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ARENE TRANSITION METAL CHEMISTRY

III *. ARENE EXCHANGE PHENOMENA **

E.L. MUETTERTIES ★, JOHN R. BLEEKE, and ALLEN C. SIEVERT
Department of Chemistry, University of California, Berkeley, California 94720 (U.S.A.)
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Summary

Arene exchange between free arene and an arene—transition metal complex is reviewed with respect to structure, thermodynamics, kinetics and reaction mechanism. Catalysis of such arene exchange is also examined. Experimental results are presented for arene exchange between arene and the arene—metal complexes: η^6-arene-1,5-cyclooctadieneruthenium, the cationic η^6-arene-1,5-cyclooctadieneiridium and η^6-arenetricarbonylmolybdenum. Mechanistic features of these exchange reactions are discussed.

Introduction

An important class of reactions in the aromatic hydrocarbon chemistry of transition metals is the exchange of the arene molecule between free and bound states. A thermodynamic, kinetic and mechanistic definition of this type of reaction is important to the design of new arene—metal syntheses and to an understanding of arene reactions catalyzed by transition metals [2,3]. These issues are important in organometallic [3] and surface chemistry [4]. We review in this introductory section the essential structural, thermodynamic and kinetic features of the arene exchange reactions.

Aromatic hydrocarbon molecules form three idealized classes *** of isolable complexes with transition metals: (a) the most common class that has a *hexahapto* interaction (I) with a coplanar or nearly coplanar arene C_6 skeleton normal or nearly normal to the C_6 centroid-metal atom vector †, (b) an unusual class,

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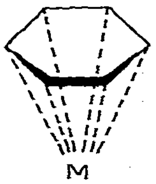
* For Part II see ref. 1.

** Dedicated to Prof. Eugene G. Rochow on the occasion of his 70th birthday.

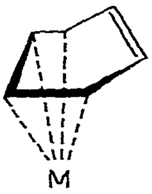
*** These are the three classes structurally defined to date. Additional classes may be established in future studies.

† Reviews of crystallographically defined η^6-arene—metal complexes may be found in articles by Silverthorn [5] and by Gastinger and Klabunde [6].

presently established by X-ray crystallography for at least seven complexes [7—13], that has a *tetrahapto* interaction (II) with diene-like bonding and with



(I)



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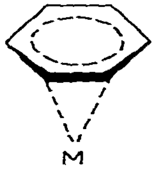
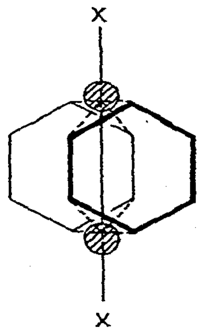


(III)

two aromatic carbon atoms bent out of the plane of the other four carbon atoms and bent away from the metal atom, and (c) a class, crystallographically established only for d^{10} metal complexes [5,14,15] that has a *dihapto* interaction (III), with a nearly coplanar set of aromatic carbon atoms of which only two are within bonding distance of the metal atom. Another type of structure, to date limited to palladium chemistry, has two metal atoms placed between two benzene rings to give a centrosymmetric complex (IV) in which the indivi-



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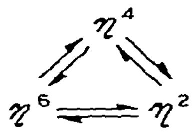

(V)

dual metal—arene interactions may be described as a special case of η^2-arene binding [16] and of class III structure. We exclude from discussion here the Dewar benzene—metal complexes. Complexes exhibiting arene—metal bonding intermediate between classes I and II and between classes II and III probably will be found. A shape analysis of crystallographically defined arene—metal structures is in progress to discern whether available structural data begin to geometrically limn the reaction cycle V and whether new idealized structural classes may be implicated.

Thermodynamic data are not available for a detailed comparison of metal—arene bond energies in the three structural classes although qualitative molecular orbital theory suggests that the bond energies would be I > II > III with other factors being approximately equal [17]. Bond energies within class I appear to have a large range varying from 79.8 kcal/mol in η^6-1,3,5-C_6H_3-$(CH_3)_3W(CO)_3$ [19] to an apparently low value in η^6-$C_6H_5CH_3Ni(C_6F_5)_2$ [23,24] which is partially dissociated to "$Ni(C_6F_5)_2$" and toluene in chloroform solution at 25°C. Selected bond enthalpy data for the η^6-arenetricarbonylchromium series are presented in Table 1. Available data show that bond

TABLE 1

ARENE—CHROMIUM BOND ENTHALPIES IN η^6-ARENETRICARBONYLCHROMIUM [19]

Arene ligand	D (Arene—Cr) (kcal/mol)
$C_6(CH_3)_6$	55 ± 4
1,3,5-$C_6(CH_3)_3H_3$	45 ± 3
C_6H_6	42.5 ± 3
$C_6H_5CH_3$	41.5 ± 3
C_6H_5Cl	38 ± 5

energies for class III complexes are much smaller than those for class I. The formation constants for d^{10} silver(I)—arene complexes in water/methanol are only in the range of 0.6—1.7 $(mol/l)^{-1}$ at 25°C which, though not directly comparable with the bond enthalpy data cited above, suggest a low silver– arene bond energy (see Table 2). (By comparison the analogous ethylenesilver(I) formation constant is 85 $(mol/l)^{-1}$ at 25°C [21d]). It should be noted that these formation constants rise to 10^4 to 10^8 in anhydrous hydrogen fluoride (see Table 2). No thermodynamic data exist for η^4-arene—metal complexes. However, an interpretation of the NMR line shape changes [22] in the fluxional η^6-$C_6(CH_3)_6$Ru-η^4-$C_6(CH_3)_6$ is that the activation energy ($\Delta H^{\neq}$) for generation of the $[\eta^4\text{-}C_6(CH_3)_6]_2$Ru state is 16.1 kcal/mol which is a maximum value for the difference in energy between η^6 and η^4 states in this specific system.

Within a specific set of η^6-arene—metal complexes, the stability or displacement series for the arene ligand typically follows the order $C_6(CH_3)_6 > C_6(CH_3)_3H_3 > C_6(CH_3)_2H_4 > C_6H_5CH_3 > C_6H_6 > C_6H_5F$ *. Stereochemistry of alkyl substituents appears to have a small effect on the stability of η^6-arene—metal complexes **. No data are available for η^4-arene complexes although in η^6-arene-η^4-areneruthenium(0) complexes it appears that the more basic arene will preferentially residue at the η^6 site ***. Stereochemistry of alkyl substituents should substantially affect the stability of η^4-arene—metal complexes, e.g., *o*-xylene should form a more stable η^4 complex than *m*- or *p*-xylene. In the unknown bis(*o*-xylene) and bis(1,2,3,4-tetramethylbenzene) derivatives of ruthenium(0), the η^4 ligand should have the methyl substituents at the noncomplexed carbon sites ****. If η^2-arene-metal complexes are truly isoelectronic analogs of η^2-olefin—metal complexes, an η^2-binding of 1,2,3,4-tetramethylbenzene should be localized at the aromatic carbon sites bearing the hydrogen substituents; however, the avilable crystallographic data are insufficient to address the issue for discrete or monomolecular η^2-arene—metal complexes. However, it is notable that the formation constants for η^2-arene—Ag^+ complexes are generally lower for arenes that do not have at least two adjacent aromatic carbon atoms with hydrogen substituents than those that do. These stability

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* A number of studies have pointed to a consistent stability series [5,6,17].

** As shown in this study, η^6-*m*-xyleneMo$(CO)_3$ is more stable than the *o*- and *p*-xelene complexes, and η^6-mesityleneMo$(CO)_3$ is more stable than η^6-1,2,3-trimethylbenzeneMo$(CO)_3$ (see Table 7).

*** In $C_6H_6RuC_6(C_6H_5)_6$ the more basic benzene ligand resides at the η^6-arene—metal position [12].

**** Note, however, that in η^4-1,2-$(CF_3)_2$-3,4,5,6-$(CH_3)_4C_6Fe(CO)_3$ the stereochemistry of the arene binding is unsymmetric and the "olefinic" sites have a CF_3 and a CH_3 substituent [9].

TABLE 2

FORMATION CONSTANTS OF Arene-Ag$^+$ COMPLEXES

Arene	K_1 [a]	K'_1 [b]	IP [c] (eV)
C_6H_6	1.10	$10^{4.90}$	9.24
$C_6H_5CH_3$	1.19	$10^{5.15}$	8.82
1,2-$C_6H_4(CH_3)_2$	1.43	—	8.56
1,3-$C_6H_4(CH_3)_2$	1.35	$10^{5.07}$	8.58
1,4-$C_6H_4(CH_3)_2$	1.14	—	8.44
1,3,5-$C_6H_3(CH_3)_3$	0.80	$10^{4.47}$	8.4
1,2,4-$C_6H_3(CH_3)_3$	1.30	—	8.27
1,2,4,5-$C_6H_2(CH_3)_4$	0.88	—	8.03
1,2,3,5-$C_6H_2(CH_3)_4$	0.88	—	8.47
1,2,3,4-$C_6H_2(CH_3)_4$	1.69	—	—
$C_6(CH_3)_6$	0.63	$10^{4.94}$	7.85
Anthracene	1.35 [d]	10^{7-8}	7.55

[a] Formation constants for arene—silver complexes ([Ag(arene)$^+$]/[Ag$^+$][arene]) at 25°C, $\mu = 0.5$ in 1/1 CH_3OH/H_2O [21a]. [b] Formation constants for arene—silver complexes ([Ag(arene)$^+$]/[Ag$^+$][arene]) at 0°C in ahydrous hydrogen fluoride [21b]. [c] Ionization potentials [25]. [a] Ref. 21c.

trends with alkyl substitution and with the stereochemistry of the alkyl substitution are apparent by inspection of Table 2 and are in sharp contrast to stability trends in η^6-arene—metal complexes (see Table 1 and the discussion above). Note also that there is not a simple correlation between formation constants and arene ionization potentials.

Arene exchange between free arene and an η^6-arene—transition metal complex generally requires very high temperatures if the solvent is either an aromatic hydrocarbon or a non-coordinating solvent. This feature of η^6-arene—transition metal chemistry is documented in Table 3. There are exceptions among which the most notable is η^6-$C_6H_5CH_3Ni(C_6F_5)_2$ which is partially dissociated in chloroform solution [23]. No datum relevant to η^4-arene—metal complexes in arene exchange is available. Arene exchange in the d^{10} η^2-arene—metal complexes is typically a facile process [14b] which reflects the fact that the η^2-arene—metal bond energies are low and that effectively the arene ligand in η^2 complexes only occupies a single coordination site. By contrast, the arene ligand in η^6 complexes effectively occupies three coordination sites and dissociation requires generation of a high coordinately unsaturated and ostensibly high energy ML_x species.

Arene exchange in η^6-arene—metal complexes, in the absence of catalysts or donor solvents, could proceed by the intramolecular or intermolecular dissociative and associative schemes discussed in the following sections.

Intramolecular dissociative processes

Dissociative reaction schemes could involve complete arene dissociation or a single stepped or multistepped ligand dissociation (in arene-ML_x species) prior to a binding of the new arene molecule:

$$\begin{aligned} &\eta^6\text{-arene-}ML_x \rightleftharpoons \text{arene} + ML_x \\ &\text{arene}' + ML_x \rightleftharpoons \eta^6\text{-arene}'\text{-}ML_x \end{aligned} \qquad (1)$$

The dissociative reaction could be one step or comprise up to three discrete steps as in the sequence

$$\eta^6\text{-arene-ML}_x \rightleftharpoons \eta^4\text{-arene-ML}_x \rightleftharpoons \eta^2\text{-arene-ML}_x \rightleftharpoons \text{arene} + \text{ML}_x$$

This type of process will not be common because the ML_x intermediate will typically have only twelve valence electrons and will therefore be a relatively high energy species.

$$\begin{tikzcd}
\eta^6\text{-arene-ML}_x \arrow[r, shift left, harpoon, "-(L)"] & \eta^6\text{-arene-ML}_{x-1} \arrow[l, shift left, harpoon] \arrow[r, shift left, harpoon, "-(L)"] \arrow[dl, shift left, harpoon, "\text{arene}'"] & \eta^6\text{-arene-ML}_{x-2} \arrow[l, shift left, harpoon] \arrow[d, shift left, harpoon, "\text{arene}'"] \\
\eta^6\text{-arene-ML}_{x-1}(\eta^2\text{-arene}') \arrow[ur, shift left, harpoon] \arrow[rr, shift left, harpoon, "-(L)"] \arrow[d, shift left, harpoon] & & \eta^6\text{-arene-LM}_{x-2}(\eta^4\text{-arene}') \arrow[ll, shift left, harpoon] \arrow[u, shift left, harpoon] \arrow[d, shift left, harpoon] \\
\eta^4\text{-arene-ML}_{x-1}(\eta^4\text{-arene}') \arrow[u, shift left, harpoon] \arrow[rr, shift left, harpoon, "-(L)"] \arrow[d, shift left, harpoon, "\text{several steps}"] & & \eta^4\text{-arene-ML}_{x-2}(\eta^6\text{-arene}') \arrow[ll, shift left, harpoon] \arrow[u, shift left, harpoon] \arrow[d, shift left, harpoon, "\text{several steps}"] \\
\eta^6\text{-arene}'\text{-ML}_x \arrow[u, shift left, harpoon] & & \eta^6\text{-arene}'\text{-ML}_x \arrow[u, shift left, harpoon]
\end{tikzcd}$$

(2)

Detection of ligand (L) dissociative processes can be achieved by isotopic labelling experiments. The relative probabilities of processes (1) and (2) will depend largely upon the thermodynamic stabilities of the M—arene and M—L bonds. In the typical case, a process like (2) should be more likely than (1).

Intramolecular arene′ associative processes

Plausible associative processes are depicted in schemes (3) and (4) which differ only in that (3) involves a preliminary rearrangement.

$$\begin{tikzcd}
\eta^6\text{-arene-ML}_x \arrow[r, shift left, harpoon] & \eta^4\text{-arene-ML}_x \arrow[l, shift left, harpoon] \arrow[d, shift left, harpoon, "\text{arene}'"] \\
& \eta^4\text{-arene-ML}_x(\eta^2\text{-arene}') \arrow[u, shift left, harpoon] \arrow[d, shift left, harpoon, "\text{one or more steps}"] \\
& \eta^6\text{-arene}'\text{-ML}_x \arrow[u, shift left, harpoon]
\end{tikzcd}$$

(3)

$$\begin{tikzcd}
\eta^6\text{-arene-ML}_x + \text{arene}' \arrow[r, shift left, harpoon] & \eta^4\text{-arene-ML}_x(\eta^2\text{-arene}') \arrow[l, shift left, harpoon] \arrow[d, shift left, harpoon, "\text{one or more steps}"] \\
& \eta^6\text{-arene}'\text{-ML}_x \arrow[u, shift left, harpoon]
\end{tikzcd}$$

(4)

In (4) the first step could involve a twenty-electron transition state or intermediate (if η^6-arene—ML_x is an 18-electron species). The probability of associative processes like (3) and (4) with respect to process (2) above will depend largely upon the relative activation energies for the η^6-arene—metal $\rightleftharpoons$ η^4-arene—metal step and the ligand (L) dissociation step.

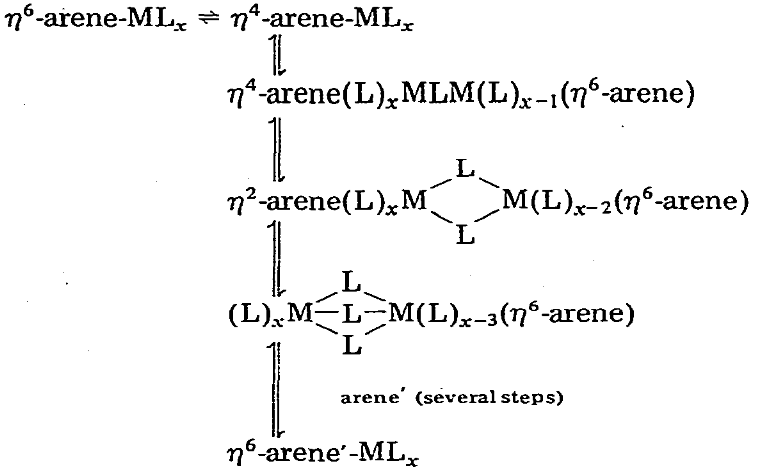
TABLE 3

REPORTED UNCATALYZED η^6-ARENE EXCHANGE REACTIONS

Arene—transition metal compound	Replacing arene′	Solvent	Temperature (°C)	Reference
$(\eta^6\text{-Benzene})\text{Ti}(\text{AlCl}_4)_2$	1,2,3,4-tetramethylbenzene, pentamethylbenzene, hexamethylbenzene	Benzene	20	46
$(\eta^6\text{-Benzene})\text{Cr}(\text{CO})_3$	phenol, methylbenzoate, aniline, *N,N*-dimethylaniline (excess)	Arene′	165	47
$(\eta^6\text{-Toluene})\text{Cr}(\text{CO})_3$	*N,N*-dimethylaniline (excess)	Arene′	193	34
$(\eta^6\text{-Benzene})\text{Cr}(\text{CO})_3$	1-*N,N*-dimethylamino-2-isopropylbenzene, 2-isopropylaniline, 2-isopropylanisole (excess)	Arene′	200	49
$(\eta^6\text{-}p\text{-Isopropyltoluene})\text{W}(\text{CO})_3$	hexamethylbenzene	Hydrocarbons	>100	50
$(\eta^6\text{-Benzene})\text{Ru}(\text{CO})(\text{GeCl}_3)_2$	1,3,5-trimethylbenzene (excess)	Arene′	163	51
$(\eta^6\text{-}p\text{-Isopropyltoluene})\text{Ru}(\text{Cl})_2(\text{PBu}_3)$	benzene, toluene, hexamethylbenzene (excess)	Arene′ or n-heptane	70—110	52
$(\eta^6\text{-Mesitylene})\text{Co}_3(\text{CO})_6\text{CPh}$	benzene (excess)	Arene′	100	53
$[(\eta^6\text{-Benzene})\text{Ir}(\eta^5\text{-C}_5(\text{CH}_3)_5)](\text{PF}_6)_2$	indole	CH_3NO_2	20	54
$(\eta^6\text{-Toluene})\text{Ni}(\text{C}_6\text{F}_5)_2$	1,3,5-trimethylbenzene, benzene, fluorobenzene	CHCl_3	20	23

Intermolecular processes

High energy species generated in multistep dissociative processes, as for example ML_x and arene-ML_{x-2} described in processes (1) and (2) above, could be partially stabilized by interaction with the parent arene-ML_x molecule either through M—L—M or M—arene—M interactions with the former probable only in complexes where L is an effective bridging molecule, e.g., carbon monoxide, hydride and isocyanide. One of several possible mechanistic scenarios is sketched in (5).



$$\begin{array}{l}
\eta^6\text{-arene-}ML_x \rightleftharpoons \eta^4\text{-arene-}ML_x \\
\qquad \updownarrow \\
\qquad \eta^4\text{-arene}(L)_xMLM(L)_{x-1}(\eta^6\text{-arene}) \\
\qquad \updownarrow \\
\qquad \eta^2\text{-arene}(L)_xM(\mu\text{-}L)_2M(L)_{x-2}(\eta^6\text{-arene}) \\
\qquad \updownarrow \\
\qquad (L)_xM(\mu\text{-}L)_3M(L)_{x-3}(\eta^6\text{-arene}) \\
\qquad \Big\updownarrow \text{ arene}' \text{ (several steps)} \\
\qquad \eta^6\text{-arene}'\text{-}ML_x
\end{array} \tag{5}$$

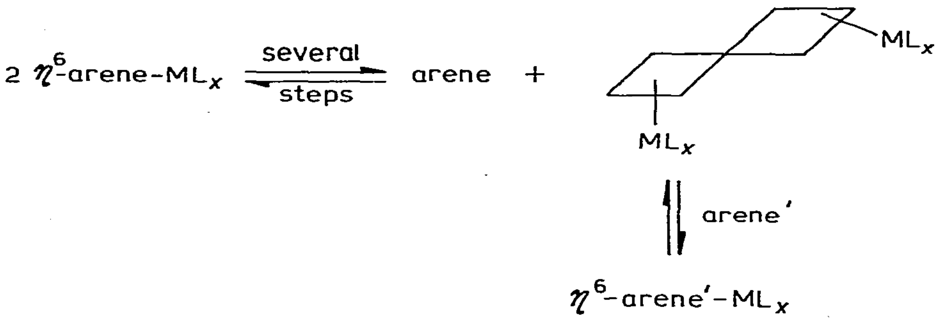
Note that the second intermediate in (5), η^4-arene$(L)_xMLM(L)_{x-1}(\eta^6$-arene) could dissociate to give a coordinately unsaturated fragment as shown in (6) which could then undergo arene exchange.

$$\begin{array}{l}
\eta^4\text{-arene}(L)_xMLM(L)_{x-1}(\eta^6\text{-arene}) \\
\qquad \updownarrow \\
\eta^4\text{-arene-}ML_{x+1} + \eta^6\text{-arene-}ML_{x-1} \\
\qquad\qquad\qquad \Big\updownarrow \text{ arene}' \text{ (several steps as shown in (2))} \\
\qquad\qquad\qquad \eta^6\text{-arene}'\text{-}ML_x
\end{array} \tag{6}$$

In an alternative to (2), a highly coordinately unsaturated arene-ML_{x-y} species could be partially stabilized by M—L—M bonding with a second, parent arene-ML_x molecule.

In the second type of intermolecular stabilization, the arene ligand could be bound to more than one metal site. For example, an ML_x fragment could be stabilized by a second arene-ML_x molecule as shown in (7). An intermediate of this type is perhaps unlikely in the presence of free arene but could be important in arene exchange between arene—metal complexes (i.e., arene-ML_x and arene′-ML_x). There are crystallographically established examples of a single aromatic ring interacting with more than one metal atom [5,11]. Fascinating in many of the above hypothetical mechanistic schemes for uncatalyzed arene exchange is the issue of "unzipping" of an

η^6-arene ligand. Must the exchange protocol follow a sequential $\eta^6 \rightleftharpoons \eta^4 \rightleftharpoons \eta^2$



(7)

sequence or can η^6-arene $\rightleftharpoons$ free arene, η^6-arene $\rightleftharpoons$ η^2-arene $\rightleftharpoons$ free arene, or η^6-arene $\rightleftharpoons$ η^4-arene $\rightleftharpoons$ free arene sequences prevail? Geometrically, the η^6-arene—metal to η^2-arene—metal traverse is simpler than $\eta^6 \rightarrow \eta^4$. Sequences of such forms can be hidden from kinetic definition in the typically ambiguous rate expressions and a full sequence of $\eta^6 \rightleftharpoons \eta^4 \rightleftharpoons \eta^2$ transformations may be discernible, if at all, only by spectroscopic studies provided that intermediate accumulation can be achieved by temperature or stoichiometry control.

Catalyzed arene exchange

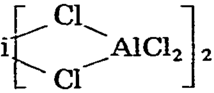
Arene exchange between free arene and an η^6-arene—metal complex can be catalyzed by a strong Lewis acid like an alane or by a "hard" Lewis base. Several alane catalyzed arene exchange reactions have been described (Table 4) but no kinetic or mechanistic studies of these reactions have been reported [5,6]. In the complexes  η^6-arene-Ti$\left[\overset{\text{Cl}}{\underset{\text{Cl}}{\quad}}\text{AlCl}_2\right]_2$, which undergo relatively facile arene exchange [1], partial dissociation of the $AlCl_4^-$ ligand to give species like arene-Ti($ClAlCl_3$)$_2$ yields coordinately unsaturated states that could interact with the free arene′. On the other hand, aluminum halide catalysis of arene exchange in (η^6-arene)$_2$M complexes must proceed by a different mechansim. However, we defer mechanistic comment on this class of catalyzed exchange. A more clearly defined set of catalyzed arene exchange reactions is based on donor ligands or solvents such as ethers, ketones and nitriles [26,27a—c]. Such ligands catalyze arene exchange in complexes like η^6-arenetricarbonylmetal (M = Cr, Mo, W) and η^6-arene-diene-metal (M = Ru and Ir^+). Formal reaction

TABLE 4

LEWIS ACID CATALYZED EXCHANGE

Arene—transition metal compound	Replacing arene′	Catalyst	Temperature (°C)	Ref.
(η^6-Benzene)$_2$Cr	biphenyl	$AlCl_3$	115	56
(η^6-Mesitylene)$_2$Cr$^+$	benzene	$AlCl_3$	78	57
η^6-$C_6(CH_3)_6$Ru-η^4-$C_6(CH_3)_6$	$C_6(CD_3)_6$	$Al_2(CH_3)_6$	80	22

schemes for these ligand (Lewis base) catalyzed reactions include the following:

$$\eta^6\text{-arene-ML}_x \rightleftharpoons \eta^6\text{-arene-ML}_{x-1} + \text{L} \qquad (8)$$

$$\eta^6\text{-arene-ML}_{x-1}+\text{L}' \rightleftharpoons \eta^6\text{-arene-ML}_{x-1}\text{L}'$$

$$\eta^6\text{-arene-ML}_{x-1}\text{L}' \rightleftharpoons \eta^4\text{-arene-ML}_{x-1}\text{L}'$$

$$\begin{tikzcd}
\eta^4\text{-arene-ML}_{x-1}\text{L}' + \text{arene}' \arrow[r, phantom, "\rightleftharpoons"] & \eta^4\text{-arene-ML}_{x-1}\text{L}'\text{-}\eta^2\text{-arene}' \arrow[d, shift left, "\text{L (one or more steps)}"] \\
 & \eta^6\text{-arene}'\text{-ML}_x + \text{arene} \arrow[u, shift left]
\end{tikzcd}$$

$$\begin{tikzcd}
\eta^6\text{-arene-ML}_x + \text{L}' \arrow[r, phantom, "\rightleftharpoons"] & \eta^4\text{-arene-ML}_x\text{L}' \arrow[r, phantom, "\rightleftharpoons"] \arrow[d, shift left, "\text{one or more steps}"] & \eta^2\text{-arene-ML}_x\text{L}'_2 \arrow[d, shift left, "\text{one or more steps}"] \\
 & \eta^6\text{-arene}'\text{-ML}_x \arrow[u, shift left] & \eta^6\text{-arene}'\text{-ML}_x \arrow[u, shift left]
\end{tikzcd} \qquad (9)$$

$$\eta^6\text{-arene-ML}_x + 3\ \text{L}' \underset{\text{steps}}{\overset{\text{several}}{\rightleftharpoons}} \text{ML}_x\text{L}'_3 \qquad (10)$$

$$\text{ML}_x\text{L}'_3 \rightleftharpoons \text{ML}_x\text{L}'_2 + \text{L}'$$

$$\text{ML}_x\text{L}'_3 + \text{arene}' \underset{\text{steps}}{\overset{\text{several}}{\rightleftharpoons}} \eta^6\text{-arene}'\text{-ML}_x + 3\ \text{L}'$$

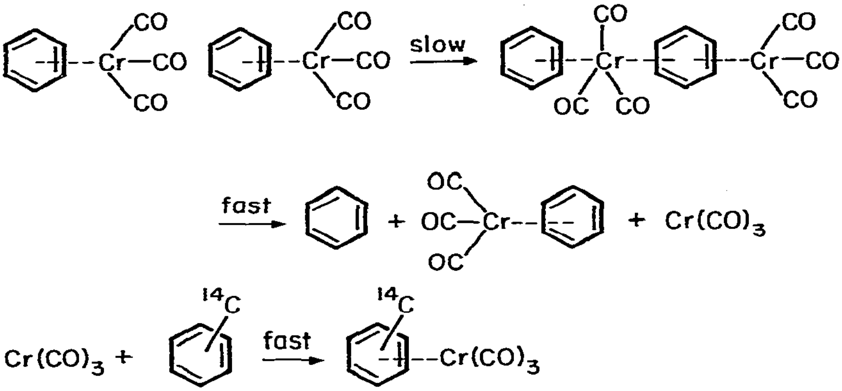
Exchange in scheme (9) occurs from an intermediate or transition state in which both arene and arene′ are bound to the metal. In scheme (10) arene is completely displaced from the metal center prior to interaction with arene′.

Interchange reactions like those depicted in (9) and (10) are more likely processes than (8). Interchange scheme (10) is a solvent stabilized formal analog of the intermolecular scheme (5) above and it has been proposed by Willeford et al. [27d]. Mechanisms of interchange reactions like (9) and (10) have been considered (see below) by Cais et al. [28] and by Mahaffy and Pauson [27a—c].

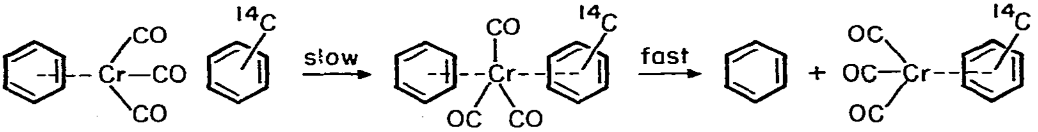
In all these ligand catalyzed schemes, the same fundamental issue arises, does a full sequential unzipping reaction prevail followed by a rezipping sequence or is arene dissociation possible directly from η^6- or η^4-arene—metal states?

Analysis of experimental data in arene exchange reactions

A preliminary report for arene exchange between free arene and $\eta^6\text{-C}_6\text{H}_5\text{CH}_3\text{Ni(C}_6\text{F}_5)_2$ described a rate expression of the form $k_2[\text{arene}'][\text{C}_6\text{H}_5\text{CH}_3\text{Ni(C}_6\text{F}_5)_2]$ [23,24]. In addition, a dissociative solution process for the nickel complex in the common solvent of chloroform was reported. An associative process was proposed although the rate expression and the reported solution dissociation process are also consistent with the sequence $\text{arene-Ni(C}_6\text{F}_5)_2 \overset{-\text{arene}}{\rightleftharpoons} \{\text{Ni(C}_6\text{F}_5)_2\} \overset{+\text{arene}'}{\rightleftharpoons} \text{arene}'\text{-Ni(C}_6\text{F}_5)_2$ [23,24]. No other kinetic data exist for arene exchange between free arene and an η^6-arene—metal complex in a noncoordinating solvent except for a set of high temperature (140—180°C) exchange reactions between ^{14}C labeled benzene and η^6-benzenetricarbonylmetal complexes of the Group VIA metals, Cr, Mo, and W. The derived rate expression for these reactions was unusual, the rate of exchange was second order in [arene-$M(CO)_3$] and about one-third order in [^{14}C-benzene] [29]. The mechanistic conclusion from these kinetic studies was that two different mechanisms were operative and that the rate expression was of the form rate = $k_2[C_6H_6Cr(CO)_3]^2 + k_2'[C_6H_6Cr(CO)_3][^{14}C_6H_6]$. Both proposed mechanisms (Schemes A and B) are



SCHEME A. Proposed mechanism outlined for one pathway of arene exchange in η^6-arenetricarbonylchromium, which could account for the observed second order dependence in the η^6-arenetricarbonylchromium concentration [32].



SCHEME B. Mechanism for an apparent second pathway of arene exchange in η^6-arenetricarbonylchromium which could account for the observed fractional order dependence in arene′ [32].

chemically improbable as explicitly formulated although the essential concept of intermolecular processes has merit. The proposed mechanism appears to be incorrect because sequence A requires an inversion in arene binding yet Jackson et al. [30] found no interconversion of the *cis* and *trans* isomers of the η^6-1-methylindane-$Cr(CO)_3$ complexes at elevated temperatures although interconversion was rapid in the presence of free arene. Similar evidence has been presented by Mahaffy and Pauson [27a—c].

Catalysis of arene exchange by donor solvents was demonstrated in the η^6-arene-$Cr(CO)_3$ system by Mahaffy and Pauson [27a—c]. The use of benzonitrile and di-n-butyl ether mixtures, tetrahydrofuran, acetone or methylformate as the solvent was found to significantly increase the rate of arene exchange. In the catalyzed reactions, equilibrium between the arenes and the arene-$Cr(CO)_3$ complexes was attained in 18 hrs. at 142°C, while in the uncatalyzed reactions, equilibration required days. Mahaffy and Pauson proposed that exchange in this system is initiated by partial arene displacement from the metal by the donor solvent. They favor exchange from the η^4-arene-$Cr(CO)_3D$ (D = donor solvent) species but do not rule out the possiblity of exchange occurring from η^2-arene-$Cr(CO)_3D_2$ or even $Cr(CO)_3D_3$ where the first arene is completely displaced prior to attack by the incoming arene(arene') *.

Meyer and Jaouen [31] as well as Goasmat, Dabard and Patin [32] have recently described acid-catalyzed arene exchange with (η^6-α-hydroxyarene)-$Cr(CO)_3$ compounds. The authors postulate that the acid catalyst, 2-methyl-1,3-cyclopentadione, protonates the hydroxy group and then loss of water generates an α-carbonium ion which reduces the basicity of the arene and promotes arene exchange. Complete exchange in these systems typically requires several hours at 100°C.

Experimental

General. All manipulations were performed in an argon- or helium-filled drybox or under argon or nitrogen using standard Schlenk techniques. Acetone was dried by refluxing over potassium carbonate under argon or nitrogen for approximately two days before distillation. CH_2Cl_2 was dried by refluxing over phosphorous pentoxide under nitrogen prior to distillation. CD_2Cl_2 and $CDCl_3$ were dried over phosphorous pentoxide at room temperature prior to trap-to-trap distillation on a vacuum line. Cyclohexane-d_{12} (approximately 99.6 atom %d) was prepared by Rh-catalyzed reduction of C_6D_6 under D_2 (1 atm) at room temperature and dried over active alumina prior to trap-to-trap distillation. Tetrahydrofuran, diethyl ether, n-pentane and hexanes were distilled from sodium benzophenone ketyl. Acetonitrile was purified by successive distillation from calcium hydride and phosphorous pentoxide under nitrogen. Pyridine was pre-dried over potassium hydroxide and distilled from barium oxide. Diethyl sulfide was vacuum distilled and degassed in vacuo. Benzene, toluene and *m*-xylene were distilled from sodium benzophenone ketyl. *o*-Xylene, *p*-xylene, mesitylene and 1,2,3,4-tetramethylbenzene were purified by passage down a column of active alumina followed by vacuum distillation. 1,2,4,5-tetramethylbenzene and hexamethylbenzene were sublimed in vacuo.

Proton NMR spectra were recorded at 90 MHz on a Varian EM-390 spectrometer or at 180 MHz on the U.C.B., Department of Chemistry pulse-FT NMR spectrometer. Chemical shifts are reported as δ values, positive values being downfield from tetramethylsilane.

Microanalyses were performed by Mr. Vazken Tashinian at the U.C.B., Department of Chemistry Microanalytical Laboratory.

Preparation of η^6-arene-$Mo(CO)_3$ compounds. η^6-$C_6H_6Mo(CO)_3$ was prepared by treatment of $(pyridine)_3Mo(CO)_3$ [33a] with $BF_3 \cdot O(C_2H_5)_2$ in the presence of benzene, as described by Nesmeyanov et al. [33b]. η^6-$C_6H_5CH_3Mo(CO)_3$ and η^6-1,3,5-$C_6(CH_3)_3H_3Mo(CO)_3$ were prepared by refluxing $Mo(CO)_6$ in excess arene [34]. A small amount of tetrahydrofuran was added to wash sublimed $Mo(CO)_6$ back into the reaction vessel. η^6-$C_6(CH_3)_6Mo(CO)_3$ was prepared by

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* Others have shown that donor solvents can assist in labilizing arene ligands. For example, Nesmeyanov [26] has reported that the reaction of η^6-benzene-$\eta^{5'}$ cyclopentadienyliron with excess naphthalene in ether/tetrahydrofuran at 30—40°C generates η^6-naphthalene-η^5-cyclopentadieneiron in low yield. The reaction does not proceed in ether alone. And Cais [28] has shown that in the η^6-arenetricarbonylchromium-catalyzed hydrogenation of dienes, donor molecules like tetrahydrofuran can partially displace the arene and therby open up coordination sites for diene complexation.

reacting $(CH_3CN)_3Mo(CO)_3$ [35] with hexamethylbenzene in refluxing tetrahydrofuran. The η^6-arene-$Mo(CO)_3$ compounds were purified by recrystallization from a methylene chloride/hexane mixture and were characterized by their infrared and proton NMR spectra.

Preparation of η^6-C_6H_6Ru-*1,5*-C_8H_{12}. η^6-C_6H_6Ru-1,5-C_8H_{12} [36] was prepared according to the method suggested by Singleton and co-workers [37]. $[Ru(H)(1,5\text{-}C_8H_{12})(NH_2N(CH_3)_2)_3](B(C_6H_5)_4)$ [38] (1.82 g, 2.56 mmol) was placed in a 100 ml three-neck flask under an inert atmosphere. The flask was fitted with an addition funnel, a ground-glass stopper, and a reflux condenser with nitrogen inlet. The complex was dissolved in approximately 22 ml of acetone and 3 ml of benzene to give a red-brown solution. As the solution was heated to reflux, an additional 20 ml of benzene was added dropwise. After 4 h at reflux, the flask was allowed to cool to room temperature and the volatiles were removed in vacuo. Subsequent extraction with n-pentane, filtration of the extract and concentration of the yellow filtrate afforded a crop of analytically pure, yellow needles (47%; m.p. 134—135.5°C; analysis: Found: C, 58.61; H, 6.33; N, 0.00. $RuC_{14}H_{18}$ calcd.: C, 58.51; H, 6.31; N, 0.00%. Mass spectrum *m/e*: Obsd.: 288. $[Ru^{102}C_{14}H_{18}]^+$ calcd.: 288; ^1H NMR (90 MHz, 35°C, C_6D_6) δ 4.77 (s, 6 H), 3.49 (broad s, 4 H), 2.28 (broad s, 8 H) ppm; ^1H NMR (180 MHz, —85°C, $C_6D_5CD_3$) δ 4.62 (s, 6 H), 3.54 (broad s, 4 H), 2.37 (broad multiplet, 8 H)) *.

Preparation of $[\eta^6$-*arene-Ir-1,5*-$C_8H_{12}](BF_4)$ *complexes.* The (η^6-arene-Ir-1,5-C_8H_{12})(BF_4) complexes were prepared by three methods; specific examples of each method are given below. Methods I and II are similar to the procedure used by Schrock and Osborn [39]. Method I employed arene as the reaction solvent while Method II used either a methylene chloride/acetone mixture of tetrahydrofuran solvent system to generate a solvated "1,5-C_8H_{12}-Ir^+" species which formed the desired complex upon addition of arene. Method III involved removal of coordinated acetylacetone with the triphenylmethyl cation in the presence of arene as described by Green and Kuc [40]. Tables 5 and 6 summarize the synthetic details and ^1H NMR data for these complexes, respectively.

Method I. Preparation of (η^6-C_6H_6-*Ir-1,5*-C_8H_{12})(BF_4). A solution of (1,5-C_8H_{12}-$IrCl)_2$ [41] (1 g, 1.49 mmol) in freshly distilled benzene (approximately 9 ml) was added dropwise to a rapidly stirred slurry of $AgBF_4$ (0.58 g, 2.98 mmol) in benzene (approximately 14 ml) over the course of about 0.5 h. The tan mixture was stirred for an additional ten minutes and then filtered through a fine frit; the filtrate was discarded. The tan insoluble powder was washed with CH_2Cl_2 (approximately 11 ml) and the filtrate was collected in a separate vessel. This tea-colored filtrate was treated with approximately 0.2 ml of C_6H_6 and 9 ml of tetrahydrofuran (added about 1 ml at a time) with rapid stirring. Two crops of tan crystals were collected and recrystallized twice from a methylene chloride/tetrahydrofuran mixture in the presence of benzene to give 0.61 g of white powder (44%). Generally, good analyses could only be obtained after powdering the complex in a mortar and heating for several hours at about 55°C in vacuo.

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* We note that previous workers [36] reported a decomposition point of 60°C and ^1H NMR peaks at δ 4.18, 2.90 and 1.68 ppm in C_6D_6.

TABLE 5

SYNTHETIC AND ANALYTICAL DATA FOR η^6-ARENE-1,5-CYCLOOCTADIENYLIRIDIUM TETRAFLUOROBORATE COMPLEXES

Arene	Method of preparation [d]	Color	Yield (%) [c]	Analysis (Found (calcd.) (%))	
				C	H
C_6H_6	I	white	44	36.14 (36.14)	3.82 (3.90)
$C_6H_5CH_3$	III	white	31	37.73 (37.58)	4.22 (4.21)
1,2-$C_6H_4(CH_3)_2$	II [a]	light tan	28	39.25 (38.95)	4.61 (4.50)
1,3-$C_6H_4(CH_3)_2$	II [a]	white	10	39.35 (38.95)	4.67 (4.50)
1,4-$C_6H_4(CH_3)_2$	II [b]	light tan	41	39.03 (38.95)	4.45 (4.50)
1,3,5-$C_6H_3(CH_3)_3$	III	white	40	40.53 (40.24)	4.79 (4.77)
1,2,3,4-$C_6H_2(CH_3)_4$	II [b]	cream	55	41.28 (41.46)	4.96 (5.03)
1,2,4,5-$C_6H_2(CH_3)_4$	II [b]	white	38	41.29 (41.46)	5.00 (5.03)
$C_6(CH_3)_6$	II [b]	off-white	44	43.90 (43.72)	5.46 (5.50)

[a] Tetrahydrofuran used as reaction solvent. [b] CH_2Cl_2/acetone solvent system. [c] Yields after two recrystallizations. [d] See Experimental.

Method II. Preparation of (η^6-1,2,3,4-$C_6H_2(CH_3)_4Ir$-1,5-C_8H_{12})(BF_4). A methylene chloride solution of (1,5-$C_8H_{12}IrCl)_2$ (0.20 g, 0.30 mmol) was treated with an acetone solution of $AgBF_4$ (0.12 g, 0.60 mmol). The color of the reaction mixture rapidly changed from orange to yellow with the accompanying precipitation of AgCl. After stirring overnight at room temperature, the mixture was filtered through celite. The yellow filtrate was treated with

TABLE 6

^1H NMR DATA FOR η^6-ARENE-1,5-CYCLOOCTADIENYLIRIDIUM TETRAFLUOROBORATE COMPLEXES AND FREE ARENES [a]

Arene	Free arene		Coordinated arene		Coordinated COD [b]	
	aromatic H	methyl H	aromatic H	methyl H	vinyl H	methylene H
C_6H_6	7.35	—	7.07	—	4.83	2.30—2.12
$C_6H_5CH_3$	7.18(m)	2.31	7.01—6.92	2.59	4.66	2.30—2.09
1,2-$C_6H_4(CH_3)_2$	7.07(m)	2.23	6.96—6.82	2.51	4.49	2.23—2.13
1,3-$C_6H_4(CH_3)_2$	6.93—7.11(m)	2.27	6.94—6.75	2.54	4.49	2.30—2.14
1,4-$C_6H_4(CH_3)_2$	7.05	2.26	6.83	2.55	4.49	2.23—2.15
1,3,5-$C_6H_3(CH_3)_3$	6.77	2.23	6.84	2.49	4.32	2.24—2.15
1,2,3,4-$C_6H_2(CH_3)_4$	6.85	2.12, 2.15	6.73	2.48, 2.35	4.11	2.27—2.11
1,2,4,5-$C_6H_2(CH_3)_4$	6.86	2.15	6.57	2.46	4.18	2.32—2.11
$C_6(CH_3)_6$	—	2.23 [c]	—	2.28 [c]	3.54 [c]	2.22—1.92 [c]

[a] Determined at 180 MHz in acetone-d_6 at approximately 25°C. [b] 1,5-Cyclooctadiene. [c] Determined in chloroform-d.

1 ml of 1,2,3,4-tetramethylbenzene and stirred for 1 h. The yellow solution was then concentrated in vacuo to the appearance of an off-white solid. 30 ml of diethyl ether were then added dropwise to precipitate the crude product. Two recrystallizations from a methylene chloride/diethyl ether mixture gave a total of 0.17 g of cream-colored crystals (55%).

Method III. Preparation of $(\eta^6\text{-}1,3,5\text{-}C_6H_3(CH_3)_3Ir\text{-}1,5\text{-}C_8H_{12})(BF_4)$. Triphenylmethyltetrafluoroborate (0.66 g, 20 mmol) was dissolved in methylene chloride (approximately 6 ml) and added dropwise to a solution of $1,5\text{-}C_8H_{12}\text{-}IrC_5H_7O_2$ [42] (0.80 g, 2.0 mmol) dissolved in a 55/45 mixture of mesitylene/methylene chloride (approximately 9 ml). After the addition was complete, an additional 8 ml portion of methylene chloride was added to the reaction mixture, and stirring was continued for ~18 h. The resulting dark red solution was added dropwise to about 170 ml of diethyl ether. A white powder precipitated which was separated from the supernatant by decantation and dried in vacuo. The complex was recrystallized twice from a methylene chloride-diethylether mixture to yield 0.40 g of white microcrystals (40%).

Determination of equilibrium constants in η^6*-arene-Mo(CO)*$_3$*–arene′ systems.* A standard solution of η^6-arene-Mo(CO)$_3$ in CD_2Cl_2 was prepared by adding a known quantity of η^6-arene-Mo(CO)$_3$ to a volumetric flask and filling to the mark with solvent. For liquid arene′ (arene′ = benzene, toluene, xylenes, mesitylene, 1,2,3,4-tetramethylbenzene), 0.50 ml of the above standard solution was transferred to an NMR tube via syringe and stoichiometric quantities of arene′ and $(CD_3)_2CO$ (one equivalent of each per equivalent of η^6-arene-Mo(CO)$_3$) were added via microsyringe. For solid arene′ (arene′ = 1,2,4,5-tetramethylbenzene, hexamethylbenzene), a weighed quantity of arene′ was added to an NMR tube and stoichiometric amounts of standard η^6-arene-Mo(CO)$_3$ solution and $(CD_3)_2CO$ were added through a syringe. Tetramethylsilane was added to each sample. The tubes were capped with airtight pressure caps obtained from Wilmad Glass Company and wrapped in aluminum foil to prevent photolytic decomposition. Periodically, the proton NMR spectra were recorded, and the free arene and arene′ signals were integrated. When the relative magnitudes of these two signals remained constant for two successive measurements, the reaction was assumed to be complete and the equilibrium constant was calculated from the equation $K_{eq} = \left(\frac{[\text{arene}]}{[\text{arene}']}\right)^2$. Approximately three days were required to reach equilibrium in the molybdenum system, while the iridium and ruthenium systems typically required weeks and months, respectively.

The reactions of the $(\eta^6\text{-arene-Ir-}1,5\text{-}C_8H_{12})(BF_4)$ and $\eta^6\text{-}C_6H_6\text{-Ru-}1,5\text{-}C_8H_{12}$ complexes were monitored by ^{1}H NMR in a manner similar to that outlined above. All NMR tubes were heat-sealed in vacuo.

Competition studies. Standard solutions of $\eta^6\text{-}C_6H_6Mo(CO)_3$ in CD_2Cl_2, $\eta^6\text{-}C_6H_6Ru\text{-}1,5\text{-}C_8H_{12}$ in C_6D_{12}, and $(\eta^6\text{-}C_6H_6Ir\text{-}1,5\text{-}C_8H_{12})(BF_4)$ in $(CD_3)_2CO$ were prepared. Equivalent quantities of *o*- and *p*-xylene or 1,2,3,4- and 1,2,4,5-tetramethylbenzene were combined with aliquots of the standard solutions in NMR tubes. Arene exchange was catalyzed by addition of one equivalent of acetone to the Mo system and three equivalents of acetonitrile to the Ru system; the Ir system was solvent catalyzed. The progress of the exchange reactions was monitored by observation of the ^{1}H NMR spectrum at 180 MHz.

Results and discussion

General considerations

Our preliminary investigation of the thermodynamic, kinetic and mechanistic features of arene exchange in the d^6 η^6-arene-Mo(CO)$_3$ system and the two isoelectronic and presumably isotructural * d^8 η^6-arene-1,5-cyclooctadienemetal ($M = Ru^0$ and Ir^+) systems has established several key qualitative and quantitative points. Facility of arene exchange, for both the uncatalyzed and the catalyzed processes, drops sharply in going from the molybdenum to the iridium to the ruthenium systems. In fact, the ruthenium complexes undergo no detectible uncatalyzed arene exchange up to temperatures where the complex undergoes thermal decomposition. Consistent with other literature reports, the η^6-arene—metal interaction increases in strength with increase in the number of methyl substituents. Stereochemistry of methyl substituents does not materially affect the interaction strength in the ruthenium system for the xylene and the tetramethylbenzene series, but there are differences in the molybdenum and iridiums systems. Specific results for these arene exchange reactions are discussed below for each metal system.

Molybdenum; Exchange between η^6-arene-Mo(CO)$_3$ and free arene$'$ is far more facile than in the analogous chromium system [5,27,29]. This exchange in the molybdenum system, in the absence of a catalyst, is measurable at temperatures as low at 60°C. In contrast, exchange in the chromium system with no catalyst requires temperatures of 140—160°C. Since the thermodynamic stability of the arene—molybdenum bond is large and is substantially larger than for arene—chromium **, a purely dissociative process to M(CO)$_3$ fragments may be unequivocally excluded for the molybdenum complexes. In fact, a process that is associative in character seems much more probable; this issue should be answered by kinetic studies now in progress.

Arene exchange in the molybdenum complexes is greatly catalyzed by simple Lewis bases such as acetone and tetrahydrofuran. This catalyzed exchange proceeds at a modest rate at 20°, again in sharp contrast to the chromium system which requires temperatures of ~80°C for measurable exchange rates in the presence of excess (solvent medium) Lewis base [27]. For the molybdenum system, equilibrium between toluene-d_8 and η^6-C_6H_5-$CH_3Mo(CO)_3$ is reached in approximately 8 h at 20°C in the presence of acetone (1 mol per mol of complex). The reaction rate is dependent upon the acetone concentration; rate studies in progress will establish the overall rate expression for this exchange reaction. Actually, dissolution of η^6-$C_6H_6Mo(CO)_3$ in either tetrahydrofuran or acetone leads to rapid (minutes or less) and complete displacement of arene and formation of $(C_4H_8O)_3Mo(CO)_3$ * or $[(CH_3)_2CO]_3$-$Mo(CO)_3$ ***. These solvated "Mo(CO)$_3$" species can then be dissolved in

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* Both are diamagnetic and should be isostructural. The precise stereochemistry is established only in the ruthenium system for η^6-C_6H_6-1,5-cyclooctadiene-ruthenium [44].

** For example, the bond energies for the mesitylene complex are 45.6 and 66.7 kcal/mol for the chromium and molybdenum complexes, respectively [19].

*** The tetrahydrofuran complex can be isolated as yellow crystals by "recrystallizing" η^6-$C_6H_6Mo(CO)_3$ from tetrahydrofuran. $(C_4H_8O)_3Mo(CO)_3$ was first reported by Werner and Coffield [45] and was described as an olive-brown crystalline solid.

TABLE 7

EQUILIBRIUM DATA FOR η^6-ARENETRICARBONYLMOLYBDENUM/ARENE′ SYSTEM [a] (22°C)

Complex	Arene′	^{1}H NMR Shifts (δ)		$K_{eq} = \left(\frac{[\text{free arene}]}{[\text{free arene}']}\right)^2$
		Free arene	Free arene′	
η^6-Mesitylene-Mo(CO)$_3$	Benzene	6.77	7.35	8.6×10^{-3} [b]
η^6-Mesitylene-Mo(CO)$_3$	Toluene	6.77	7.18(m)	3.4×10^{-2}
η^6-Mesitylene-Mo(CO)$_3$	*o*-Xylene	6.77	7.07(m)	7.4×10^{-2}
η^6-Mesitylene-Mo(CO)$_3$	*m*-Xylene	6.77	6.93–7.11(m)	1.6×10^{-1}
η^6-Mesitylene-Mo(CO)$_3$	*p*-Xylene	6.77	7.05	9.8×10^{-2} [b]
η^6-Mesitylene-Mo(CO)$_3$	1,2,3,4-Tetramethylbenzene	6.77	6.85	6.1×10^{-1} [b]
η^6-Mesitylene-Mo(CO)$_3$	1,2,4,5-Tetramethylbenzene	6.77	6.86	1.2 [b]
η^6-Toluene-Mo(CO)$_3$	Benzene	7.18(m)	7.35	3.2×10^{-1} [c]
η^6-Toluene-Mo(CO)$_3$	*p*-Xylene	7.18(m)	7.05	3.2
η^6-Toluene-Mo(CO)$_3$	Mesitylene	7.18(m)	6.77	3.6×10^{1}
η^6-Toluene-Mo(CO)$_3$	1,2,3-Trimethylbenzene	7.18(m)	6.90	8.4
η^6-Toluene-Mo(CO)$_3$	1,2,3,4-Tetramethylbenzene	7.18(m)	6.85	2.0×10^{1}
η^6-Toluene-Mo(CO)$_3$	1,2,4,5-Tetramethylbenzene	7.18(m)	6.86	3.5×10^{1}
η^6-Hexamethylbenzene-Mo(CO)$_3$	1,2,3,4-Tetramethylbenzene	—	6.85	2.1×10^{-2} [d, e]

[a] Reaction mixtures contained one equivalent of η^6-arenetricarbonylmolybdenum, arene′, and $(CD_3)_2CO$ in CD_2Cl_2 solvent. [b] Complexed arene′ signal was integrated and used as a check on free mesitylene integration. [c] Equilibrium constant was checked by integrating free and complexed toluene methyl signals.

[d] Free and complexed aromatic 1,2,3,4-tetramethylbenzene (TMB) signals were integrated and K_{eq} was calculated from the equation, $K_{eq} = \left(\frac{[\text{complexed TMB}]}{[\text{free TMB}]}\right)^2$.

[e] The η^6-mesitylene-Mo(CO)$_3$ $\rightleftharpoons$ η^6-hexamethylbenzene-Mo(CO)$_3$ equilibrium constant (K_1) can be calculated from the η^6-mesitylene-Mo(CO)$_3$ $\rightleftharpoons$ η^6-1,2,3,4-tetramethylbenzene-Mo(CO)$_3$ equilibrium constant (K_2) and the η^6-hexamethylbenzene-Mo(CO)$_3$ $\rightleftharpoons$ η^6-1,2,3,4-tetramethylbenzene equilibrium constant (K_3) with the equation $K_1 = K_2/K_3$. Substitution of the appropriate values for K_2 and K_3 yields $K_1 = 2.9 \times 10^{1}$.

arene solvent to regenerate the arene—metal complex. Attempts to study the rate of this back reaction have been frustrated by the failure to find a nonreactive solvent (vide infra). This chemistry has clearly established the "end" reaction products in the interaction of Lewis bases (D) and η^6-arene-Mo(CO)$_3$ complex as shown in reaction (11), but spectroscopic studies to date have not

$$\eta^6\text{-arene-Mo(CO)}_3 + 3\ \mathrm{D} \rightleftharpoons \text{arene} + \mathrm{D_3Mo(CO)_3} \tag{11}$$

revealed any of the necessary intermediates. We do not envisage a species such as $D_3Mo(CO)_3$ as the key intermediate in the Lewis base catalyzed arene exchange reactions. In fact, the irreversible decomposition of $D_3Mo(CO)_3$ complexes in solvents like methylene chloride †, a decomposition that is largely suppressed by the addition of arene, suggests a facile dissociation of the complex (reaction 12) to give $D_2Mo(CO)_3$ which could react associatively with

$$\mathrm{D_3Mo(CO)_3} \rightleftharpoons \mathrm{D} + \mathrm{D_2Mo(CO)_3} \tag{12}$$

arenes and which perhaps more closely resembles the type of intermediate important in the catalyzed arene exchange reaction (cf. reaction 10). The fact that the analogous chromium complexes do not show this type of chemistry at modest temperatures may be largely thermodynamic in character. Thus although the arene—metal bond is stronger in the molybdenum case, the overall solvation-displacement reaction is still more favored for molybdenum because of a larger Mo—O bond strength in the solvates than in the chromium system *.

Equilibrium constants for reaction (13) have been established in the catalyzed

$$\eta^6\text{-arene-Mo(CO)}_3 + \text{arene}' \rightleftharpoons \eta^6\text{-arene}'\text{-Mo(CO)}_3 + \text{arene} \tag{13}$$

reaction (Table 7). Generally, stabilities of the arene complexes increase with the degree of methyl substitution. The stereochemistry of the methyl substituents has a small effect on complex stability; meta substitution is most favorable. Hence, η^6-1,3,5-trimethylbenzeneMo(CO)$_3$ is more stable than η^6-1,2,3-trimethylbenzeneMo(CO)$_3$ and even η^6-1,2,3,4-tetramethylbenzeneMo(CO)$_3$. *m*-XyleneMo(CO)$_3$ is the most stable of the three xylene complexes.

In a competitive reaction of *o*- and *p*-xylene with η^6-C$_6$H$_6$Mo(CO)$_3$, the initial rates of formation of η^6-*o*-xyleneMo(CO)$_3$ and η^6-*p*-xyleneMo(CO)$_3$ were identical.

Ruthenium. No arene exchange was observed between η^6-C$_6$H$_6$Ru-1,5-C$_8$H$_{12}$ and benzene-d_6, *o*-xylene or hexamethylbenzene at temperatures up to 97°C. These observations are consistent with those of earlier workers [12]. Above 97°C, an irreversible decomposition of the complex ensues **. Arene exchange can be effected by the addition of acetonitrile to non-polar solvent systems like cyclohexane or benzene. However, even in this catalyzed mode, the exchange is slow at 50°C ***. Rate of exchange is dependent on acetonitrile concentration

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* An attempt is being made to evaluate these thermodynamic considerations by the synthesis of the tris-tetrahydrofuran or acetone complex of "Cr(CO)$_3$" and subsequent study of the "back reaction" with arene to ensure that purely kinetic considerations are not the overriding factor.

** At 118°C, free benzene along with black solids were formed.

*** In the η^6-C$_6$H$_6$-1,5-cyclooctadieneruthenium-C$_6$D$_6$ system in cyclohexane with 3 mol of CH$_3$CN per mol of complex, the exchange was only 22% complete within 204 h at 50°C.

† Decomposition is also observed in chloroform and nitromethane.

but the order of the reaction in acetonitrile concentration is not precisely established. No intermediate 1,5-$C_8H_{12}Ru(CH_3CN)_x$ species were spectroscopically detected; apparently such intermediate complexes in this catalyzed reaction are low concentration species.

Diethyl sulfide is a far less effective catalyst for the arene exchange reaction in this ruthenium system. Acetone is not a very effective exchange catalyst and this Lewis base, as a solvent, decomposes the ruthenium complex at 60°C.

Competitive exchange studies of isomeric alkylbenzenes with η^6-C_6H_6Ru-1,5-C_8H_{12} (e.g., between *o*- and *p*-xylene and also between 1,2,3,4- and 1,2,4,5-tetramethylbenzene) showed that the exchange rates were independent of the methyl substituent stereo-chemistry. Significantly the tetramethylbenzenes reacted more slowly than the xylenes, which suggests that either a steric or electronic factor may operate in the rate determining step of the exchange process.

Iridium. In sharp contrast to the isoelectronic ruthenium complex, the cationic η^6-arene-1,5-cyclooctadieneiridium complex undergoes arene exchange, although at low rates, with free arene in chloroform solvent at 25°C. This qualitative chemical difference does not necessarily reflect some fundamental thermodynamic difference between the two complexes. In the cationic complex, the associated anion could partially stabilize (or preserve) a coordinately unsaturated or even a "1,5-cyclooctadieneiridium cation" intermediate for an arene′ association process. Like the ruthenium system, the exchange rate is dependent upon the degree of methyl substitution in the incoming arene. Hexamethylbenzene exchanges for benzene in η^6-C_6H_6Ir-1,5-$C_8H_{12}{}^+$ more slowly than does benzene-d_6 although rate difference is less than an order of magnitude.

Arene exchange with the iridium complex is about an order of magnitude more rapid in acetone than in chloroform. In this solvent, the competitive exchange between *o*-xylene and *p*-xylene with η^6-C_6H_6Ir-1,5-$C_8H_{12}{}^+$ showed the initial rates and the equilibria to be identical and thus established the insensitivity of rate and of η^6-xylene—metal complex stability to substituent stereochemistry. However, similar studies did show a greater stability for cationic 1,2,3,4-tetramethylbenzene-1,5-cyclooctadieneiridium than for the isomeric 1,2,4,5-tetramethylbenzene complex.

In the acetone catalyzed exchange reactions, direct spectroscopic evidence for an intermediate with coordinated acetone was obtained. In the exchange reaction between C_6D_6 and (η^6-C_6H_6Ir-1,5-C_8H_{12})(BF_4) in acetone, a new set of proton resonances were observed (δ 4.13 (broad), 2.34 (broad) and 1.57 ppm (multiplet)). These same resonances appeared upon dissolution of the benzene complex in acetone and by reaction of $AgBF_4$ with (1,5-$C_8H_{12}IrCl)_2$ in acetone. Although this 1,5-$C_8H_{12}Ir(acetone)_x{}^+$ complex has not yet been isolated in crystalline form, it appears to be a high concentration intermediate in the exchange reactions. (Actually a species like 1,5-$C_8H_{12}Ir(acetone)_{x-1}{}^+$ would be the reactive intermediate.) An acetonitrile analog has been isolated [43] and evidence for solvated species in the analogous rhodium(I) system has been presented [39].

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* This implies that there would then be a substantial counterion effect, and this aspect of the exchange process is now under investigation.

Spectroscopic NMR studies of arene exchange between η^6-C_6H_6-Ir-1,5-$C_8H_{12}^+$ and arenes much more basic than benzene, e.g., xylenes and hexamethylbenzene, and also between η^6-1,3,5-$C_6(CH_3)_3H_3$Ir-1,5-$C_8H_{12}^+$ and alkyl-substituted arenes gave no evidence of the acetone solvated iridium intermediate. We presume that the exchange mechanism is the same for all of these catalyzed iridium reactions (cf. scheme (10)); for the more basic arenes, equilibrium (14) apparently lies far to the left.

$$\eta^6\text{-arene-Ir-1,5-}C_8H_{12}^+ + x \text{ acetone} \rightleftharpoons \text{1,5-}C_8H_{12}\text{-Ir(acetone)}_x^+ + \text{arene} \qquad (14)$$

Attempts to increase the rate of arene exchange in equation (15) by

$$(\eta^6\text{-1,3,5-}C_6H_3(CH_3)_3\text{-Ir-1,5-}C_8H_{12})(BF_4) + \text{1,2,4,5-}C_6H_2(CH_3)_4 \rightleftharpoons \qquad (15)$$
$$(\eta^6\text{-1,2,4,5-}C_6H_2(CH_3)_4\text{-Ir-1,5-}C_8H_{12})(BF_4) + \text{1,3,5-}C_6H_3(CH_3)_3$$

addition of "catalytic" amounts of various Lewis bases (two moles per mole of arene complex) were not successful. Tetrahydrofuran was ineffective at promoting the exchange. In the acetone experiment, products were barely detectable in the ^{1}H NMR spectrum after 739h at room temperature. Diethyl sulfide and acetonitrile initially effected slow displacement of coordinated mesitylene to generate (1,5-C_8H_{12}-IrL_x)$^+$, L = CH_3CN [43], $S(C_2H_5)_2$, *without* formation of a new arene complex. Slow formation of the durene complex was observed in the presence of acetonitrile only after a significant amount (> 50%) of the mesitylene complex had been converted to the acetonitrile adduct.

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