_2(CSe)[(PhO)_3P]_3$ was detected in higher concentration than the *mer* I isomer while the final product was predominantly the *mer* I isomer, suggesting that rearrangement to the thermodynamically more stable *mer* I isomer occurs subsequent to the formation of the more kinetically favored *fac* product. The initial detection of the *fac* isomer in the case of $(PhO)_3P$ but not $(MeO)_3P$ may be the result of a slower rate of isomerization in the former case due to steric effects imposed by the bulky phenoxy groups.

The reactions of the tridentate ligands triphos-U and triphos $[(Ph_2PCH_2CH_2)_2PPh]$ with (η-arene)$Cr(CO)_2(CX)$ afford *fac*-$Cr(CO)_2(CX)$(triphos-U) and *fac*-$Cr(CO)_2(CX)$(triphos), respectively, in quantitative yield giving added support to the hypothesis that the *fac* product is formed first in the reactions with the monodentate tertiary phosphite ligands.

It is interesting to note that, in earlier studies of arene displacement from (η-arene)$M(CO)_3$ by monodentate ligands (L), kinetic investigations were not undertaken for the chromium complexes because these reactions yielded products other than the expected *fac*-$Cr(CO)_3L_3$.[4] We have identified the products of arene displacement from (η-arene)$Cr(CO)_3$ [(η-arene) = monoarene] by $(MeO)_3P$ as mixtures of *fac*- and *mer*-$Cr(CO)_3[(MeO)_3P]_3$, with the *mer* isomer predominant. However, we have been unable to obtain kinetic data for such reactions due to the slow reactivity of the (η-arene)$Cr(CO)_3$ complexes. Even for (η-$PhNMe_2$)$Cr(CO)_3$ (the most reactive tricarbonyl complex studied), there was no spectroscopic evidence (UV-vis, FT-IR) of reaction with $(MeO)_3P$ after heating under rigorous conditions [83.3 °C, $[(MeO)_3P]$:[complex] = 3000:1] for 48 h. This observation allows us to estimate that the upper limit for k_{obsd} of this reaction is 10^{-6} s^{-1}. This rate is slower than that rate we have measured for *fac* → *mer* isomerization of $Cr(CO)_3[(MeO)_3P]_3$ by 2 orders of magnitude.[35] Therefore, just as for the thio- and selenocarbonyl analogues, the formation of predominantly *mer*-$Cr(CO)_3[(MeO)_3P]_3$ may be attributed to isomerization of the expected *fac* isomer at a much faster rate than its rate of formation. On the other hand, the rates reported for the reactions of (cht)$Cr(CO)_3$[26] and (η-naphthalene)$Cr(CO)_3$[15] with $(MeO)_3P$, in both cases yielding *fac*-$Cr(CO)_3[(MeO)_3P]_3$, are faster than the rate of isomerization of *fac*-$Cr(CO)_3[(MeO)_3P]_3$, thus accounting for the formation of the *fac* isomer.

Conclusions

The kinetic data presented here demonstrate that the effect of the CS and CSe ligands on the reactivity of the arene complexes is quite dramatic. Even placing the most electron-withdrawing substituent on the arene ring in a tricarbonyl complex does not result in as great a labilizing effect on the metal–arene bond as does substitution of one CO group by CS. The effect is even more pronounced for the CSe ligand. The kinetic data provide a good quantitative measure of the increased reactivity of (η-arene)$Cr(CO)_2(CSe)$ complexes compared to that of their CS counterparts, the enhancement in ring lability being close to 5-fold at 50 °C.

The utility of (η-arene)$Cr(CO)_3$ complexes as catalysts for the hydrogenation of dienes is well-known. The catalytically active species has been shown to result from the partial or total loss of the arene, and the induction period of the catalytic cycle can be decreased by introducing substituents on the ring that increase arene lability.[36] On the basis of the results of our study, it could therefore reasonably be anticipated that (η-arene)$Cr(CO)_2(CX)$ (X = S, Se) complexes would be superior catalysts to their tricarbonyl analogues in such processes. However, investigation of the thiocarbonyl complexes as catalysts has revealed that they completely lack activity.[37] A possible explanation may be that the *fac*-$Cr(CO)_2(CX)L_3$ products obtained from the reactions of the arene thio- and selenocarbonyl derivatives with tertiary phosphite ligands (L) exhibit much faster intramolecular isomerization than the corresponding *fac*-$Cr(CO)_3L_3$ complexes. Such rapid rearrangements would not afford the necessary *fac* configuration for the intermediates believed to be responsible for the catalytic hydrogenation activity.[36] In addition, the crystal structure of $Cr(CO)_2(CS)[(MeO)_3P]_3$ evidences a large amount of electron density on the thiocarbonyl ligand—the C–S bond distance approximating that found for a bridging CS group.[24] Nucleophilic attack by the S atom of the CS ligand has been reported for complexes with long C–S bonds.[38] Since hydrogenation studies are performed in the presence of donor solvents, $Cr(CO)_2(CS)(solvent)_3$ species are probably formed. It is likely that the electron density on the CS ligand in such species is sufficient to cause it to act as a nucleophile, leading to side reactions for autodecomposition.

Finally, although there have been no catalytic studies yet performed for the selenocarbonyl complexes, their catalytic activity will amost certainly be the same as that of the thiocarbonyls because of their closely similar chemical reactivities.

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