Kinetics and Mechanism of Substitution Reactions of Arene Molybdenum Tricarbonyl

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Abstract: The rates of reaction of (arene)$Mo(CO)_3$ with different reagents to yield $Mo(CO)_3L_3$ are reported, where arene = toluene, *p*-xylene, and mesitylene, and L = PCl_3, $PCl_2(C_6H_5)$, and $P(n\text{-}C_4H_9)_3$. The rates of reaction are first order in both the metal carbonyl and the ligand concentrations, and the rates are not greatly affected by changes in solvent. For the same reagent the rates decrease with changes in arene in the order toluene $\simeq$ *p*-xylene > mesitylene, and for the same metal carbonyl the rates decrease with changes in reagent in the order $P(n\text{-}C_4H_9)_3 \gg PCl_2(C_6H_5) > PCl_3$. These results are discussed in terms of a possible mechanism of reaction.

The recent review[1] of insertion reactions (or ligand migration reactions[2]) by Heck provides an excellent summary of the importance of such reactions and of the interesting problems involved. Although considerable work has been done on the kinetics and mechanism of reactions of metal carbonyls and their derivatives, only a very limited amount of research of this type has been reported on the reactions of (arene)$M(CO)_3$, where M = Cr, Mo, and W.

Pajaro, Calderazzo, and Ercoli[3] observed no exchange of ^{14}CO with $(CH_3C_6H_5)Cr(CO)_3$ at 140° over a period of several hours. However, under these conditions Strohmeier and his co-workers[4] find that ^{14}C-arenes exchange with (arene)$M(CO)_3$. The rates of exchange follow a two-term rate law: one term is second order in the metal carbonyl and zero order in arene, and the other term is first order in both. On this basis it was suggested that exchange takes place by means of a bimolecular displacement mechanism.

Abel, Bennett, and Wilkinson[5] have reported the syntheses of compounds of the type *cis*-$M(CO)_3L_3$ by the reaction of (arene)$M(CO)_3$ with different ligands. This paper reports the results of a kinetic study of some of these substitution reactions.

Experimental Section

Compounds and Solvents. The hexacarbonyls $Mo(CO)_6$ and $W(CO)_6$ were obtained from the Climax Molybdenum Co., and $Cr(CO)_6$ was prepared by the method described in the literature.[6] The method of Nicholls and Whiting[7] was followed to prepare the (arene)$M(CO)_3$ compounds. The identity and purity of these compounds were confirmed by their carbon and hydrogen analyses and by a comparison of their infrared spectra with those reported in the literature (Table I).

The reaction products, *cis*-$Mo(CO)_3(PCl_3)_3$, *cis*-$Mo(CO)_3(PCl_2C_6H_5)_3$, and *cis*-$Mo(CO)_3[P(n\text{-}C_4H_9)_3]_3$, were prepared by the reaction of (mesitylene)$Mo(CO)_3$ with the different ligands. Carbon and hydrogen analyses were performed to make certain of the identity of all samples. In addition the infrared spectra (Table I) checked well with those reported for the compounds and also with the infinite time spectrum of a reaction mixture in a kinetic run for a particular compound.

Table I. CO Stretching Frequencies (in *n*-Heptane)

Compound	Stretching frequency, cm^{-1}	
(mesitylene)$Mo(CO)_3$	1975	1903
(*p*-xylene)$Mo(CO)_3$	1979	1907
(toluene)$Mo(CO)_3$	1984	1912
cis-$Mo(CO)_3(PCl_3)_3$	2045	1995
cis-$Mo(CO)_3[PCl_2(C_6H_5)]_3$	2015	1955
cis-$Mo(CO)_3[P(n\text{-}C_4H_9)_3]_3$	1930	1835

The reagents PCl_3 (British Drug Houses Ltd.), $PCl_2C_6H_5$ (Eastman Kodak Co.), and $P(n\text{-}C_4H_9)_3$ (Fluka) were used as obtained without further purification. The solvent $CHCl_3$ (Analar, British Drug Houses Ltd.) was also used as obtained. The *n*-heptane was dried over sodium wire and then fractionally distilled. The *s*-tetrachloroethane was shaken with concentrated H_2SO_4, washed with water, dried over $CaCl_2$, and distilled.

Kinetic Studies. The rates of reaction were followed by monitoring the disappeareance of the lowest frequency carbonyl absorption of (arene)$M(CO)_3$ as it reacts with the various reagents. A Perkin-Elmer spectrophotometer Model 621 and 1-mm infrared cells were used. An aluminum foil-wrapped flask containing the solution of metal carbonyl and one containing a solution of the reagent, both under nitrogen, were brought to constant (±0.1°) temperature in a thermostated bath. The ligand solution was then poured into the foil-wrapped flask and mixed well. Samples of the reaction mixture were removed at various times with an eye dropper, under nitrogen, and placed in an infrared cell, and the spectrum was quickly measured. For the reactions with $P(n\text{-}C_4H_9)_3$, which were fast, the reaction mixture was kept in a thermostated Perkin-Elmer 1-mm infrared cell and the change in transmittance with time was recorded.

All the kinetic studies were carried out under pseudo-first-order conditions, using at least a tenfold excess of reagent. All reactions proceed to completion, and the infinite time spectra were in good agreement with those of the known products prepared independently. The data obtained gave good linear plots of ln $(A - A_\infty)$ *vs.* time, and the k_{obsd} values were calculated in the usual way from the slopes of these lines. In these calculations A is the absorbance at time t ($A = \log 1/T$, where T is the transmittance) and A_∞ is the absorbance at $t = \infty$, as estimated for every spectra from the base line because the observed bands disappeared completely. The second-order rate constants were calculated by dividing k_{obsd} by the concentration of the ligand reagents. A 10% or better precision is obtained for the values of the rate constants. It was also determined that in the solvents used the variations of the absorption intensities with changes in concentration of (arene)$Mo(CO)_3$ follow the Beer–Lambert law.

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Results

The experimentally observed pseudo-first-order rate constants at various reagent concentrations and the estimated second-order rate constants for reaction 1 in

$$(\text{arene})\text{Mo(CO)}_3 + 3\text{L} \longrightarrow cis\text{-Mo(CO)}_3\text{L}_3 + \text{arene} \quad (1)$$

n-heptane solution are given in Tables II and III. The activation parameters are given in Table IV.

Table II. Rates of Reaction of (arene)$Mo(CO)_3$ with Different Ligands in *n*-Heptane Solution at 25°

Ligand	Ligand concn, mole/l.	$10^5 k_{obsd}$, sec^{-1}	$10^4 k$, M^{-1} sec^{-1}
	0.0013 *M* (mesitylene)$Mo(CO)_3$		
PCl_3	0.090	1.40	1.55
	0.163	2.22	1.36
	0.291	4.15	1.43
	0.355	5.10	1.44
	0.469	6.84	1.46
	0.575	8.24	1.43
$PCl_2(C_6H_5)$	0.072	2.09	2.90
	0.098	2.96	3.02
	0.156	4.48	2.87
	0.218	6.06	2.78
	0.278	7.75	2.79
$P(n\text{-}C_4H_9)_3$	0.031	20.0	64.5
	0.057	40.3	70.7
	0.080	54.0	67.5
	0.111	74.5	67.1
	0.210	135	64.3
	0.0015 *M* (*p*-xylene)$Mo(CO)_3$		
PCl_3	0.041	1.98	4.83
	0.092	3.86	4.20
	0.167	6.93	4.15
	0.329	13.7	4.16
	0.331	14.1	4.26
	0.528	22.1	4.19
$PCl_2(C_6H_5)$	0.034	2.60	7.65
	0.075	6.43	8.57
	0.134	11.3	8.43
	0.150	12.1	8.07
	0.242	20.1	8.31
	0.001 *M* (*p*-xylene)$Mo(CO)_3$		
$P(n\text{-}C_4H_9)_3$	0.011	54.5	495
	0.014	70.8	506
	0.016	82.9	518
	0.020	96.0	480
	0.0015 *M* (toluene)$Mo(CO)_3$		
PCl_3	0.070	2.20	3.14
	0.150	4.86	3.24
	0.210	7.64	3.64
	0.364	11.9	3.27
	0.401	13.1	3.27
	0.570	19.6	3.44
$PCl_2(C_6H_5)$	0.032	2.40	7.50
	0.066	5.59	8.47
	0.095	8.12	8.54
	0.151	12.8	8.48
	0.245	20.4	8.33
	0.001 *M* (toluene)$Mo(CO)_3$		
$P(n\text{-}C_4H_9)_3$	0.009	44.9	499
	0.011	59.7	543
	0.015	76.0	507
	0.021	109	519

Similar data for the reaction of (mesitylene)$Mo(CO)_3$ with PCl_3 in $CHCl_3$ and in *s*-$C_2H_2Cl_4$ solutions are collected in Table V. A typical plot of k_{obsd} *vs.* ligand concentration is shown in Figure 1.

Table III. Rates of Reaction of (arene)$Mo(CO)_3$ with PCl_3 in *n*-Heptane Solution at 40°

(arene)$Mo(CO)_3$	Concn, *M*	Ligand concn, mole/l.	k_{obsd}, sec^{-1}	$10^4 k$, M^{-1} sec^{-1}
(mesitylene)$Mo(CO)_3$	0.0013	0.051	3.0	5.88
	0.0010	0.150	8.0	5.33
	0.0013	0.251	13.6	5.42
	0.0007	0.285	16.2	5.68
	0.0013	0.374	22.1	5.91
(*p*-xylene)$Mo(CO)_3$	0.0015	0.029	4.1	14.1
	0.0010	0.131	20.4	15.6
	0.0015	0.264	37.5	14.2
	0.0007	0.270	38.9	14.4
	0.0015	0.465	69.2	14.9
(toluene)$Mo(CO)_3$	0.0015	0.025	3.2	12.8
	0.0015	0.152	18.0	11.8
	0.0008	0.160	20.0	12.5
	0.0010	0.285	36.9	12.9
	0.0015	0.379	46.7	12.3

Table IV. Activation Parameters for the Reaction (arene)$Mo(CO)_3$ + $3PCl_3 \rightarrow cis$-$Mo(CO)_3(PCl_3)_3$ in *n*-Heptane

(arene)$Mo(CO)_3$	ΔH^*, kcal/mole	ΔS^*, eu
(mesitylene)$Mo(CO)_3$	17 ± 2	−20 ± 5
(*p*-xylene)$Mo(CO)_3$	15 ± 2	−24 ± 5
(toluene)$Mo(CO)_3$	16 ± 2	−21 ± 5

Table V. Rates of Reaction of (mesitylene)$Mo(CO)_3$ with PCl_3 in Solution of Chloroform and *s*-Tetrachloroethane at 25° and 0.0013 *M* Carbonyl[a]

Solvent	Ligand concn, mole/l.	$10^5 k_{obsd}$, sec^{-1}	$10^4 k$, M^{-1} sec^{-1}
Chloroform	0.065	2.08	3.20
	0.134	4.44	3.31
	0.228	7.80	3.42
	0.341	10.4	3.05
	0.437	13.7	3.13
	0.578	17.7	3.06
s-Tetrachloroethane	0.070	2.02	2.89
	0.139	3.27	2.35
	0.267	6.36	2.38
	0.396	10.0	2.52
	0.556	15.5	2.79

[a] The dielectric constants of *n*-heptane, chloroform, and *s*-tetrachloroethane at 25° are 1.92, 4.71, and 8.00, respectively.

Attempt were made to use other solvents, but with no success. In the solvents benzene, tetrahydrofuran, toluene, and nitrobenzene, the infrared spectra of (arene)$Mo(CO)_3$ in the C–O stretching region does not show two bands of equal intensity, as is expected for C_{3v} symmetry. In CH_3NO_2 solution reaction takes place with decomposition, and in acetone the metal carbonyl itself decomposes even under nitrogen. Reactions were also attempted with the ligands pyridine, β-picoline, γ-picoline, triphenylphosphine, triphenylarsine, thiophene, tetrahydrothiopene, triphenyl phosphite, and chlorodiphenylphosphine. However in no case were the results obtained amenable to quantitative treatment, because either the product that formed was insoluble or reactions other than reaction 1 take place.

At the condition of these experiments, it was also not possible to investigate the kinetics of reaction 1 for the Cr and the W systems. In the case of (arene)$Cr(CO)_3$, the changes in the infrared spectra of reaction mixtures

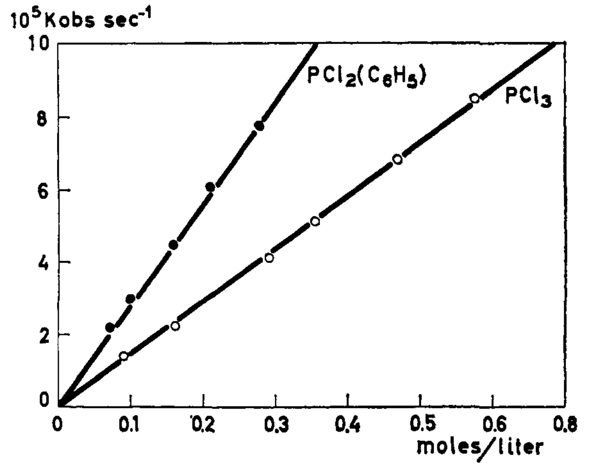

Figure 1. The rate of reaction of (mesitylene)$Mo(CO)_3$ with PCl_3 and $PCl_2C_6H_5$ as a function of their concentrations in *n*-heptane at 25°.

indicate that species other than the desired *cis*-$Cr(CO)_3L_3$ are also formed. For (arene)$W(CO)_3$, the reaction in *n*-heptane solution at 25° is too slow to be examined and at much higher temperatures decomposition takes place which complicates any attempt to make a quantitative study of reaction 1.

Discussion

An examination of the kinetic data in Table II, III, and V reveals the following experimental facts: (1) the rates of reaction 1 are second order, being first order in both the concentrations of (arene)$Mo(CO)_3$ and of the ligands; (2) the rates of reaction decrease for changes in arene in the order toluene $\simeq$ *p*-xylene $>>$ mesitylene; (3) the rates of reaction decrease for changes in reagent in the order $P(n\text{-}C_4H_9)_3 >> PCl_2C_6H_5 > PCl_3$; and (4) the rates of reaction are about the same in the solvents *n*-heptane, chloroform, and *s*-tetrachloroethane.

That the rates of reaction are second order is consistent with the observations on the rates of arene exchange in these systems.[4] Also, that the mesitylene compound is the slowest to react is in accord with the arene exchange studies. The striking difference between the substitution reactions reported here and the arene exchange reactions is that exchange is extremely slow and it had to be studied at temperatures of 100° and higher. This difference is readily understood, since the rates of reaction depend on the concentration and the nature of the entering ligand. Thus, arene compounds are poor reagents toward the substrate (arene)$Mo(CO)_3$, whereas phosphines are, in comparison with arenes, extremely good reagents.

That $P(n\text{-}C_4H_9)_3$ is a much better nucleophile than $PCl_2C_6H_5$, which is better than PCl_3, for reaction 1 is in agreement with the nucleophilic strengths of different reagents toward $\pi\text{-}C_5H_5Rh(CO)_2$.[8] This supports the view that the more polarizable phosphorus ligand atom is the better nucleophile toward substrates of this type. The metals in such systems are presumably of the class b[9] or soft[10] type and prefer ligands that are highly polarizable.

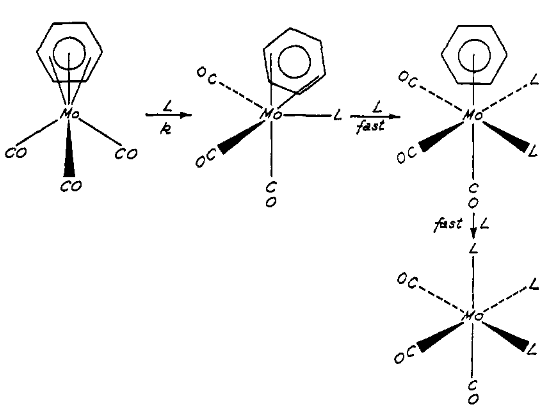

Figure 2. Mechanism proposed for the reaction of (arene)$Mo(CO)_3$ with L to form *cis*-$Mo(CO)_3L_3$.

Since there is no arene and no CO exchange with (arene)$Mo(CO)_3$ at these conditions and since the rate of reaction is second order it appears that the rate-determining step involves a bimolecular displacement reaction. This can be followed by further rapid reaction to give the final product as shown by

$$\begin{tikzcd}
\text{(arene)Mo(CO)}_3 + \text{L} \arrow[r, "k"] & \text{(arene)Mo(CO)}_3\text{L} \arrow[r, "\text{fast}"] \arrow[d, "\text{fast}"', "\text{L}"] & \text{Mo(CO)}_3\text{L} \arrow[d, "\text{fast}"', "\text{L}"] \\
 & \text{(arene)Mo(CO)}_3\text{L}_2 \arrow[d, "\text{fast}"', "\text{L}"] & \text{Mo(CO)}_3\text{L}_2 \arrow[dl, "\text{fast}"', "\text{L}"] \\
 & cis\text{-Mo(CO)}_3\text{L}_3 &
\end{tikzcd} \quad (2)$$

Graham and Angelici[11] have recently reported what appears to be a bimolecular displacement reaction for $Mo(CO)_4$bipy, and King[12] has isolated salts of the seven-coordinated complex ion $[Mo(CO)_4I_3]^-$. These observations support the formation of (arene)$Mo(CO)_3L$ as the rate-determining step in reaction scheme 2. What happens beyond this point is not known, but either of two paths seem plausible. One of these results in the immediate loss of arene to form the very reactive four-coordinated (or six-coordinated if solvated) $Mo(CO)_3L$ which readily takes on two additional ligands to form $Mo(CO)_3L_3$. An alternative path, also shown by (2), involves the rapid addition of two more ligands to the reactive species (arene)$Mo(CO)_3L$.

This path would normally not seem as plausible as the one with the immediate loss of arene. However, Stolz, Haas, and Sheline[13] have reported infrared evidence for the formation of (arene)$W(CO)_5$ at low temperature which is analogous to the proposed (arene)$Mo(CO)_3L_2$. On this basis it is interesting to speculate that the mechanism for the reaction of (arene)$Mo(CO)_3$ with L to form *cis*-$Mo(CO)_3L_3$ is that shown by Figure 2. Because of the nature of the arene–Mo bonding, it is possible that this can change in response to the approach of another ligand to the metal

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atom. This is shown by the formalism of three bonds going to two bonds with the addition of a pair of electrons by the entering nucleophile, to one bond with the addition of a second ligand, and finally arene leaves with the addition of the third ligand and the third pair of electrons. Such a suggestion is in keeping with the somewhat general observation[8,14] that whereas simple metal carbonyls react by first-order processes, the π complexes of metal carbonyls react by second-order mechanisms.

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Carbon-13 Magnetic Resonance of Diene–Iron Tricarbonyl Complexes[1]

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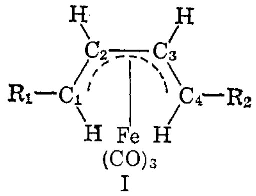
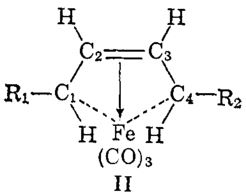
Abstract: The ^{13}C nmr spectra of butadiene–iron tricarbonyl and methyl octadecadienoate–iron tricarbonyl were obtained to elucidate the structure of these complexes. The ^{13}C–H coupling constants indicate that all of the C–H bonds in the butadiene complex are essentially sp^2 hybrids. This observation, the ^{13}C and proton chemical shifts, the H–H coupling constants, and other data are consistent with a structure in which the bonding of Fe at $C_{2,3}$ in the diene complexes is very similar to that in ferrocene, but in which the terminal CH_2 and CHR groups are rotated about the C_1–C_2 and C_3–C_4 bonds of the ligand. This steric distortion of the ligand from planarity makes the bonding of the Fe at $C_{1,4}$ differ somewhat from that at $C_{2,3}$, but both instances involve π orbitals on the carbons.

Recent interest in the structure of diene–iron tricarbonyl complexes has prompted us to obtain and analyze the ^{13}C nmr spectra of butadiene–iron tricarbonyl and methyl octadecadienoate–iron tricarbonyl. It has been uncertain whether these complexes involve delocalization of the π electrons in the diene system (structure I) or 1,4 addition of iron to the diene (structure II). We define structure I to be a butadiene system containing only sp^2-hybridized carbon atoms which are π bonded to the iron, and II to be a structure which has some localized bonding between iron and carbon atoms 1 and 4 with the bonding orbitals of the latter being sp^3 hybrids.



I



II

Much chemical and other evidence indicates that the structure represented by I is the most appropriate.[3] However, the nmr spectra of protons in such complexes exhibit features which can be interpreted as supporting or being consistent with structure II. Thus, the resonance of the central hydrogen atoms in butadiene–iron tricarbonyl appears in the normal region for olefinic protons, whereas those of the terminal atoms exhibit large upfield shifts into the region generally associated with aliphatic protons.[4] But it has been pointed out[5] that this result has little bearing on the bonding in methyl octadecadienoate–iron tricarbonyl[6] because the upfield shifts could result from magnetic anisotropy effects of the CO groups, or of the Fe to diene bonds, rather than from any aliphatic character of the terminal protons.

Recent interpretations of the proton spectra of the iron tricarbonyl complexes of 1,1′-bicycloalkenyls[7] favor structure II. On the other hand, the infrared and ultraviolet spectra of various conjugated diene–iron tricarbonyl complexes have been considered[8] to indicate no loss of conjugation, in support of structure I. Also, electron absorption studies of various metal complexes of cyclopentadienone derivatives[9,10] show that the π-electron system of the ligand is not sufficiently perturbed to support a structure involving

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