

Arene Transition-Metal Chemistry. 5. Arene Ligand Exchange and Reactivity in η^6 -Arene Iridium(I) Complexes¹

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The arene-exchange behavior of a number of arene complexes of the type $[\text{Ir}(\eta^6\text{-arene})(\eta^4\text{-}i\text{-}1,5\text{-C}_8\text{H}_{12})^+](\text{X}^-)$ was examined in acetone and chloroform solution. In acetone, the reaction $[\text{Ir}(\eta^6\text{-arene})(\eta^4\text{-}i\text{-}1,5\text{-C}_8\text{H}_{12})^+](\text{BF}_4^-) + \text{arene}' = [\text{Ir}(\eta^6\text{-arene}')(\eta^4\text{-}i\text{-}1,5\text{-C}_8\text{H}_{12})^+](\text{BF}_4^-) + \text{arene}$ proceeded via solvent displacement of coordinated arene to yield a spectroscopically observable intermediate, $[\text{Ir}(\eta^4\text{-}i\text{-}1,5\text{-C}_8\text{H}_{12})(\text{acetone})_2]^+$, which subsequently reacted with arene' to form the new arene' complex. The rate of exchange was independent of arene' concentration and the extent of methyl substitution on arene' while it was dependent on the extent of methyl substitution of the initially coordinated arene. Competitive exchange reactions established that the rate of exchange was independent of the stereochemistry of methyl substitution if the incoming arene had three or fewer methyl substituents. However, for more highly substituted arenes, a steric effect was operative; the 1,2,3,4- $\text{C}_6\text{H}_2(\text{CH}_3)_4$ complex was the preferred kinetic product in competitive exchanges between 1,2,3,4- $\text{C}_6\text{H}_2(\text{CH}_3)_4$ and 1,2,3,5- $\text{C}_6\text{H}_2(\text{CH}_3)_4$, 1,2,4,5- $\text{C}_6\text{H}_2(\text{CH}_3)_4$, or $\text{C}_6(\text{CH}_3)_6$. Arene exchange proceeded much more slowly in chloroform than in acetone and was anion dependent. Equilibrium constants for a number of arene-exchange reactions were measured. In accord with literature data for other transition-metal complexes, the stabilities of the iridium arene complexes were independent of the stereochemistry of methyl substitution and increased with increasing methyl substitution on the arene ring.

Introduction

Our observation that $[\text{Co}(\eta^3\text{-C}_3\text{H}_5)(\text{PR}_3)_3]$ complexes (PR_3 = tertiary phosphite or phosphine) are precursors for the unique homogeneous hydrogenation of arenes under mild conditions²⁻⁴ initiated our research interest in the chemistry of transition-metal arene complexes.⁵ Subsequent work in our laboratory has shown that $\{\text{Ru}[\eta^6\text{-C}_6(\text{CH}_3)_6][\eta^4\text{-C}_6(\text{CH}_3)_6]\}$ ⁶ and $\{\text{HRh}[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_2\}$ ⁷ are also arene hydrogenation catalysts or catalyst precursors although the mechanistic features of these systems differ from the cobalt-catalyzed reaction in detail. Maitlis,⁸ Bennett,⁹ and Klabunde¹⁰ have recently reported homogeneous hydrogenation of arenes using $\{\text{Rh}[\eta^5\text{-C}_5(\text{CH}_3)_5]\text{Cl}\}_2$, $\{\text{Ru}[\eta^6\text{-C}_6(\text{CH}_3)_6](\text{H})(\text{Cl})[\text{P}(\text{C}_6\text{H}_5)_3]_3\}$ or $[\text{Ru}_2[\eta^6\text{-C}_6(\text{CH}_3)_6]_2(\mu\text{-H})_2(\mu\text{-Cl})](\text{Cl})$, and $\{\text{Ni}[\eta^6\text{-C}_6\text{H}_5(\text{CH}_3)](\eta^1\text{-C}_6\text{F}_5)_2\}$, respectively, as catalysts or catalyst precursors.

One of the salient steps in any catalytic reaction is the interaction of a substrate with the metal complex catalyst. If the substrate is an arene, initial complexation between the arene and the metal center could occur via any one of several binding modes (η^2 , η^4 , etc.). In order to further understand the reactivity trends and systematics of the interaction between aromatic hydrocarbons and metal complexes, a study of the arene-exchange behavior of $[\text{M}(\eta^6\text{-arene})(\text{CO})_3]$ ($\text{M} = \text{Cr}$,

Mo , and W) and $[\text{M}(\eta^6\text{-arene})(\eta^4\text{-}i\text{-}1,5\text{-C}_8\text{H}_{12})]^{n+}$ ($\text{M} = \text{Ru}$, $n = 0$; $\text{M} = \text{Ir}$, $n = 1$) complexes was initiated.¹¹ We report here our results with the iridium system.

Experimental Section

General. All manipulations were performed in a helium-filled drybox or under nitrogen with use of standard Schlenk and serum cap techniques. Extensive use was made of the "three-needle technique" described by Shriver.¹² Acetone and dichloromethane were dried by refluxing over K_2CO_3 and P_4O_{10} , respectively, before distillation. Benzene, diethyl ether, pentane, tetrahydrofuran, toluene, and *m*-xylene were distilled from sodium benzophenone ketyl. Acetonitrile was purified by successive distillation from CaH_2 and P_4O_{10} under nitrogen. Methanol and ethanol were dried by refluxing over the appropriate magnesium alkoxide under nitrogen prior to distillation. Acetylacetone and diethyl sulfide were vacuum distilled and degassed under vacuum prior to use. Allylbenzene, indene, *cis*- and *trans*-propenylbenzene, tetralin, 1,2,3,4- and 1,2,3,5-tetramethylbenzene, 1,2,3- and 1,2,4-trimethylbenzene, and *o*- and *p*-xylene were purified by passage down a column of active alumina followed by vacuum distillation and storage under nitrogen. Anthracene, biphenyl, 9,10-dihydroanthracene, durene, hexamethylbenzene, naphthalene, and phenol were sublimed under vacuum.

Solvents for ¹H NMR spectroscopy were treated in the following manner: acetone-*d*₆ was refluxed over K_2CO_3 ; CD_3CN , CD_2Cl_2 , and CDCl_3 were dried over P_4O_{10} at room temperature; C_6D_6 and $\text{C}_6\text{D}_5\text{CD}_3$ were dried by refluxing over sodium; *p*-xylene-*d*₈ was dried over CaH_2 at room temperature. After the treatments described above, the solvents were degassed by freeze-thaw cycles and vacuum transferred into a dry receiver on a vacuum line.

$[\text{Ir}(\eta^4\text{-}i\text{-}1,5\text{-C}_8\text{H}_{12})\text{HCl}]_2$, $[\text{Ir}(\eta^4\text{-}i\text{-}1,5\text{-C}_8\text{H}_{12})(\text{C}_5\text{H}_7\text{O}_2)]$ ($\text{C}_5\text{H}_7\text{O}_2$ = acetylacetonate), and $[\text{Ir}(\eta^4\text{-}i\text{-}1,5\text{-C}_8\text{H}_{12})(\mu\text{-OCH}_3)]_2$ were prepared by the methods of Shaw.¹³ $[\text{Ir}(\eta^4\text{-}i\text{-}1,5\text{-C}_8\text{H}_{12})\text{Cl}]_2$ (mp 210-211 °C) was prepared by the procedure of Crabtree¹⁴ except that sodium oxalate was used instead of sodium acetate.

AgBF_4 was purchased from Ozark-Mahoning, Tulsa, OK, purified by Soxhlet extraction with diethyl ether. Subsequent evaporation of the extract under vacuum gave a white powder (percent Ag found by gravimetry, 55.38 and 53.71; percent required for AgBF_4 , 55.41). AgPF_6 was used as received from Ozark-Mahoning. $\text{AgOSO}_2\text{CF}_3$ was prepared by treating freshly precipitated Ag_2O with the acid in water. Subsequent filtration and removal of the water under vacuum

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Table X. Synthetic and Analytical Data for $[\text{Ir}(\eta^6\text{-arene})(\eta^4\text{-c-1,5-C}_6\text{H}_{12})^+](\text{BF}_4^-)$ Complexes

arene	method of prepn ^a	color	yield, %	% C		% H	
				obsd	calcd	obsd	calcd
1,2,3-C ₆ H ₃ (CH ₃) ₃	IV ^b	white	24 ^e	39.99	40.24	4.74	4.77
1,2,4-C ₆ H ₃ (CH ₃) ₃	IV ^b	white	74 ^e	40.34	40.24	4.85	4.77
1,2,3,5-C ₆ H ₂ (CH ₃) ₄	II ^c	tan	25 ^f	41.25	41.46	4.99	5.03
C ₆ H ₅ OH	IV ^d	white	42 ^e	35.02	34.94	3.83	3.77
C ₆ H ₅ C ₆ H ₅	II ^c	cream	68 ^g	44.18	44.36	4.18	4.10
CH ₂ (C ₆ H ₅)CH=CH ₂	IV ^b	cream	36 ^k	40.36	40.40	4.32	4.39
<i>cis</i> -(C ₆ H ₅)CH=CHCH ₃	IV ^b	light tan	52 ⁱ	40.55	40.40	4.44	4.39
<i>trans</i> -(C ₆ H ₅)CH=CHCH ₃	II ^c	yellow	50 ^g	40.24	40.40	4.44	4.39
indene	II ^c	pale yellow	9 ^h	40.32	40.56	4.14	4.01
tetralin	II ^c	white	40 ^g	41.93	41.62	4.82	4.66
naphthalene	IV ^d	yellow	22 ^g	41.10	41.95	3.82	3.91
9,10-dihydroanthracene	II ^c	white	29 ^j	46.41	46.57	4.34	4.26
anthracene	IV ^d	dark yellow	29 ^g	47.37	46.73	3.97	3.92

^a See text. ^b Arene-acetone solvent system. ^c CH₂Cl₂-acetone solvent system. ^d Diethyl ether-acetone solvent system. ^e Yield after one recrystallization from CH₂Cl₂-(C₂H₅)₂O. ^f Yield after three recrystallizations from CH₂Cl₂-(C₂H₅)₂O. ^g Yield after two recrystallizations from CH₂Cl₂-(C₂H₅)₂O. ^h Yield after two recrystallizations from acetone-(C₂H₅)₂O. ⁱ Yield after two recrystallizations from CH₂Cl₂-tetrahydrofuran. ^j Recrystallized once from warm acetone. ^k Recrystallized once by adding diethyl ether to a 50:50 tetrahydrofuran-CH₂Cl₂ solution of the complex.

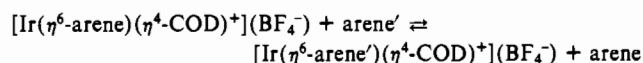
gave a white powder.¹⁵ AgOSO₂C₆H₄CH₃¹⁶ and Ag₂B₁₂Cl₁₂¹⁷ were prepared by literature procedures.

Infrared spectra were recorded on a Perkin-Elmer 597 spectrophotometer. Proton NMR spectra were recorded at 90 MHz on a Varian EM-390 spectrometer or at 180 MHz on a modified Bruker 42 kG multinuclear, pulse-FT NMR spectrometer equipped with Nicolet Technology Corp. software. Carbon-13 NMR spectra were recorded on the latter instrument at 45 MHz. Chemical shifts of all ¹H NMR spectra are reported in ppm with respect to internal Me₄Si standard; positive shifts are downfield. Chemical shifts of ¹³C NMR spectra were referred to the solvent and are reported as δ values in ppm units from Me₄Si according to the equations $\delta_{\text{CHCl}_3} = \delta_{\text{Me}_4\text{Si}} - 77.0$, $\delta_{\text{CH}_2\text{Cl}_2} = \delta_{\text{Me}_4\text{Si}} - 53.8$, and $\delta_{\text{C}_6\text{H}_6\text{O}} = \delta_{\text{Me}_4\text{Si}} - 25.3$. ¹³C chemical shifts are reported for ¹H-decoupled spectra; coupling constants were obtained from a separate gated decoupled spectrum.

Microanalyses were performed by Mr. Vazenken Tashinian at the Microanalytical Laboratory, Department of Chemistry, University of California at Berkeley.

Preparation of Solutions for Arene-Exchange Studies and Determination of Equilibrium Constants. Solutions for these experiments were normally prepared in a helium-filled drybox. A standard solution of the starting complex was prepared by dissolving a known quantity of the complex in the appropriate solvent and diluting to the mark in a 2- or 3-mL volumetric flask. Aliquots (0.50 mL) of the standard solution as well as any arenes (usually 1 equiv) or catalysts were directly syringed into an NMR tube which was sealed to a standard taper joint. The NMR tube was then attached to an appropriate stopcock assembly, passed out of the drybox, and attached to a high-vacuum line. All NMR tubes were torch sealed under vacuum. ¹H NMR spectra were recorded periodically, and progress of the reaction was followed by integration of the arene or cyclooctadiene vinyl protons. Equilibrium constants were calculated after no further change occurred in ratio of the two arene complexes. Temperature control, where necessary, was maintained by placing the NMR tubes in a heated oil bath. Most of the equilibrium constants were obtained at ambient temperature (24 ± 3 °C).

The full equilibrium constant expression for the arene-exchange equilibrium



is

$$K_{\text{eq}} = \frac{[[\text{Ir}(\eta^6\text{-arene}')(\eta^4\text{-COD})^+](\text{BF}_4^-)][\text{arene}]}{[[\text{Ir}(\eta^6\text{-arene})(\eta^4\text{-COD})^+](\text{BF}_4^-)][\text{arene}']}$$

Since equimolar quantities of arene' and $[\text{Ir}(\eta^6\text{-arene})(\eta^4\text{-COD})^+](\text{BF}_4^-)$ were present, this expression simplifies to

$$K_{\text{eq}} = \left(\frac{[[\text{Ir}(\eta^6\text{-arene}')(\eta^4\text{-COD})^+](\text{BF}_4^-)]}{[[\text{Ir}(\eta^6\text{-arene})(\eta^4\text{-COD})^+](\text{BF}_4^-)]} \right)^2 = R^2$$

where R is the ratio of the two complexes as determined by integration of the COD vinyl resonances in the ¹H NMR spectrum. Tables I-V, available as supplementary material, present data for a number of arene-exchange reactions. The data in Tables II-IV were used to prepare Figure 4.

Samples for the competitive arene-exchange experiments were prepared by the procedure given above. One molar equivalent of each arene was added per mole of starting arene complex. The results of three competition experiments between coordinated benzene and the isomeric xylenes as well as 1,2,3,4- and 1,2,4,5-C₆H₂(CH₃)₄ are shown in Table VI (see supplementary material). Another set of competition experiments between the C₆H₆ complex and 1,2,3- and 1,3,5-C₆H₃(CH₃)₃ and 1,2,3,4- and 1,2,4,5-C₆H₂(CH₃)₄ run at slightly lower concentrations (0.0719 M in acetone-*d*₆, 24 ± 3 °C) indicated that there was no dependence on the stereochemistry of methyl substitution in the formation of trimethylbenzene complexes. In good agreement with the data in Table VI, the ratio of coordinated 1,2,3,4-C₆H₂(CH₃)₄ to coordinated 1,2,4,5-C₆H₂(CH₃)₄ at the completion of the experiment (defined as complete displacement of coordinated benzene) was 4.63.

A final set of competitive arene-exchange experiments were run between $[\text{Ir}(\eta^6\text{-C}_6\text{H}_6)(\eta^4\text{-COD})^+](\text{BF}_4^-)$ (0.0605 M in acetone-*d*₆, 24 ± 3 °C) and three pairs of methylbenzenes: 1,2,3,4-C₆H₂(CH₃)₄ and 1,2,3,5-C₆H₂(CH₃)₄; 1,2,3,4-C₆H₂(CH₃)₄ and 1,3,5-C₆H₃(CH₃)₃; 1,2,3,4-C₆H₂(CH₃)₄ and C₆(CH₃)₆. The results of these experiments are discussed in the text.

Tables VII-IX, available as supplementary material, summarize kinetic data for some arene-exchange and isomerization reactions. These data are graphically presented in Figures 2, 3, and 5, respectively; vide infra.

Preparation of $[\text{Ir}(\eta^6\text{-arene})(\eta^4\text{-c-1,5-C}_6\text{H}_{12})^+](\text{X}^-)$ Complexes (X = BF₄⁻, PF₆⁻, OSO₂CF₃⁻, *p*-OSO₂C₆H₄CH₃⁻, or (B₁₂Cl₁₂)_{1/2}⁻). The $[\text{Ir}(\eta^6\text{-arene})(\eta^4\text{-c-1,5-C}_6\text{H}_{12})^+](\text{X}^-)$ complexes were prepared by five methods. Examples of methods I-III were given in our previous report;¹¹ examples of methods IV and V are given below. We previously reported the preparation of nine tetrafluoroborate salts;¹¹ the synthetic details and ¹H NMR data for the remaining complexes prepared during the course of this study are presented in Tables X-XIII. ¹³C NMR data are presented in Table XIV.

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Table XI. Synthetic and Analytical Data for $[\text{Ir}(\eta^6\text{-arene})(\eta^4\text{-}o\text{-}1,5\text{-C}_8\text{H}_{12})^+](\text{X}^-)$ Complexes

arene	X	method of prepn	color	yield, %	% C		% H	
					obsd	calcd	obsd	calcd
C_6H_6	OSO_2CF_3	I ^a	white	16 ^b	34.13	34.15	3.50	3.44
1,4- $\text{C}_6\text{H}_4(\text{CH}_3)_2$	OSO_2CF_3	II ^c	ivory	62 ^b	36.72	36.75	4.04	3.99 ^d
1,4- $\text{C}_6\text{H}_4(\text{CH}_3)_2$	PF_6	IV ^j	white	22 ^b	34.95	34.84	4.09	4.02 ^e
1,4- $\text{C}_6\text{H}_4(\text{CH}_3)_2$	$(\text{B}_{12}\text{Cl}_{12})_{1/2}$	II ^c	white	14 ^f	28.25	28.09	3.36	3.24
1,2,3,4- $\text{C}_6\text{H}_2(\text{CH}_3)_4$	1,4- $\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_3$	II ^g	white	97 ^h	49.61	49.56	5.55	5.49 ⁱ

^a Benzene solvent system. ^b Yield after two recrystallizations from dichloromethane–diethyl ether. ^c Acetone–dichloromethane solvent system. ^d % S: obsd, 5.65; calcd, 5.77. ^e % P: obsd, 5.74; calcd, 5.62. ^f Crystallized from reaction upon addition of diethyl ether.

^g Acetone–dichloromethane–ethanol solvent system. ^h Yield after two recrystallizations from dichloromethane–diethyl ether–pentane. ⁱ % S: obsd, 5.16; calcd, 5.29. ^j Arene–dichloromethane–acetone solvent system.

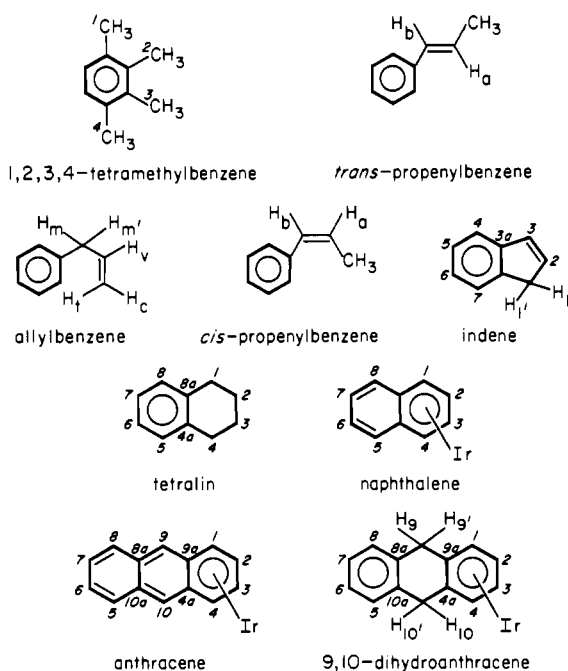


Figure 1. Labeling scheme used in Tables XII and XIV.

Method IV. Preparation of $[\text{Ir}(\eta^6\text{-C}_6\text{H}_5\text{OH})(\eta^4\text{-}o\text{-}1,5\text{-C}_8\text{H}_{12})^+](\text{BF}_4^-)$. A 50-mL round-bottom flask equipped with a side-arm stopcock was charged with a Teflon-coated stirring bar, 0.20 g (0.27 mmol) of $[\text{Ir}(\eta^4\text{-}o\text{-}1,5\text{-C}_8\text{H}_{12})\text{HCl}]_2$, and 0.5 g (5.3 mmol) of phenol under an inert atmosphere. The flask was sealed with a rubber septum, and 5 mL of diethyl ether added via syringe. In a separate flask 0.21 g (1.1 mmol) of AgBF_4 was dissolved in 5 mL of acetone under N_2 . The solution of the silver salt was then added to the stirred slurry of the iridium complex via catheter tubing at room temperature. An immediate reaction occurred; the mixture developed a pale orange cast, and AgCl precipitated. After stirring 1 h at room temperature, the reaction mixture was filtered through a fine frit (0.12 g of AgCl were recovered; 0.16 g were calculated). The pale yellow filtrate was concentrated to a volume of about 5 mL and the solution was flooded with 50 mL of diethyl ether. The supernatant was discarded, and the resulting white solid was washed with diethyl ether and dried under vacuum. The crude material was recrystallized from dichloromethane–diethyl ether to yield 110 mg of white microcrystals (42%).

Method V. Preparation of $[\text{Ir}(\eta^6\text{-}1,2\text{-C}_6\text{H}_4(\text{CH}_3)_2)(\eta^4\text{-}o\text{-}1,5\text{-C}_8\text{H}_{12})^+](\text{BF}_4^-)$. $[\text{Ir}(\eta^4\text{-}o\text{-}1,5\text{-C}_8\text{H}_{12})(\mu\text{-OCH}_3)]_2$ (0.10 g, 0.15 mmol) was dissolved in 7 mL of tetrahydrofuran under nitrogen. The dark yellow solution was treated with 1 mL of *o*-xylene and 0.26 mL (1.2 mmol, 48% aqueous solution) of HBF_4 . As the reaction was stirred at room temperature, a white solid gradually precipitated from solution. After ca. 36 h the white solid was separated from the supernatant by decantation, washed with diethyl ether, and dried under vacuum.

Subsequent recrystallization of the crude material from dichloromethane–diethyl ether yielded 40 mg (27%) of white needles which were characterized by comparison of their IR and NMR spectra with an authentic sample of the *o*-xylene complex prepared via method II. The nonvolatile materials from the reaction filtrate were examined by ^1H NMR and found to consist primarily of the *o*-xylene complex; no starting material was observed.

Preparation of $[\text{Ir}(\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{CH}=\text{CH}_2)(\eta^4\text{-}o\text{-}1,5\text{-C}_8\text{H}_{12})^+](\text{BF}_4^-)$. $[\text{Ir}(\eta^4\text{-}o\text{-}1,5\text{-C}_8\text{H}_{12})\text{HCl}]_2$ (0.30 g, 0.40 mmol) was slurried in 1 mL of freshly distilled acetone and 1 mL of distilled allylbenzene. The buff-colored slurry was treated with an acetone solution of AgBF_4 (0.31 g, 1.6 mmol, 3 mL) via catheter tubing. The reaction was stirred for 0.75 h at ambient temperature. The initial yellow coloration of the reaction mixture was then filtered through a fine frit and the AgCl washed with acetone (3×1 mL). The light yellow filtrate and washings were concentrated under vacuum to a volume of 5 mL and subsequently flooded with 50 mL of diethyl ether. The white solid was separated from the yellow supernatant by decantation, washed with pentane, and dried under vacuum. The crude product was dissolved in 6 mL of 1:1 tetrahydrofuran–dichloromethane mixture; the resulting solution was filtered under nitrogen. Diethyl ether was carefully added to the stirred filtrate until the solution became cloudy. Cooling to ca. -25°C yielded 100 mg (25%) of analytically pure cream crystals. Unnecessarily long reaction times or recrystallization procedures usually resulted in the isolation of the *cis*-propenylbenzene complex.

Preparation of $[\text{Ir}(\eta^6\text{-}1,5\text{-C}_8\text{H}_{12})(\text{CH}_3\text{CN})_2^+](\text{BF}_4^-)$. The acetonitrile adduct was prepared by reacting $[\text{Ir}(\eta^4\text{-}o\text{-}1,5\text{-C}_8\text{H}_{12})\text{Cl}]_2$ with AgBF_4 in the presence of CH_3CN . Green prepared the complex from $[\text{Ir}(\eta^4\text{-}1,5\text{-C}_8\text{H}_{12})_2^+](\text{BF}_4^-)$.²⁵ In contrast to the reported melting point ($107\text{--}108^\circ\text{C}$)²⁵ the complex only darkened up to 150°C . However, the compound was characterized by analysis, IR, and ^1H NMR. Anal. Calcd for $\text{IrC}_{12}\text{H}_{18}\text{N}_2\text{BF}_4$: C, 30.71; H, 3.87; N, 5.97. Found: C, 30.64; H, 3.92; N, 6.04. ^1H NMR (90 MHz, CDCl_3 , 35°C): δ 4.20 (br, 4.0 H, $\text{CH}=\text{CH}$), 2.59 (s, 6.1 H, CH_3CN), 2.25 and 1.73 (br m, 8.5 H, CH_2CH_2) (lit. δ 4.17, 2.39, 2.20, 1.74–1.65). IR (Nujol mull) $\nu(\text{CN})$: 2326, 2296 cm^{-1} (lit. 2317, 2292 cm^{-1}).

Preparation of $[\text{Ir}(\eta^4\text{-}o\text{-}1,5\text{-C}_8\text{H}_{12})(\text{acetone})_x](\text{BF}_4^-)$. $[\text{Ir}(\eta^4\text{-}o\text{-}1,5\text{-C}_8\text{H}_{12})\text{Cl}]_2$ (8.8 mg, 0.013 mmol) and AgBF_4 (5.1 mg, 0.026 mmol) were reacted in about 1 mL of acetone- d_6 in a helium-filled drybox. The reaction was allowed to stand overnight. Filtration gave a yellow solution. ^1H NMR (180 MHz, 25°C): δ 4.13 (br, 4.0 H, COD vinyl H), 2.34 (br m, COD methylene H), 1.54 (m, 4.4 H, COD methylene H).

Preparation of $[\text{Ir}(\eta^4\text{-}o\text{-}1,5\text{-C}_8\text{H}_{12})(\text{acetone})_x^+](\text{BF}_4^-)$. Alternative Procedure. AgBF_4 (0.18 g, 0.92 mmol) was dissolved in 3 mL of freshly distilled acetone and added to a suspension of $[\text{Ir}(\eta^4\text{-}o\text{-}1,5\text{-C}_8\text{H}_{12})\text{Cl}]_2$ (0.30 g, 0.45 mmol) in acetone (10 mL) under a nitrogen atmosphere. The mixture was stirred for 5 h at room temperature. The reaction was then filtered through a fine frit, and the resulting yellow filtrate was concentrated to a volume of ca. 1 mL. This yielded a small crop of orange crystals (starting material). The yellow supernatant was decanted into the bottom of a Schlenk tube containing a test tube. The test tube was filled with diethyl ether. After the Schlenk tube was sealed with a standard taper glass stopper, a slight vacuum was applied to the system, and the apparatus was placed in a refrigerator at -15°C . The resulting red oil was dried under vacuum at room temperature after decantation of the supernatant and removal

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Table XII. ¹H NMR Data for [Ir(η⁴-arene)(η⁴-c-1,5-C₆H₁₂)⁺](BF₄⁻) Complexes and Free Arenes

arene	free arene		coordinated arene		coordinated COD ^b	
	aromatic H	methyl or other H	aromatic H	methyl or other H	vinyl H	methylene H
C ₆ H ₆ ^c	7.36		6.83		4.80	2.28-2.05
1,2-C ₆ H ₄ (CH ₃) ₂ ^{c,d}	7.11 (br)	2.26	6.78 and 6.57 (AA'BB')	2.38	4.41	2.26-2.03
1,3-C ₆ H ₄ (CH ₃) ₂ ^c	7.19-6.95 (m)	2.31	6.83-6.50 (m)	2.47	4.42	2.23-1.99
1,2,3-C ₆ H ₃ (CH ₃) ₃	6.95 (br)	2.24 (6 H), 2.14 (3 H)	6.82 (m)	2.48 (6 H), 2.37 (3 H)	4.30	2.30-2.11
1,2,4-C ₆ H ₃ (CH ₃) ₃	6.94 (m)	2.23 (3 H), 2.18 (6 H)	6.86 (d, J = 6.2 Hz), 6.71 (s), 6.63 (d, J = 6.2 Hz)	2.52, 2.48, 2.47	4.32	2.29-2.12
1,3,5-C ₆ H ₃ (CH ₃) ₃ ^c	6.80	2.28	6.56	2.43	4.23	2.28-2.05
1,2,3,4-C ₆ H ₂ (CH ₃) ₄ ^c	6.90	2.26, 2.19	6.62	2.39, 2.21	3.99	2.18-2.02
1,2,3,5-C ₆ H ₂ (CH ₃) ₄	6.78 (br)	2.20 (9 H), 2.09 (3 H)	6.77 (br)	2.47 (3 H), 2.43 (6 H), 2.35 (3 H)	4.13	2.28-2.11
1,2,4,5-C ₆ H ₂ (CH ₃) ₄ ^c	6.84	2.17	6.35	2.37	4.09	2.16-2.02
C ₆ H ₅ OH ^e	7.25 (m), 6.93 (m), 6.85 (m)	ca. 4.8 (br, OH)	6.62 (m), 6.49 (m), 6.37 (m)	9.04 (br, OH)	4.57	2.32-2.05
C ₆ H ₅ C ₆ H ₅ ^c	7.62-7.56 (m), 7.49-7.34 (m)		7.10-6.88 (m)	7.73-7.67 (m, free aryl), 7.54-7.50 (m, free aryl)	4.58	2.22-1.93
C ₆ H ₅ CH ₂ CH=CH ₂ ^e	7.29-7.18 (m)	6.00 (q of t, J _{v,m} = 6.7, J _{v,t} = 17.0, J _{v,c} = 10.0 Hz, H _v), ca. 5.08 (d of "q", J _{t,v} = ca. 17, J _{t,m} = ca. 1.4, J _{t,c} = ca. 2.1 Hz, H _t), 5.03 (d of "q", J _{c,v} = ca. 1.0, J _{c,m} = ca. 1.3, J _{c,t} = ca. 2.1 Hz, H _c), 3.38 (d, J _{m,v} = 6.7 Hz, H _m)	7.21-6.87 (m)	6.12 (q of t, J _{v,m} = 6.9, J _{v,t} = 17.0, J _{v,c} = 10.1 Hz, H _v), 5.35 (d of "q", J _{t,v} = 17.1, J _{t,c} = 1.6 Hz, H _t), 5.28 (d of "q", J _{c,v} = 10.1, J _{c,t} = 1.7 Hz, H _c), 3.62 (d of t, J _{m,v} = 6.9, J _{m,c/t} = ca. 1.3 Hz, H _m)	4.72	2.28-2.13
C ₆ H ₅ CH ₂ CH=CH ₂ ^{e,e}	7.34-7.17 (m)	5.98 (q of t, J _{v,m} = 6.7, J _{v,t} = 17.6, J _{v,c} = 9.5 Hz, H _v), 5.12, 5.10, 5.04 (m, H _c and H _t), 3.40 (d, J _{m,v} = 6.6 Hz, H _m)	7.02-6.61 (m)	5.96 (q of t, J _{v,m} = 6.9, J _{v,t} = 17.1, J _{v,c} = 9.8 Hz, H _v), 5.34, 5.26 (m, H _c and H _t), 3.48 (d, J _{m,v} = 6.9 Hz, H _m)	4.66	2.26-2.03
cis-C ₆ H ₅ CH=CHCH ₃ ^e	7.35-7.17 (m)	6.44 (d of m, J _{b,Me} = 1.6, J _{a,a} = 11.7 Hz, H _b), 5.78 (d of q, J _{a,Me} = 7.1, J _{a,b} = 11.6 Hz, H _a), 1.87 (d of d, J _{Me,a} = 7.2, J _{Me,b} = 1.8 Hz, H _{Me})	ca. 7.2-6.9 (m)	6.43 (d of m, J _{b,Me} = ca. 1.3, J _{a,b} = 11.6 Hz, H _b), 6.29 (d of q, J _{a,Me} = ca. 7, J _{a,b} = 11.6 Hz, H _a), 2.10 (d of d, J _{Me,a} = 7, J _{Me,b} = 1.4 Hz, H _{Me})	4.69	2.27-2.12
cis-C ₆ H ₅ CH=CHCH ₃ ^{e,e}	7.39-7.18 (m)	6.43 (d of m, J _{b,Me} = 1.7, J _{a,a} = 11.6 Hz, H _b), 5.79 (d of q, J _{a,Me} = 7.2, J _{a,b} = 11.6 Hz, H _a), 1.91 (d of d, J _{Me,a} = 7.1, J _{Me,b} = 1.8 Hz, H _{Me})	6.98 ("t", J = 6 Hz), 6.81 ("t", J = 6 Hz), 6.67 ("d", J = 6 Hz)	6.22 (m, H _a and H _b), ca. 2.07 (H _{Me})	4.66	2.26-2.02
trans-C ₆ H ₅ CH=CHCH ₃ ^e	7.39-7.17 (m)	6.43 (d of m, J _{b,a} = 16.1 Hz, H _b), 6.28 (d of q, J _{a,b} = 15.8, J _{a,Me} = 6 Hz), 1.85 (d of m, J _{Me,a} = 6 Hz, H _{Me})	7.10-6.92 (m)	6.74 (d of q, J _{a,b} = 15.8, J _{a,Me} = 6.6 Hz, H _a), 6.45 (d of m, J _{b,a} = 15.8, J _{b,Me} = 1.5 Hz, H _b), 2.00 (d of d, J _{Me,a} = 6.6, J _{Me,b} = 1.5 Hz, H _{Me})	4.62	2.35-2.14
trans-C ₆ H ₅ CH=CHCH ₃ ^{e,e}	7.35-7.13 (m)	6.41 (d of m, J _{b,a} = 15.8, J _{b,Me} = 1.0 Hz, H _b), 6.23 (d of q, J _{a,b} = 15.7, J _{a,Me} = 6.2 Hz, H _a), 1.88 (d of d, J _{Me,a} = 6.2, J _{Me,b} = 0.8 Hz, H _{Me})	6.89-6.76 (m)	6.59 (d of q, J _{a,b} = 15.7, J _{a,Me} = 6.6 Hz, H _a), 6.21 (d of q, J _{b,a} = 15.8, J _{b,Me} = 1.5 Hz, H _b), 2.01 (d of d, J _{Me,a} = 6.5, J _{Me,b} = 1.5 Hz, H _{Me})	4.56	2.25-2.07

tetraline	7.07 (br)	2.77 (m, H(1,4) or H(2,3)), 1.79 (m, H(2,3) or H(1,4))	6.99 and 6.07 (AA'BB')	2.88 (m, H(1)-H(4))	4.44	2.27-1.88
naphthalene ^{c,g}	7.85 (H(1,4)) and 7.48 (H(2,3)) (AA'BB')		7.32 (H(1,4)) and 6.89 (H(2,3)) (AA'BB')	7.89 (m, H(5)-H(8))	4.76	1.88 (br)
9,10-dihydroanthracene ^h	7.30 (H(1,4)) and 7.17 (H(2,3)) (AA'BB')	3.91 (s, H(9,10))	7.28 (H(1,4)) and 6.60 (H(2,3)) (AA'BB')	7.5-7.35 (m, H(5)-H(8)), 4.30 (^c q, ^j A,B = 17, Δ = 33 Hz, H(9,9') and H(10,10'))	4.39	1.84-1.66
anthracene ^{c,g,i} (7)	8.42 (s, H(9,10)), 8.00 (H(1,4)), and 7.46 (H(2,3)) (AA'BB')		ca. 7.27 (H(1,4)) and 7.09 (H(2,3)) (AA'BB')	8.10 (H(5,8)) and 7.90 (H(6,7)) (AA'BB'), 8.43 (s, H(9,10))	4.93	1.87 (br)
indene ^{c,f} (8)	7.50-7.39 (m, H(5,8)) or H(6,7)), 7.31-7.14 (m, H(6,7) or H(5,8))	6.89 (m, H(3)), 6.56 (m, H(2)), 3.40 (br, H(1,1'))	7.70 (s, H(9,10))	7.70 (H(1,4) or H(2,3)), 8.10 (H(2,3) or H(1,4)) (AA'BB')	4.67	1.87 (br)

^a Unless otherwise noted, spectra were measured at 180 MHz in acetone-*d*₆ solution at approximately 25 °C. Chemical shifts are referred to internal Me₄Si standard; downfield shifts are positive. A labeling scheme is provided in Figure 1. ^b Uncoordinated 1,5-cyclooctadiene (COD) exhibits broad peaks at 5.59 and 2.37 ppm. ^c Determined in CDCl₃. ^d ¹H NMR methyl resonances for all of the methyl substituted benzenes have been assigned by Woolfenden and Grant.¹⁸ ^e The resonances for H_a and H_b in *cis*- and *trans*-propenylbenzene and their complexes are interpreted in a first-order fashion with all coupling constants positive. These resonances appear as an AB "quartet" with one pair of "doublets" clearly split by the methyl group. Similarly a simplistic, first-order interpretation of the H_c and H_e resonances is employed for the allylbenzene case. ^f Resonances for indene were assigned by Elleman and Manatt.¹⁹ ^g ¹H NMR resonances for naphthalene and anthracene were assigned by Jonathon, Gordon, and Dailley.²⁰ ^h ¹H NMR resonances for 9,10-dihydroanthracene were assigned by analogy with anthracene. ⁱ ¹H NMR resonances for the anthracene complex were assigned by analogy with the naphthalene complex and [Cr(η⁶-anthracene)(CO)]₂.²¹ See ref 38 for an explanation of complexes 7 and 8.

of the test tube from the Schlenk tube. This material gave a red-brown solution in acetone-*d*₆. ¹H NMR (90 MHz, acetone-*d*₆, 35 °C): δ 4.07 (br, COD, vinyl H), 2.26 (m, COD methylene H), 2.07 (s, acetone methyl), 1.50 (m, COD methylene H). ¹H NMR (180 MHz, acetone-*d*₆, 30 °C) δ 4.11 (br), 2.30 (br m), 2.10 (s), 1.51 (m).

Preparation of [Ir(η⁴-c-1,5-C₈H₁₂)[S(C₂H₅)₂]⁺](BF₄⁻). [Ir(η⁴-c-1,5-C₈H₁₂)(acac)] (0.20 g, 0.50 mmol) was dissolved in 5 mL of a 4:1 dichloromethane-diethyl sulfide mixture under nitrogen. The yellow solution was then treated with a solution of trityl tetrafluoroborate (0.16 g, 0.50 mmol) dissolved in 4:1 dichloromethane-diethyl sulfide (5 mL). The homogeneous reaction developed an orange-red color and was stirred overnight at room temperature. Addition of 85 mL of diethyl ether gave a red oil. After the flask was chilled to ca. -25 °C, the orange supernatant was decanted via catheter tubing. The red oil was "recrystallized" by diffusing diethyl ether into an acetone solution of the complex in the same manner as for the acetone complex above. ¹H NMR (90 MHz, acetone-*d*₆, 35 °C): δ 4.41 (br, 4.0 H, COD vinyl H), 3.09 (q, *J* = 7.2 Hz, 9.3 H, methylene H of S(C₂H₅)₂), ca. 2.2 (m, COD methylene H), 1.87 (m, COD, methylene H), 1.45 (t, *J* = 7.5 Hz, methyl H of S(C₂H₅)₂). ¹H NMR (90 MHz, CDCl₃, 35 °C): δ 4.28 (br, 4.0 H, COD vinyl H), 3.00 (q, *J* = 7.5 Hz, 9.1 H, methylene H of S(C₂H₅)₂), 2.23 (br m, COD methylene H), 1.86 (m, COD methylene H), 1.45 (t, *J* = ca. 7.5, methyl H of S(C₂H₅)₂). Addition of excess diethyl sulfide to a chloroform solution of [Ir(η⁴-COD)[S(C₂H₅)₂]⁺](BF₄⁻) at room temperature resulted in a shift of the methylene and methyl resonances of diethyl sulfide to 2.59 and 1.29 ppm, respectively.

Preparation of [Ir(η⁶-CH₃C₆H₄SO₃)(η⁴-c-1,5-C₈H₁₂)] (1). [Ir(η⁴-c-1,5-C₈H₁₂)(μ-OCH₃)₂] (0.16 g, 0.24 mmol) and a Teflon-coated stirring bar were placed in a 50-mL round-bottom flask equipped with a side-arm stopcock. The complex was dissolved in 6 mL of a 1:1 tetrahydrofuran-dichloromethane solution under nitrogen to give a dark yellow solution. *p*-Toluenesulfonic acid monohydrate (ca. 0.1 g, 0.53 mmol) was added to the solution against an N₂ counterstream. No obvious reaction occurred. After the solution was stirred for 11 h at room temperature, the volatiles were removed under vacuum. The residue was twice recrystallized from dichloromethane-diethyl ether to yield 60 mg of an ivory microcrystalline powder (26%) (mp 189-191 °C, darkened above ca. 70 °C). Anal. Calcd for IrC₁₅H₁₉O₃S: C, 38.20; H, 4.06; N, 0.00. Found: C, 38.20; H, 4.33; N, 0.03. ¹H NMR (90 MHz, CDCl₃, 35 °C): δ 7.16 (d, *J* = 6.4 Hz, tosylate phenyl), 6.59 (d, *J* = 6.4 Hz, 2.0 H, tosylate phenyl), 4.63 (br, 3.8 H, COD vinyl H), 2.34 (s, tosylate methyl), 2.17 (m, COD methylene H), the last two peaks integrate as 10.5 H. IR (Nujol mull) ν(SO): 1240 (s, br), 1100 (s), 1040 cm⁻¹ (s). A chloroform solution of **1** stood for ca. 4 h at room temperature. A new set of resonances in the ¹H NMR spectrum attributed to an O-bonded tosylate complex, **2**, grew in at the expense of the starting material. Evaporation of the yellow solution gave a yellow oil. ¹H NMR (90 MHz, CDCl₃, 35 °C): δ 7.52 (d, *J* = 7.8 Hz, tosylate phenyl), 7.03 (d, *J* = ca. 8.1 Hz, tosylate phenyl), 4.45 (br, COD vinyl H), 2.31 (s, tosylate methyl), ca. 2.2 (m, COD methylene H), 1.36 (m, COD methylene H). IR (Nujol mull) ν(SO): 1263 (s, br), 1158 (s), 1103 (s), 1028 (s), 1000 cm⁻¹ (s, br). See ref 71 and Table XV in the supplementary material.

Preparation of [Ir(η⁶-C₆H₆)(η⁴-c-1,5-C₈H₁₂)](OSO₂C₆H₄CH₃⁻) (3). [Ir(η⁴-c-1,5-C₈H₁₂)Cl]₂ (0.20 g, 0.30 mmol) was dissolved in 5 mL of tetrahydrofuran under nitrogen. The orange solution was added to a rapidly stirred slurry of silver tosylate (0.17 g, 0.60 mmol) in 5 mL of tetrahydrofuran. Addition of ca. 0.5 mL of absolute ethanol to the orange mixture resulted in an immediate yellow coloration. The reaction was stirred for 18 h at room temperature and then filtered through a fine frit. Approximately 80 mg of AgCl was recovered (calculated 86 mg). The yellow filtrate was concentrated to a volume of ca. 7 mL and treated with 50 mL of benzene. The solution was set aside for 24 h and then evaporated under vacuum. The crude product was precipitated from benzene-heptane and dichloromethane-benzene-heptane mixtures to yield 0.13 g of a yellow powder. Anal. Calcd for IrCl₂H₂₅SO₃: C, 45.88; H, 4.58; N, 0.00. Found: C, 42.47; H, 4.41; N, 0.02. ¹H NMR (90 MHz, CDCl₃, 35 °C): δ 7.70 (d, *J* = 8.3 Hz, tosylate phenyl), 7.08 (d, *J* = 8.3 Hz, tosylate phenyl), 6.89 (s, coordinated C₆H₆), 4.75 (br, COD vinyl H), 2.33 (s, tosylate methyl), 2.1 (m, COD methylene H). IR (Nujol mull) ν(SO): 1270 (s), 1175 (ms), 1158 (s), 1108 (s), 1030 (ms), 997 cm⁻¹ (s). The benzene in this compound could not be removed by heating for 31 h at temperatures up to 90 °C. In addition to resonances

Table XIII. ^1H NMR Data for $[\text{Ir}(\eta^6\text{-arene})(\eta^4\text{-c-1,5-C}_8\text{H}_{12})^+](\text{X}^-)$ Complexes

arene	X	X	^1H chemical shifts, ppm ^a			
			coordinated arene		coordinated COD	
			aromatic H	methyl H	vinyl H	methylene H
C_6H_6	OSO_2CF_3		7.02		4.76	2.14
1,4- $\text{C}_6\text{H}_4(\text{CH}_3)_2$	$\text{OSO}_2\text{CF}_3^b$		6.58	2.45	4.36	2.11
1,4- $\text{C}_6\text{H}_4(\text{CH}_3)_2$	PF_6		6.73	2.50	4.39	2.13
1,4- $\text{C}_6\text{H}_4(\text{CH}_3)_2$	$(\text{B}_{12}\text{Cl}_{12})_{1/2}^c$		6.83	2.56	4.50	2.31-2.15
1,2,3,4- $\text{C}_6\text{H}_2(\text{CH}_3)_4$	1,4- $\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_3^b$	7.73 (d), 7.03 (d, $J = 8.0$ Hz), 2.29 (s)	6.89	2.36, 2.14	3.92	2.07

^a Unless otherwise noted, spectra were measured at 90 MHz in acetone- d_6 at approximately 35 °C; downfield shifts are positive. ^b Determined in CDCl_3 . ^c Determined at 180 MHz (27 °C).

Table XIV. ^{13}C NMR Data for Selected Iridium Complexes

complex	^{13}C chemical shift, ppm ($J^{13}\text{C-H}$, Hz) ^a		
	arene carbon	COD vinyl C ^b	COD methylene C
$[\text{Ir}(\eta^4\text{-c-1,5-C}_8\text{H}_{12})\text{Cl}]_2$		62.19 (d, $J = 160$)	31.78 (t, $J = 127$)
$[\text{Ir}(\eta^6\text{-C}_6\text{H}_6)(\eta^4\text{-COD})^+](\text{BF}_4^-)^d$	98.75 (d, $J = 180$)	63.29 (d, $J = 158$)	32.80 (t, $J = 129$)
$\{\text{Ir}[\eta^6\text{-1,2-C}_6\text{H}_4(\text{CH}_3)_2](\eta^4\text{-COD})^+\}(\text{BF}_4^-)$	113.96 (s, C(1,2)), 98.32 (d, $J = 174$, C(3,6)), ^c 97.21 (d, $J = 174$, C(4,5)), ^c 17.14 (q, $J = 129$, CH_3)	64.32 (d, $J = 154$)	32.53 (t, $J = 128$)
$\{\text{Ir}[\eta^6\text{-1,3,5-C}_6\text{H}_3(\text{CH}_3)_3](\eta^4\text{-COD})^+\}(\text{BF}_4^-)$	113.29 (s, C(1)), 98.43 (d, $J = 175$, C(2)), 18.04 (q, $J = 130$, CH_3)	64.78 (d, $J = 155$)	32.46 (t, $J = 128$)
$\{\text{Ir}[\eta^6\text{-1,2,3,4-C}_6\text{H}_2(\text{CH}_3)_4](\eta^4\text{-COD})^+\}(\text{BF}_4^-)$	112.97 (s, C(1,4)), 110.66 (s, C(2,3)), 97.02 (d, $J = 177$, C(5,6)), 18.03 (q, $J = 130$, C(Me1,Me4)), ^c 14.12 (q, $J = 130$, C(Me2,Me3)) ^c	65.72 (d, $J = 158$)	32.48 (t, $J = 129$)
$\{\text{Ir}[\eta^6\text{-C}_6(\text{CH}_3)_6](\eta^4\text{-COD})^+\}(\text{BF}_4^-)$	109.97 (s, C(1)), 15.60 (q, $J = 129$, CH_3)	67.45 (d, $J = 155$)	32.72 (t, $J = 128$)
$[\text{Ir}(\eta^4\text{-tetralin})(\eta^4\text{-COD})^+](\text{BF}_4^-)$	117.90 (s, C(4a,8a)), 100.29 (d, $J = 179$, C(6,7)), 91.12 (d, $J = 176$, C(5,8)), 26.79 (t, $J = 132$, C(1,4)), ^c 21.62 (t, $J = 129$, C(2,3)) ^c	65.04 (d, $J = 157$)	32.68 (t, $J = 131$)
$[\text{Ir}(\eta^6\text{-naphthalene})(\eta^4\text{-COD})^+](\text{BF}_4^-)^d$	111.71 (s, C(4a,8a)), 100.87 (d, $J = 179$, C(2,3)), 87.20 (d, $J = 176$, C(1,4)), 133.35 (d, $J = 165$, C(6,7)), 127.30 (d, $J = 168$, C(5,8))	66.22 (d, $J = 158$)	32.15 (t, $J = 130$)
$[\text{Ir}(\text{anthracene})(\eta^4\text{-COD})^+](\text{BF}_4^-)^d, e$ (7)	99.87 (d, $J = 180$, C(2,3)), 86.12 (d, $J = 174$, C(1,4)), 109.60 (s, C(4a,9a)), 127.11 (d, $J = 164$, C(9,10) or C(5,8)), 129.09 (d, $J = 162$, C(5,8) or C(9,10)), 132.67 (d of d, $J = 165$, $J = \text{ca. } 8.5$, C(6,7)), 135.29 (s, C(8a,10a))	68.40 (d, $J = 159$)	32.20 (t, $J = 129$)
(8)	81.12 (d, $J = 172$, C(9,10)), 110.07 (s, C(4a,9a,8a,10a)), 126.97 (d, $J = \text{ca. } 165$, C(1,4) or C(2,3)), 128.82 (d, $J = 162$, C(2,3) or (1,4))	66.97 (d, $J = 161$)	31.41 (t, $J = 125$)

^a Unless otherwise indicated, spectra were determined at 45 MHz in CDCl_3 at 20 °C. Chemical shifts are relative to external Me_4Si standard (see Experimental Section); downfield shifts are positive. A labeling scheme is provided in Figure 1. ^b ^{13}C NMR data for uncoordinated *o*-xylene, mesitylene, 1,2,3,4- $\text{C}_6\text{H}_2(\text{CH}_3)_4$, tetralin, and hexamethylbenzene are given in ref 22. ^c ^{13}C data for naphthalene and benzene appear in ref 23 and 24, respectively. ^d The chemical shift of the vinyl carbon of free 1,5-cyclooctadiene (COD) is 128.5 ppm.¹⁴ ^e Assignments of these peaks may be interchanged. ^d Determined in CD_2Cl_2 . ^e See ref 38 for an explanation of these assignments.

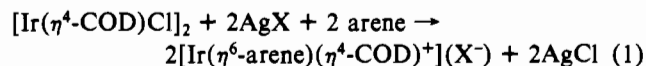
attributed to the benzene complex, another set of resonances were present which were attributed to an O-bonded complex, **4**. ^1H NMR (90 MHz, CDCl_3 , 35 °C): δ 4.35 (br, COD vinyl H), 1.23 (mult, COD methylene H) (the other resonances for this complex were superimposed on **3**). Allowing the mixture of **3** and **4** to stand at room temperature eventually gave an equilibrium mixture of **1**, **3**, **5**, and free C_6H_6 . A tentative proposal for the structures of complexes **2**, **4**, and **5** is given in ref 71 (see also Table XV in the supplementary material).

Preparation of $[\text{Ir}(\eta^6\text{-1,2,3,4-C}_6\text{H}_2(\text{CH}_3)_4)(\eta^4\text{-c-1,5-C}_8\text{H}_{12})^+](\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_3^-)$ (6**).** Silver tosylate (0.13 g, 0.45 mmol) was treated with 4 mL of acetone, 0.3 mL of absolute ethanol, and 0.5 mL of 1,2,3,4-tetramethylbenzene under nitrogen. This rapidly stirred slurry was treated with a solution of $[\text{Ir}(\eta^4\text{-c-1,5-C}_8\text{H}_{12})\text{Cl}]_2$ (0.15 g, 0.22 mmol) in dichloromethane (4 mL). The resulting yellow mixture was stirred for 14 h at room temperature and then filtered through a fine frit. The pale yellow filtrate was concentrated to a volume of ca. 4 mL and treated with ca. 70 mL of diethyl ether. The clear supernatant was separated by decantation and the crude product dried under vacuum. Successive recrystallizations from dichloromethane–diethyl ether–pentane and dichloromethane–diethyl ether gave 260 mg (97%) of white acicular crystals. (See Tables XI and XIII.) IR (Nujol mull)

$\nu(\text{SO})$: 1210 (s, br), 1120 (s), 1035 (s), 1013 cm^{-1} (s).

Results and Discussion

Synthesis and Characterization of $[\text{Ir}(\eta^6\text{-arene})(\eta^4\text{-c-1,5-C}_8\text{H}_{12})^+](\text{X}^-)$ Complexes. Five methods were used in the preparation of salts of the cationic iridium arene complexes. Two methods were minor modifications of the Schrock–Osborn^{26,27} procedure (eq 1) and differed only in the solvent

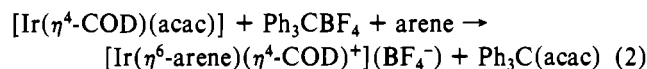


system employed: benzene or toluene in method I and tetrahydrofuran or, more commonly, a dichloromethane–acetone mixture in method II. (Occasional polymerization of tetrahydrofuran under the reaction conditions limited the utility of this solvent.) Electrophilic attack on coordinated 2,4-

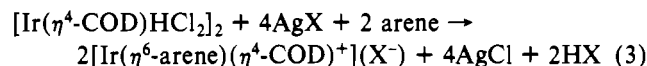
(26) R. R. Schrock and J. A. Osborn, *J. Am. Chem. Soc.*, **93**, 3089 (1971).

(27) R. R. Schrock, Ph.D. Thesis, Harvard University.

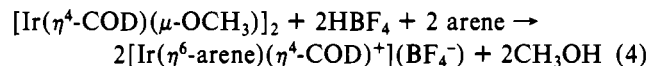
pentanedionate in $[\text{Ir}(\eta^4\text{-COD})(\text{acac})]$ in the presence of an arene was used in method III (eq 2).^{28,29} The most convenient,



general route to the arene complexes was method IV (eq 3).



The fifth method (eq 4) involved protonation of $[\text{Ir}(\eta^4\text{-COD})(\mu\text{-OCH}_3)]_2$



$[\text{Ir}(\eta^4\text{-COD})(\mu\text{-OCH}_3)]_2$ ¹³ in the presence of an arene; presumably protonation generated a highly coordinately unsaturated species, $[\text{Ir}(\eta^4\text{-COD})(\text{CH}_3\text{OH})^+]$, by dimer cleavage. This reaction was useful in preparing the π -tosylate derivative (see ref 71).³⁰ A summary of synthetic details for the $[\text{Ir}(\eta^6\text{-arene})(\eta^4\text{-COD})^+](\text{X}^-)$ complexes prepared in this work is presented in Tables X and XI.

Proton NMR data for the iridium arene complexes are presented in Tables XII and XIII. Arene resonances were temperature independent as observed by Schrock^{26,27} and Green²⁸ as was expected since arene rotation about the M-C₆ centroid is rapid.³³ Resonances of protons directly bound to the arene ring generally shifted upfield by 0.1–0.5 ppm upon coordination. No correlation between the magnitude of the upfield shift and the stability of the arene complex was discernible.^{32,37a} Arenes containing two or more possible coordination sites (e.g., biphenyl or naphthalene) always showed sharp, discrete signals for the free and coordinated ring sections in the ¹H NMR of the complex.³⁸ ¹H NMR spectra of the

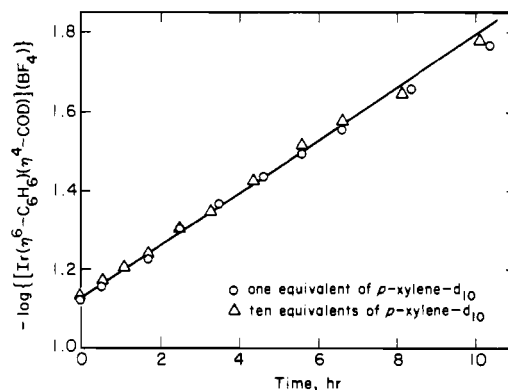
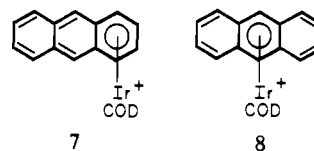


Figure 2. Plot of $-\log [[\text{Ir}(\eta^6\text{-C}_6\text{H}_6)(\eta^4\text{-c-1,5-C}_6\text{H}_{12})^+](\text{BF}_4^-)]$ vs. time for the exchange between $[\text{Ir}(\eta^6\text{-C}_6\text{H}_6)(\eta^4\text{-c-1,5-C}_6\text{H}_{12})^+](\text{BF}_4^-)$ and 1 or 10 equiv of *p*-xylene-*d*₁₀ in acetone-*d*₆ at 35 °C. Both sets of data are plotted on the graph. A first-order dependence on the benzene complex is indicated (see Table VII).

propenylbenzene complexes clearly indicated that the arene was interacting with the metal and not the olefinic moiety (a negligible or even downfield shift was observed for these protons). The coupling constants within the propenyl group, interpreted in a first-order manner, were consistent with literature values:⁴¹ J_{cis} and J_{trans} were typically 10–12 and 16–17 Hz, respectively. No change in these coupling constants occurred upon coordination. The AB pattern observed for the

- (38) The anthracene complex was unusual in that two species, **7** and **8**, were clearly present in chlorocarbon solutions of $[\text{Ir}(\text{anthracene})(\eta^4\text{-COD})^+](\text{BF}_4^-)$. On the basis of ¹H and ¹³C NMR data the following structures were assigned to species **7** and **8**:



The ¹H NMR spectrum of $[\text{Ir}(\text{anthracene})(\eta^4\text{-COD})^+](\text{BF}_4^-)$ in CDCl₃ indicated the presence of free anthracene and two $[\text{Ir}(\text{COD})]^+$ moieties which were present in a 3:1 ratio (δ 4.93 and 4.68, respectively). We attribute the free anthracene to an impurity rather than to an equilibrium of the form $[\text{Ir}(\text{anthracene})(\eta^4\text{-COD})^+](\text{BF}_4^-) \rightleftharpoons [\text{Ir}(\eta^4\text{-COD})^+](\text{BF}_4^-) + \text{anthracene}$ since this would require the presence of three $[\text{Ir}(\text{COD})]^+$ moieties in solution. An alternate interpretation that the COD vinyl resonances of **7** and **8** both appear at 4.93 ppm and the solvated $[\text{Ir}(\text{COD})]^+$ species appears at 4.68 ppm cannot be excluded without further study.

The ¹H NMR spectrum in the arene region was complicated owing to the many types of arene protons present, but by analogy to the Cr(CO)₃ analogue²¹ we were able to assign the peaks attributed to **7**. The peaks attributed to **8** partially overlap with **7** as indicated in Table XIV. The hydrogen atoms at the 9,10 position of **8** resonate at 7.70 ppm; a 0.7-ppm coordination shift from the free arene is consistent with this assignment.

The ¹³C NMR spectrum of $[\text{Ir}(\text{anthracene})(\text{COD})^+](\text{BF}_4^-)$ in CD₂Cl₂ clearly indicated the presence of two $[\text{Ir}(\text{COD})]^+$ species. Five resonances were observed in the coordinated arene region (including two quaternary carbons). Three of these are assigned to **7** and two to **8**. Ten lines were observed in the free-arene region. Four of these resonances were assigned to free anthracene;³⁹ the other six were assigned to **7** and **8** on the basis of intensity and coupling patterns expected for polycyclic aromatic hydrocarbons.³⁹

Other possible structures for species **8** such as η^4 -anthracene moieties or dinuclear complexes would not account for the spectroscopic data. The possibility of a dihydroanthracene complex as observed in the $[\text{Fe}(\eta^3\text{-C}_5\text{H}_5)]^+$ -anthracene system⁴⁰ can be excluded on the basis of the gated-decoupled ¹³C and ¹H NMR spectra.

We are not aware of any other polynuclear arene complexes in which the center ring is coordinated as in **8**.

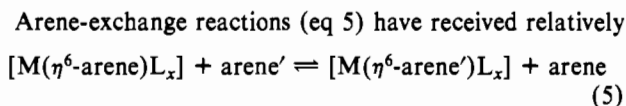
- (28) M. Green and T. A. Kuc, *J. Chem. Soc., Dalton Trans.*, 832 (1972).
 (29) B. F. G. Johnson, J. Lewis, and D. A. White, *J. Am. Chem. Soc.*, **91**, 5186 (1969).
 (30) (a) Protonation of a coordinated base has been used by Maitlis^{30b} and Bennett^{30c,d} to prepare arene complexes. Pannetier^{30e} has prepared $[\text{Ir}(\eta^4\text{-COD})(\mu\text{-OC}_6\text{H}_5)]_2$ by reaction of the $\mu\text{-OCH}_3$ complex with phenol. (b) C. White and P. M. Maitlis, *J. Chem. Soc. A*, 3322 (1971). (c) M. A. Bennett, T. W. Matheson, G. B. Robertson, W. L. Steffens, and T. W. Turney, *J. Chem. Soc., Chem. Commun.*, 32 (1979). (d) M. A. Bennett and T. W. Matheson, *J. Organomet. Chem.*, **175**, 87 (1979). (e) G. Pannetier, P. Fougeroux, R. Bonnaire, and N. Platzler, *J. Less-Common Met.*, **24**, 83 (1971). (f) The chemical shift of the proton-acetone was nearly identical with that of the solvent. A peak for coordinated acetone in $[\text{Ru}(\eta^6\text{-arene})(\text{acetone})_3]^{2+}(\text{PF}_6^-)_2$ at 2.98 ppm has been observed in dimethyl sulfoxide solution.^{30c}
 (31) (a) The naphthalene and anthracene complexes were quite labile. They dissociated completely in acetone solution to give the free arene and $[\text{Ir}(\eta^4\text{-COD})(\text{acetone})_2]^+$. The lability of metal complexes of polycyclic aromatic hydrocarbons has been noted.^{31b,c} (b) C. White, S. J. Thompson, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1654 (1977). (c) M. Cais, D. Fraenkel, and K. Weidenbaum, *Coord. Chem. Rev.*, **16**, 27 (1975), and reference 30d.
 (32) The shielding effect observed for coordinated olefins and arenes is well-known³⁴⁻³⁶ although a high positive charge on the complex can result in a downfield shift of the arene resonances.^{30b,31b} The chemical shifts of the arene methyl substituents shifted downfield by as much as 0.3 ppm upon coordination, but no general trends for the shift of the methyl group were evident.^{31b,36}
 (33) The ¹³C NMR spectrum of the naphthalene complex was consistent with its formulation as an η^6 -arene complex in solution: three resonances were observed in the coordinated arene region at room temperature (see Table XIV). See ref 38 for comments on the possible solution structure of $[\text{Ir}(\text{anthracene})(\text{COD})^+](\text{BF}_4^-)$.
 (34) J. T. Price and T. S. Sorensen, *Can. J. Chem.*, **46**, 515 (1968).
 (35) R. V. Emanuel and E. W. Randall, *J. Chem. Soc. A*, 3002 (1969).
 (36) V. Graves and J. J. Lagowski, *J. Organomet. Chem.*, **120**, 397 (1976).
 (37) (a) Occasionally, coordination of an arene resulted in a pattern of arene resonances which could be interpreted in a first-order fashion; this is illustrated for *cis*-propenylbenzene and 1,2,4-trimethylbenzene in Table XII. Wilkinson has reported a similar observation.^{37b} (b) D. J. Cole-Hamilton, R. Young, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1995 (1976).

- (39) H. Günther, H. Schmickler, and G. Jikeli, *J. Magn. Reson.*, **11**, 344 (1973).
 (40) R. G. Sutherland, S. C. Chen, J. Pannekoek, and C. C. Lee, *J. Organomet. Chem.*, **101**, 221 (1975).
 (41) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy", Vol. 2, Pergamon, Oxford, 1965, pp 710–711.

methylene protons in the indene and 9,10-dihydroanthracene complexes was consistent with observations for $[\text{Fe}(\eta^5\text{-indenyl})(\eta^6\text{-indene})]^+$.^{42,43a}

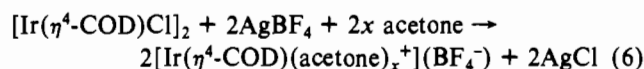
For the π -arene complexes, the ¹³C resonances of directly bound carbon atoms were shifted upfield upon coordination.⁴⁵⁻⁴⁷ ¹³C chemical shifts of methyl substituents moved 0.5–4 ppm upfield from the free-arene values, and an increase in the carbon-hydrogen coupling constant also occurred upon coordination.^{35,46}

Ligand-Exchange Reactions. A fundamental reaction in inorganic chemistry is the exchange of a free ligand in solution for one coordinated to a metal; this type of reaction is a key step for many catalytic and stoichiometric transformations which occur in the presence of transition-metal complexes.^{48,49} For arene complexes, the coordinated arene may be displaced by a new arene or by another type of ligand such as carbon monoxide or pyridine⁵ which will be referred to as "arene exchange" and "arene displacement", respectively. The latter has been the subject of kinetic studies on d⁶ Cr, Mo, W, and Mn complexes.⁵⁰⁻⁵² Recently, the displacement of the benzene ligand in $[\text{Ir}(\eta^6\text{-C}_6\text{H}_6)(\eta^4\text{-c-1,3-C}_6\text{H}_8)]^+$ (M = Rh, Ir) complexes by phosphines, pyridine, and acetonitrile has been reported.⁵³ Of the arene displacement reactions which have been studied in detail, an associative mechanism is implicated, and η^4 -arene and/or η^2 -arene intermediates have been proposed.⁵⁰⁻⁵² Infrared evidence has suggested a $[\text{Cr}(\text{naphthalene})(\text{CO})_3(\text{THF})]$ complex as an intermediate in the solvolysis of $[\text{Cr}(\eta^6\text{-naphthalene})(\text{CO})_3]$ by tetrahydrofuran.⁵⁴ An $[\text{Mn}(\eta^4\text{-arene})(\text{CO})_3\text{H}]$ intermediate in the isomerization of $[\text{Mn}(\eta^5\text{-cyclohexadienyl})(\text{CO})_3]$ complexes has been proposed⁵⁵ and supported by other studies.⁵⁶



little study; the conditions required for the reaction vary widely. For example, in nonpolar solvents complexes of the type $[\text{Cr}(\eta^6\text{-arene})(\text{CO})_3]$ typically undergo arene exchange between 100 and 200 °C.⁵⁷ This contrasts with the facile arene exchange with $[\text{Ni}(\eta^6\text{-toluene})(\text{C}_6\text{F}_5)_2]$ in chloroform at room temperature.¹⁰ Both the examples cited above are considered to be "uncatalyzed" reactions. Many workers have found that arene-exchange reactions which are sluggish in inert solvents may be accelerated by the addition of a Lewis acid or a Lewis base. An example of an acid-catalyzed system is the replacement of coordinated benzene by biphenyl in the presence of AlCl_3 ⁵⁸ and of a base-catalyzed system is the acceleration of arene exchange in $[\text{Cr}(\eta^6\text{-arene})(\text{CO})_3]$ complexes by a di-*n*-butyl ether-benzonitrile solvent system.⁵⁹

$[\text{Ir}(\eta^6\text{-C}_6\text{H}_6)(\eta^4\text{-COD})^+](\text{BF}_4^-)$ slowly reacted with C_6D_6 or $\text{C}_6(\text{CH}_3)_6$ in chloroform solution at room temperature to form the new arene complex.¹¹ The reaction with C_6D_6 was only 4% complete after 41 h at room temperature; equilibrium was reached within 1031 h. However, the reactions proceeded much more rapidly in the potentially coordinating solvent acetone. The exchange of coordinated benzene for C_6D_6 in acetone was followed by ¹H NMR spectroscopy. The first reaction process to occur was not simple arene exchange but rather the formation of a new $[\text{Ir}(\eta^4\text{-COD})^+]$ species which displayed a broad COD vinyl resonance at about 4.12 ppm and COD methylene resonances at approximately 2.3 (overlapping with the same resonance of the C_6H_6 complex) and 1.52 ppm. As these peaks increased in intensity, the solution became yellow. A yellow solution with resonances at 4.13, 2.34, and 1.54 ppm was generated by reacting AgBF_4 with $[\text{Ir}(\eta^4\text{-COD})\text{Cl}]_2$ in acetone-*d*₆ (eq 6). Hence the resonances



which developed in these positions during the exchange reaction of the benzene complex with C_6D_6 were assigned to an acetone-solvated $[\text{Ir}(\eta^4\text{-COD})^+]$ moiety. Intensity studies indicated that the acetone complex formed until it comprised about 24–30% of the iridium species in solution before the C_6D_6 complex began to form to a major extent (see Table I in the supplementary material); equilibrium was attained within 40 h at room temperature. Evidence for the related labile $[\text{Rh}(\eta^4\text{-nor-C}_7\text{H}_8)(\text{acetone})_x]^+$ ²⁷ and $[\text{M}(\eta^5\text{-C}_5\text{Me}_5)(\text{acetone})_x]^{2+}$ (M = Rh, Ir)^{31b} complexes have been presented convincingly in the literature although these complexes have not been isolated in crystalline form. Indeed an attempt to isolate $[\text{Ir}(\eta^4\text{-COD})(\text{acetone})_x]^+(\text{BF}_4^-)$ gave only a dark red oil (see Experimental Section) presumably because of facile loss of acetone. The dark oil had a ¹H NMR spectrum virtually identical with the yellow solution obtained via eq 6. ¹H DNMR studies indicated exchange between free and coordinated acetone was rapid on the NMR time scale down to at least –90 °C.^{30f} An analogous exchange between free and coordinated acetone in $[\text{IrH}_2(\text{PPh}_3)_2(\text{acetone})_2]^+$ was reported to be rapid at room temperature.⁶⁰

Interestingly, the ¹H NMR peaks attributed to $[\text{Ir}(\eta^4\text{-COD})(\text{acetone})_x]^+$ (hereafter referred to as the acetone com-

(42) P. M. Treichel and J. W. Johnson, *J. Organomet. Chem.*, **88**, 207 (1975).

(43) (a) The methylene protons of the coordinated COD ligand appeared as a broad band or complex multiplet and usually split into two distinct multiplets if iridium was also coordinated to nonpolarizable ligands.^{43b} The vinyl protons appeared as a single, broad peak between 3.5 and 5 ppm; the chemical shift of these protons was quite sensitive to the nature of other ligands present. The resonance moved upfield with increasing basicity of the bound arene, an effect which is evident for arene complexes of ruthenium,^{30c,d} rhodium,^{28,31b} and iridium.^{30b,31b} The general effect may be due partially to a greater electron density at the other ligands due to increased electron donation by the arene.⁴⁴ (b) An examination of the literature indicates that the COD methylene protons of $[\text{Ir}(\eta^4\text{-COD})\text{L}_x]^+$ complexes ($x = 2$ or 3) generally split into two distinct areas of resonance if L_x is a relatively nonpolarizable set of ligands while only a broad band is observed if L_x is a relatively polarizable ligand or set of ligands.^{14,25,30c,43c-f} The exceptions to the generality occur mainly for nitrogen ligands; no exceptions have been found for oxygen ligands (see ref 71). (c) G. Winkhaus and H. Singer, *Chem. Ber.*, **99**, 3610 (1966). (d) M. H. J. M. de Croon, H. L. M. van Gaal, and A. van der Ent, *Inorg. Nucl. Chem. Lett.*, **10**, 1081 (1974). (e) R. N. Hazeldine, R. J. Lunt, and R. V. Parrish, *J. Chem. Soc. A*, 3711 (1971). (f) L. M. Haines and E. Singleton, *J. Chem. Soc., Dalton Trans.*, 1891 (1972). (g) Maitlis has observed separate resonances for coordinated CH_3CN (2.76 ppm) and solvent CH_3CN (2.09 ppm) in $[\text{Ir}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CH}_3\text{CN})_2]^{2+}$.^{31b}

(44) D. A. Brown and H. Sloan, *J. Chem. Soc.*, 3849 (1962).

(45) D. J. Thoennes, C. L. Wilkins, and W. S. Trahanovsky, *J. Magn. Reson.*, **13**, 18 (1974).

(46) G. M. Bodner and L. J. Todd, *Inorg. Chem.*, **13**, 360 (1974).

(47) V. Graves and J. J. Lagowski, *Inorg. Chem.*, **15**, 577 (1976).

(48) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 4th ed., John Wiley, New York, 1980.

(49) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd ed., John Wiley, New York, 1967.

(50) F. Zingales, A. Chiesa, and F. Basolo, *J. Am. Chem. Soc.*, **88**, 2707 (1966).

(51) A. Pidcock, J. D. Smith, and B. W. Taylor, *J. Chem. Soc. A*, 1604 (1969), and references therein.

(52) L. A. P. Kane-Maguire and D. A. Sweigart, *Inorg. Chem.*, **18**, 700 (1979), and references therein.

(53) P. T. Draggett, M. Green, and S. F. W. Lowrie, *J. Organomet. Chem.*, **135**, C60 (1977).

(54) O. Gandolfi and M. Cais, *J. Organomet. Chem.*, **125**, 141 (1977).

(55) G. A. M. Munro and P. L. Pauson, *J. Chem. Soc., Chem. Commun.*, 134 (1976).

(56) W. Lamanna and M. Brookhart, *J. Am. Chem. Soc.*, **102**, 3490 (1980).

(57) W. Strohmeier and R. Müller, *Z. Phys. Chem. (Frankfurt/Main)*, **40**, 85 (1964), and references therein.

(58) F. Hein and K. Kartte, *Z. Anorg. Allg. Chem.*, **307**, 22 (1960).

(59) C. A. L. Mahaffy and P. L. Pauson, *J. Chem. Res. Miniprint*, 1746 (1979).

(60) J. R. Shapley, R. R. Schrock, and J. A. Osborn, *J. Am. Chem. Soc.*, **91**, 2816 (1969).

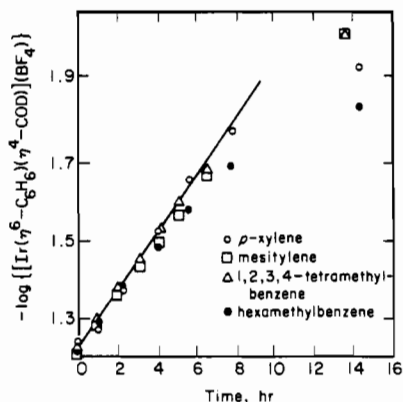


Figure 3. Plot of $-\log \{[\text{Ir}(\eta^6\text{-C}_6\text{H}_6)(\eta^4\text{-c-1,5-C}_6\text{H}_{12})^+(\text{BF}_4^-)]\}$ vs. time for the exchange between the benzene complex and *p*-xylene, mesitylene, 1,2,3,4-tetramethylbenzene, or hexamethylbenzene (see Table VIII and text).

plex) were not observed if the exchange reactions involved dimethylbenzene or more highly substituted benzenes. The presence of the acetone complex was clearly evident in exchange reactions involving $[\text{Ir}(\eta^6\text{-C}_6\text{H}_6)(\eta^4\text{-COD})^+(\text{BF}_4^-)]$ and toluene, propenylbenzenes, or phenol. A small amount (ca. 1%) of the acetone complex was detected in an exchange reaction between the benzene complex and hexamethylbenzene; however, the acetone complex was not evident after long reaction times (56–127 h at 35 °C).

The rate of arene exchange was independent of the concentration of added arene. The exchange between $[\text{Ir}(\eta^6\text{-C}_6\text{H}_6)(\eta^4\text{-COD})^+(\text{BF}_4^-)]$ and 1 or 10 equiv of *p*-xylene-*d*₁₀ was monitored by ¹H NMR spectroscopy in acetone solution (see Table VII in the supplementary material and Figure 2). Disappearance of the benzene complex and formation of the *p*-xylene complex occurred at identical rates in both experiments. The linearity of the curve in Figure 2 suggests that the exchange in acetone is first order in the benzene complex ($k_{\text{obsd}} = \text{ca. } 4 \times 10^{-5} \text{ s}^{-1}$) within the experimental conditions and errors.

Formation rate of the new arene complex was independent of the degree of the methyl substitution in the added arene. In four separate experiments the exchange between the benzene complex and (a) *p*-xylene, (b) mesitylene, (c) 1,2,3,4-tetramethylbenzene, and (d) hexamethylbenzene was examined (see Table VIII in the supplementary material and Figure 3). Virtually no difference in the rate of formation of new arene complexes was observed up to about 60% completion. At longer reaction times, the hexamethylbenzene complex and to a lesser extent the *p*-xylene complex formed at a slightly lower rate. The *p*-xylene reaction was approaching equilibrium while in the hexamethylbenzene case a kinetic factor is thought responsible (vide infra). However, formation rates were dependent upon the degree of methyl substitution in the initially bound arene. This is shown in Figure 4 for three sets of experiments run under similar conditions of temperature and concentration (referring to eq 5 ($M = \text{Ir(I)}$, $L_x = \eta^4\text{-COD}$): (i) arene = toluene and arene' = *o*-, *m*-, and *p*-xylene, 1,2,3- and 1,3,5-trimethylbenzene, and 1,2,3,4-tetramethylbenzene; (ii) arene = *p*-xylene and arene' = 1,2,3-, 1,2,4-, and 1,3,5-trimethylbenzene and 1,2,3,4- and 1,2,3,5-tetramethylbenzene; (iii) arene = mesitylene and arene' = *o*-, *m*-, and *p*-xylene and 1,2,3,4-tetramethylbenzene). The rate of exchange increased in the order arene = mesitylene < *p*-xylene < toluene; that is, the least stable arene complex (vide infra), $[\text{Ir}(\eta^6\text{-toluene})(\eta^4\text{-COD})^+(\text{BF}_4^-)]$, exchanged at the highest rate.

A stereochemical dependence on the rates of arene exchange between various isomeric methyl-substituted benzenes and an arene complex has not been mentioned in the literature.

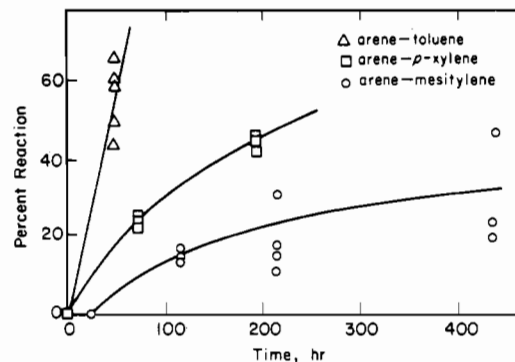


Figure 4. Plot of percent reaction vs. time for the exchange between $[\text{Ir}(\eta^6\text{-arene})(\eta^4\text{-c-1,5-C}_6\text{H}_{12})^+(\text{BF}_4^-)]$ (arene = toluene, *p*-xylene, or mesitylene) and a number of arenes (see Tables II–IV). The scatter in the data for the mesitylene complex is attributed to the fact that the xylene complexes are relatively unstable and therefore are expected to form at a lower rate.

Significant differences exist in the thermodynamic stabilities of $[\text{Ag}(\text{arene})]^+$ complexes for various isomeric methyl-substituted arenes.⁶¹ In particular, substituted arene isomers that have the maximum number of contiguous unsubstituted ring carbons form the most stable complexes.⁶² A similar effect in the transition metals has not been reported, and evidence for these types of effects was sought in competitive arene-exchange experiments between $[\text{Ir}(\eta^6\text{-C}_6\text{H}_6)(\eta^4\text{-COD})^+(\text{BF}_4^-)]$ and a number of pairs of methyl benzenes. Consistent with the data presented graphically in Figures 2 and 3, no dependence on the stereochemistry of methyl substitution was evident in competition between *o*- or *p*-xylene, *o*- and *m*-xylene, or 1,2,3- and 1,3,5-trimethylbenzene; the new complexes formed at the same rate and at equilibrium were present in equal concentrations. Exchange between the benzene complex and 1 equiv each of mesitylene and 1,2,3,4-tetramethylbenzene resulted in formation of the new arene complexes in their approximate thermodynamic ratio (the observed ratio was 1:3.3; $K_{\text{eq}} \approx 11$; see Table XVI) throughout the experiment, indicating that the two new arene complexes were also in equilibrium with each other. Significant differences were observed in competitive experiments between 1,2,3,4- and 1,2,4,5-tetramethylbenzene (durene), 1,2,3,4- and 1,2,3,5-tetramethylbenzene (isodurene), and 1,2,3,4-tetramethylbenzene and hexamethylbenzene. In all three experiments 1,2,3,4-tetramethylbenzene was the preferred kinetic product. At the “end” of the reaction, defined as the complete displacement of coordinated C_6H_6 , the ratios of coordinated 1,2,3,4-tetramethylbenzene to coordinated durene, coordinated 1,2,3,4-tetramethylbenzene to coordinated isodurene, and coordinated 1,2,3,4-tetramethylbenzene to coordinated hexamethylbenzenes were 4.63 (a second determination gave a ratio of 4.55), ca. 2.2, and ca. 9, respectively. (The last two ratios were estimated from peak heights in the methyl region of the ¹H NMR spectrum.) After 712 h at room temperature, the ratios in the last two experiments dropped to 1.7 and 5.1, respectively. Heating those two reactions for 856 h at 50 °C resulted in a further decrease in the ratios to 1.1 (essentially equilibrated) and 1.5, respectively. The durene complex crystallized out of solution under these conditions, and no further information could be obtained from that experiment. These data clearly indicate a unique dependence on the stereochemistry and extent of methyl substitution in exchange reactions of highly substituted methylbenzenes. Despite its

(61) For example, the formation constants for $\text{Ag}(\text{arene})^+$ complexes in $\text{CH}_3\text{OH-H}_2\text{O}$ for arene = 1,2,4,5- $\text{C}_6\text{H}_2(\text{CH}_3)_4$, 1,2,3,5- $\text{C}_6\text{H}_2(\text{CH}_3)_4$, and 1,2,3,4- $\text{C}_6\text{H}_2(\text{CH}_3)_4$ are 0.88, 0.88, and 1.69, respectively.⁶²

(62) N. Ogimachi, L. J. Andrews, and R. M. Keefer, *J. Am. Chem. Soc.*, **78**, 2210 (1956).

Table XVI. Equilibrium Constants for Arene Exchange

arene	arene'	K_{eq}^a	K_{eq}^b	K_{eq}^c	K_{eq}^d
C ₆ H ₆	<i>trans</i> -C ₆ H ₅ CH=CHCH ₃	2.3			
C ₆ H ₆	C ₆ H ₅ CH ₃	6.1	1.1 × 10	1.3 × 10	
C ₆ H ₆	PhOH	2.0			
C ₆ H ₅ CH ₃	C ₆ H ₆	8.0 × 10 ⁻²	7.1 × 10 ⁻²	1.6 × 10 ⁻¹	
C ₆ H ₅ CH ₃	1,2-C ₆ H ₄ (CH ₃) ₂	8.0	7.1		1.1 × 10
C ₆ H ₅ CH ₃	1,3-C ₆ H ₄ (CH ₃) ₂	7.3	7.7		9.0
C ₆ H ₅ CH ₃	1,4-C ₆ H ₄ (CH ₃) ₂	8.5	7.6		1.0 × 10
C ₆ H ₅ CH ₃	1,2,3-C ₆ H ₃ (CH ₃) ₃	5.7 × 10			4.6 × 10
C ₆ H ₅ CH ₃	1,3,5-C ₆ H ₃ (CH ₃) ₃	3.0 × 10		1.2 × 10 ²	4.8 × 10
1,4-C ₆ H ₄ (CH ₃) ₂	1,2,3-C ₆ H ₃ (CH ₃) ₃	6.6	6.1		
1,4-C ₆ H ₄ (CH ₃) ₂	1,2,4-C ₆ H ₃ (CH ₃) ₃	7.8	9.1		
1,4-C ₆ H ₄ (CH ₃) ₂	1,3,5-C ₆ H ₃ (CH ₃) ₃	5.7	5.6	8.3	4.3
1,4-C ₆ H ₄ (CH ₃) ₂	1,2,3,4-C ₆ H ₂ (CH ₃) ₄	4.3 × 10		7.7 × 10 ^e	5.7 × 10
1,4-C ₆ H ₄ (CH ₃) ₂	1,2,3,5-C ₆ H ₂ (CH ₃) ₄	5.2 × 10			
1,3,5-C ₆ H ₃ (CH ₃) ₃	C ₆ H ₅ CH ₃	8.2 × 10 ⁻³		3.3 × 10 ⁻²	1.2 × 10 ⁻²
1,3,5-C ₆ H ₃ (CH ₃) ₃	1,2-C ₆ H ₄ (CH ₃) ₂	9.2 × 10 ⁻²	9.0 × 10 ⁻²		5.8 × 10 ⁻²
1,3,5-C ₆ H ₃ (CH ₃) ₃	1,3-C ₆ H ₄ (CH ₃) ₂	8.6 × 10 ⁻²	7.5 × 10 ⁻²		6.3 × 10 ⁻²
1,3,5-C ₆ H ₃ (CH ₃) ₃	1,4-C ₆ H ₄ (CH ₃) ₂	1.2 × 10 ⁻¹	1.2 × 10 ⁻¹	1.8 × 10 ⁻¹	1.3 × 10 ⁻¹
1,3,5-C ₆ H ₃ (CH ₃) ₃	1,2,3,4-C ₆ H ₂ (CH ₃) ₄	1.0 × 10	9.3	1.0 × 10 ^e	5.2
1,2,3,4-C ₆ H ₂ (CH ₃) ₄	1,4-C ₆ H ₄ (CH ₃) ₂	1.3 × 10 ^{-2e}		2.3 × 10 ^{-2f}	
1,2,3,4-C ₆ H ₂ (CH ₃) ₄	1,3,5-C ₆ H ₃ (CH ₃) ₃	1.0 × 10 ^{-1e}		1.0 × 10 ^{-1f}	
1,2,3,4-C ₆ H ₂ (CH ₃) ₄	1,2,4,5-C ₆ H ₂ (CH ₃) ₄	6.2 × 10 ^{-1e}	1.0		
1,2,3,4-C ₆ H ₂ (CH ₃) ₄	C ₆ (CH ₃) ₆	5.0 × 10 ^{-1e}			

^a Equilibrium constants for $[\text{Ir}(\eta^6\text{-arene})(\eta^4\text{-COD})](\text{BF}_4) + \text{arene}' \rightleftharpoons [\text{Ir}(\eta^6\text{-arene}')(\eta^4\text{-COD})](\text{BF}_4) + \text{arene}$; determined in acetone-*d*₆ at 24 ± 3 °C (unless indicated otherwise). The data in this table were obtained from five standard solutions of $[\text{Ir}(\eta^6\text{-arene})(\eta^4\text{-COD})](\text{BF}_4)$ complexes. The concentrations of these five solutions, and thus the total concentrations of iridium species in solution, were 0.0987, 0.122, 0.107, 0.121, and 0.620 M for arene = benzene, toluene, *p*-xylene, mesitylene, and 1,2,3,4-tetramethylbenzene, respectively. ^b Equilibrium constants obtained by computer simulation of appropriate region of the ¹H NMR spectrum. Computer simulation of NMR spectra were accomplished by using programs available in Nicolet Technology Corp. 1180 software. ^c Equilibrium constants obtained from the back-reaction. ^d Equilibrium constants calculated by using the relation $K_{ac} = K_{ab}K_{bc}$. ^e Determined at 50 ± 2 °C; the equilibration time was 1024–1025 h. ^f Determined at 24 ± 3 °C.

presumed high thermodynamic stability, the hexamethylbenzene complex formed rather slowly. Traces of the acetone complex were observed in the exchange reaction of the benzene complex with hexamethylbenzene. This suggests that benzene was competing effectively with the hexamethylbenzene for the acetone-solvated $[\text{Ir}(\text{COD})]^+$ intermediate. Thus, it is not surprising that 1,2,3,4-tetramethylbenzene competed effectively with hexamethylbenzene in exchange reactions. The particular *stereochemistry* of the four methyl groups in the 1,2,3,4-isomer apparently minimized any steric inhibition in the reaction, while, on the other hand, the *number* of methyl groups present insured that the complex formed had thermodynamic stability comparable to that of the hexamethylbenzene complex.

Since arene exchange proceeded slowly in chloroform solution but significantly more rapidly in acetone—i.e., under catalyzed conditions—an attempt was made to accelerate arene exchange in chloroform solution by controlled addition of various Lewis bases. Accordingly, the exchange reactions between coordinated mesitylene and free durene in chloroform solution were examined in the presence of 2 equiv of tetrahydrofuran, acetone, acetonitrile, or diethyl sulfide (eq 7). No $[\text{Ir}(\eta^6\text{-mesitylene})(\eta^4\text{-COD})]^+(\text{BF}_4^-) + \text{durene} + 2 \text{ donor} \rightleftharpoons [\text{Ir}(\eta^6\text{-durene})(\eta^4\text{-COD})]^+(\text{BF}_4^-) + \text{mesitylene} + 2 \text{ donor}$ (7)

evidence of arene exchange in the presence of tetrahydrofuran was observed after 1606 h at 24 ± 3 °C; only a trace of the durene complex was observed after 2602 h. Exchange occurred somewhat more rapidly in the presence of acetone: the reaction was ca. 10% complete after 1606 h. This result contrasts sharply with the same arene-exchange reaction in acetone solution where the exchange was 26% complete after 214 h (see Table IV in the supplementary material).

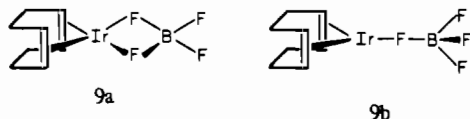
A more complicated series of equilibria were evident in the presence of either acetonitrile or diethyl sulfide. In the case of acetonitrile a distinct yellow coloration developed as the acetonitrile resonance in the ¹H NMR spectrum shifted downfield from 1.97 to 2.40 ppm concomitant with the ap-

pearance of free mesitylene (see Table V in the supplementary material). The durene complex began to form only after long reaction times. The shift of the acetonitrile resonance is attributed to formation of the known $[\text{Ir}(\eta^4\text{-COD})(\text{CH}_3\text{CN})_2]^+$.²⁵ The appearance of an additional cyclooctadiene methylene multiplet at 1.66 ppm (similar to that observed for the acetone complex) confirmed the presence of a new $[\text{Ir}(\eta^4\text{-COD})]^+$ species in solution which was coordinated by nonpolarizable ligands.^{43b} After 741 h, the solution species consisted of 10% durene complex, 30% mesitylene complex, and 60% acetonitrile complex. This distribution changed to 39%, 18%, and 43% for the durene, mesitylene, and acetonitrile complexes, respectively, after 2602 h. As the concentration of the acetonitrile complex decreased, the methyl resonance shifted back upfield to approximately 2.33 ppm. Since only one acetonitrile resonance was observed throughout the experiment, exchange with free acetonitrile must be fast on the NMR time scale. Fast exchange between free and ligated acetonitrile was evident in a chloroform solution of $[\text{Ir}(\eta^4\text{-COD})(\text{CH}_3\text{CN})_2]^+(\text{BF}_4^-)$ at -50 °C.^{43g}

In the presence of diethyl sulfide, the reaction in eq 7 took on an orange coloration and coordinated mesitylene was slowly displaced with the simultaneous downfield shift of the methylene and methyl protons of diethyl sulfide from their initial values of 2.53 and 1.25 ppm. By analogy to the acetonitrile case, these downfield shifts are attributed to the formation of $[\text{Ir}(\eta^4\text{-COD})[\text{S}(\text{C}_2\text{H}_5)_2]_2]^+$ (see Experimental Section and Table V in the supplementary material). Diethyl sulfide displaced mesitylene more slowly than acetonitrile: 17% displacement was observed after 160 h compared with 39% displacement in the acetonitrile experiment. In contrast to the acetonitrile experiment, no evidence for the formation of the durene complex was observed after 1606 h. After 2602 h at 24 ± 3 °C, the concentration distributions were <1%, 32%, and 68% for the durene, mesitylene, and diethyl sulfide complexes, respectively. The initial displacement of coordinated arene by the catalyst before a significant quantity of new arene complex began to form was also observed in ex-

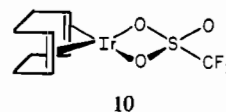
change between the benzene complex and C_6D_6 in neat acetone (vide supra).⁶³

Both $[Ir(\eta^6-C_6H_6)(\eta^4-COD)^+](BF_4^-)$ and the isoelectronic complex $[Ru(\eta^6-C_6H_6)(\eta^4-COD)]$ provide examples of arene complexes which undergo base-catalyzed arene exchange.⁶⁵ Since the ruthenium complex did not undergo arene exchange in noncoordinating solvents, the question arises as to the mechanism of arene exchange for the iridium complex in chloroform. The cationic Ir(I) complexes possess a counterion which could, in principle, interact with the metal and stabilize (possibly with solvent assistance) a coordinately unsaturated, arene-free intermediate. The existence of such an intermediate complex, formally represented as either **9a** or **9b**, is plausible based on the established coordinating ability of tetrafluoroborate.⁶⁹



Anion participation in the reaction was tested by preparing different salts and examining their exchange behavior with free arene in chloroform. The only pair of salts which exhibited comparable solubility properties were $[Ir(\eta^6-p\text{-xylene})(\eta^4-COD)^+](BF_4^-)$ and $[Ir(\eta^6-p\text{-xylene})(\eta^4-COD)^+](OSO_2CF_3^-)$. Approximately equimolar chloroform solutions of these two salts were prepared (0.0880 and 0.0875 M, respectively), and the exchange between the coordinated *p*-xylene and free mesitylene or 1,2,3,4-tetramethylbenzene was followed by ¹H NMR spectroscopy (four separate experiments). After 382

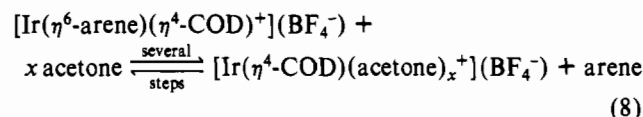
h at room temperature the BF_4^- salt of the *p*-xylene complex had not exchanged with either mesitylene or 1,2,3,4-tetramethylbenzene; however, the exchange reaction of the $OSO_2CF_3^-$ salt with mesitylene and 1,2,3,4-tetramethylbenzene had proceeded to 68% and 78% completion, respectively. On the assumption that changing the counterion did not change the reaction mechanism, the results support the proposal of an intermediate **10** (similar to **9a**). Such iridium(I) sulfonate



complexes may be isolable although they would be expected to be labile with respect to displacement by polarizable ligands.^{64a,70,71} Alteration of the counterion could be an important consideration in the design of cationic transition-metal catalysts.

Summary of Arene-Exchange Reactions

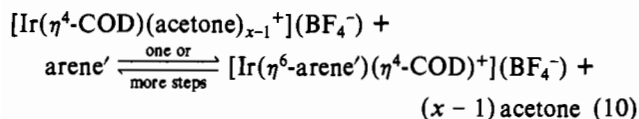
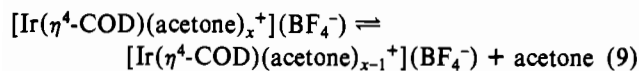
The experiments described above provide a rational framework for discussing the mechanism of arene exchange in the cationic Ir(I) system. Two types of processes are operative depending on the solvent. In acetone, the first step is considered to be solvent displacement of the arene (eq 8).⁷²



Reaction of the incoming arene with a coordinately unsaturated acetone complex generates the new arene complex (eq 9 and 10). The acetone complex was only observed in ex-

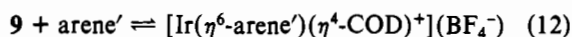
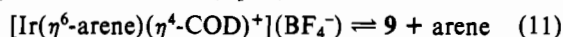
- (63) It is reasonable that Ir(I), a class B metal,^{64a} would interact strongly with diethyl sulfide, less strongly with acetonitrile, and least strongly with an O donor such as acetone. The importance of these considerations is evident from the following observations. The solution obtained by dissolving $[Ir(\eta^4\text{-COD})(CH_3CN)_2]^+(BF_4^-)$ in acetone-*d*₆ had a ¹H NMR spectrum showing a COD vinyl resonance at 4.28 ppm, a COD methylene resonances at 2.24 and 1.76 ppm, and a singlet at 2.62 ppm for coordinated acetonitrile. Virtually no change in the spectrum occurred after 118 h at room temperature; that is, coordinated acetonitrile was not exchanging with solvent. Addition of approximately 2 equiv of acetonitrile to this solution shifted the acetonitrile resonance to 2.36 ppm; no further change in the spectrum was observed after 69 h. There is also a considerable difference between acetonitrile and acetone with respect to their reactivity with the arene complexes. Two equivalents of acetonitrile react with $[Ir(\eta^6-C_6H_6)(\eta^4\text{-COD})^+](BF_4^-)$ in acetone solution at $24 \pm 3^\circ C$ to give the acetonitrile complex (arene = C_6H_6): $[Ir(\eta^6\text{-arene})(\eta^4\text{-COD})^+](BF_4^-) + 2CH_3CN \rightleftharpoons [Ir(\eta^4\text{-COD})(CH_3CN)_2]^+(BF_4^-) + \text{arene}$. The reaction is complete within 60 h; a large K_{eq} is indicated. The equilibrium constant for the above reaction for arene = *p*-xylene is in the range of 30–400. By contrast, allowing an acetone solution of $[Ir(\eta^6-C_6H_6)(\eta^4\text{-COD})^+](BF_4^-)$ (0.13 M) to stand for 70 days at room temperature resulted in only 25% conversion to the acetone complex. A similar experiment with the *p*-xylene complex indicated only a trace of the acetone complex after the 70 day reaction period. The strong interaction of diethyl sulfide and acetonitrile with Ir(I), as opposed to the weak interaction with acetone, accounts for the relative facility of arene exchange in acetone solvent. Rauchfuss and Roundhill have recently taken advantage of the lability of bonds between bases and platinum metals in their work with chelating ligands containing two classes of donors.^{64b-c} The α -(diphenylphosphino)anisole ligand appears to form particularly labile complexes with Ru(II);^{64c} in fact, only P-bonded monodentate complexes were formed with Pd(II) and Pt(II)^{64c} and Ir(I)^{64d} using this ligand.
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- (65) Our observations on the ruthenium system are reported in ref 11.
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- (69) A. P. Gaughan, Jr., Z. Dori, and J. A. Ibers, *Inorg. Chem.*, 13, 1657 (1974), and references therein.

- (70) (a) We have previously prepared stable complexes of the type $[Mn\{P(O-i-C_3H_7)_3\}_2(CO)_2(O_2SOR)]$ (R = CH₃ or CF₃),^{70b} and Troglor has recently presented evidence for the labile species $[Mn(CO)_5(OSO_2CF_3)]$.^{70c} In an interesting paper, Shriver has shown that CH_3X (X = SO₃F or SO₃CF₃) can oxidatively add to Vaska's complex to give the labile, hexacoordinate complexes $[Ir(Cl)(CO)\{P(C_6H_5)_3\}_2(CH_3)(X)]$.^{70d} Some recent examples of monodentate sulfonate complexes characterized by X-ray crystallography are $[Au(CH_3)_2(OH_2)(OSO_2CF_3)]$ ^{70e} and $[Pd(NR_2CH_2CH_2CO)(NR_2H)(OSO_2CF_3)]$.^{70f} (b) L. S. Stuhl and E. L. Muettterties, *Inorg. Chem.*, 17, 2148 (1978). (c) W. C. Troglor, *J. Am. Chem. Soc.*, 101, 6459 (1979). (d) D. Strope and D. F. Shriver, *Inorg. Chem.*, 13, 2652 (1974). (e) S. Komiya, J. C. Huffman, and J. K. Kochi, *ibid.*, 16, 2138 (1977). (f) O. P. Anderson and A. B. Packard, *ibid.*, 18, 1129 (1979).
- (71) (a) Justification for **10** as an intermediate in arene-exchange reactions in chloroform solutions was provided by the interesting (and complex) equilibria operative in the $Ir(COD)^+$ -*p*-toluenesulfonate system.^{71b} Chloroform solutions of $\{[Ir(\eta^6-1,4-C_6H_4(CH_3)_2)(SO_3)](\eta^4\text{-COD})\}$ (**1**) or $\{[Ir(\eta^6-C_6H_6)(\eta^4\text{-COD})^+](O_3SC_6H_4CH_3)^-\}$ (**3**) (see Experimental Section) were prepared and observed by ¹H NMR spectroscopy over a period of time. Changes in the chemical shift of the tosylate arene resonances, COD vinyl resonances, and in particular the appearance of COD methylene proton resonances at 1.2–1.3 ppm⁴³ provided evidence for the presence of three yellow to orange yellow O-bonded tosylate complexes, **2**, **4**, and **5**, in solution (see Table XV in the supplementary material). The solid-state infrared spectrum of one of these yellow species, **2**, was compared with the IR of the π -bound tosylate species **1**, ionic tosylate complex **6**, and a literature complex, $[Mo_2(\mu-O_2SOCH_3)_4]$.^{71c} It was consistent with the O-bonded formulation. Although the precise nature of the O-bonded tosylate complexes **2**, **4**, and **5** is not known, we tentatively propose bidentate chelate, monodentate, and bidentate bridging structures, respectively, for these three complexes. In accord with the stability of highly methyl-substituted arene complexes $\{[Ir(\eta^6-1,2,3,4-C_6H_2(CH_3)_4)(\eta^4\text{-COD})^+](O_3SC_6H_4CH_3)^-\}$ (**6**) was not labile in chloroform at room temperature. Wilkinson and Cole-Hamilton have recently prepared a π -tosylate complex of ruthenium.^{71d} (b) A. C. Sievert, Ph.D. Thesis, University of California, Berkeley, 1979. (c) F. Hochberg and E. H. Abbott, *Inorg. Chem.*, 17, 506 (1978).
- (72) Note that in competitive arene-exchange reactions the initial product distribution depended on the stereochemistry and extent of methyl substitution for highly substituted arenes. In these cases the displaced arene or another more favorably substituted arene will compete effectively with arene' for the acetone complex intermediate even if the arene' complex is the thermodynamically favored product.



change involving arenes which form relatively unstable complexes (e.g., benzene or toluene). For more highly methyl-substituted arenes the equilibrium constant for eq 8 is apparently small enough to prevent spectroscopic observation of this complex. Acetone appears to be a good catalyst for arene exchange because it does not interact strongly with the Ir(I) center in contrast to diethyl sulfide or acetonitrile but reacts strongly enough that arene displacement is fast in contrast to the exchange reactions in chloroform.

In chloroform, the counterion probably assists in the dissociation of the arene to form a low concentration of a reactive intermediate such as $[\text{Ir}(\eta^4\text{-COD})(\text{BF}_4)]$ (9) (eq 11) which rapidly reacts with arene (eq 12).



Whether sequential $\eta^6 \rightleftharpoons \eta^4 \rightleftharpoons \eta^2 \rightleftharpoons \eta^0$ rearrangements occur in the dissociation (or formation) of arene complexes has never been definitely answered.¹¹ Our study provides no evidence on this issue.

Equilibrium Constants. A summary of the equilibrium constants for a number of arene-exchange reactions is given in Table XVI. The third column of the table lists K_{eq} values obtained by integration of the arene or COD vinyl region in the ¹H NMR spectra. Since peak overlap appeared to present a complication in some of the spectra, the fourth column of the table lists K_{eq} values obtained by computer simulation of the recorded spectra; the values in the third and fourth columns agree within the experimental error. The fifth column of Table XVI lists K_{eq} values obtained by separate study of the appropriate back-reaction; the agreement between the third and fifth columns is fair (factor of 2 or less), except for the toluene-mesitylene system (where the factor was 4). The last column of the table lists K_{eq} 's calculated from other equilibria.

There appears to be little or no difference in the thermodynamic stability of the 1,2,3,4-tetramethylbenzene and durene complexes. The results of the competition experiments is therefore definitely a kinetic effect. Our data would suggest that the hexamethylbenzene complex is less stable than the 1,2,3,4-tetramethylbenzene complex; however, this system probably had still not reached equilibrium after 1024 h at 50 °C. Table XVI and our observations outlined above³¹ indicate the following order of stabilities for the $[\text{Ir}(\eta^6\text{-arene})(\eta^4\text{-COD})]^+(\text{BF}_4^-)$ complexes: anthracene \approx naphthalene \ll C₆H₆ \approx C₆H₅OH \approx *trans*-C₆H₅CH=CHCH₃ < C₆H₅CH₃ < C₆H₄(CH₃)₂ < C₆H₃(CH₃)₃ < C₆H₂(CH₃)₄ > C₆(CH₃)₆. Hexamethylbenzene excepted, the equilibrium constants are considered to reflect the metal-arene bond strengths. These trends have also been observed by other workers for η^6 -arene complexes; e.g., Mahaffy and Pauson have recently reported the following displacement order for $[\text{Cr}(\eta^6\text{-arene})(\text{CO})_3]$ complexes:⁵⁹ naphthalene < C₆H₅F \approx C₆H₅Cl < C₆H₅C-O₂CH₃ < C₆H₅OCH₃ \approx C₆H₅COCH₃ < C₆H₆ \approx C₆H₅CH₃ < C₆H₄(CH₃)₂ \leq C₆H₅N(CH₃)₂ < C₆H₃(CH₃)₃ < C₆H₂(C-H₃)₄ < C₆(CH₃)₆. These data differ from our iridium system in assigning approximately the same stability to toluene and benzene complexes which is in agreement with Connor's thermochemical data.⁷³ Klabunde et al. have shown that

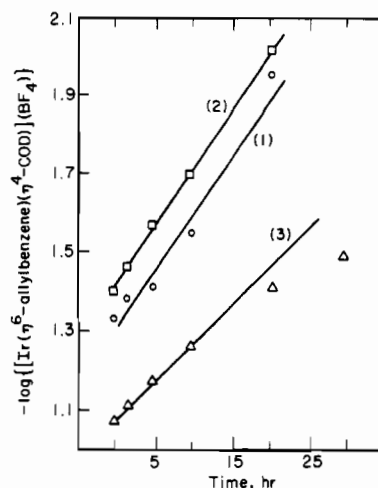
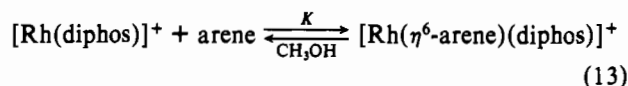


Figure 5. Plots of $-\log [[\text{Ir}(\eta^6\text{-allylbenzene})(\eta^4\text{-c-1,5-C}_8\text{H}_{12})]^+(\text{BF}_4^-)]$ vs. time for the isomerization of the allylbenzene complex (12) to the *trans*-propenylbenzene complex (11) at 35 °C. Experiments 2 and 3 were performed in chloroform; the initial concentrations of the allylbenzene complex were 0.043 and 0.093 M, respectively. Experiment 1 was performed in acetone (0.051 M) (see Table IX).

arenes with electronegative substituents are easily displaced and observed the following coordination preference for nickel(II) arene complexes:¹⁰ C₆H₅CF₃ < C₆H₅F < C₆H₆ < C₆-H₅CH₃ < C₆H₅OCH₃ \approx C₆H₃(CH₃)₃. Halpern and co-workers have found that the equilibrium constants in eq 13



are 18, 97, and 500 for arene = benzene, toluene, and xylenes, respectively.⁷⁴ All these data and the observations of others^{5,11,28} point to the increasing stability of the metal-arene bond with increasing methyl substitution on the arene.

Isomerization Reactions of Coordinated Alkenylbenzenes.

An interesting example of the solution lability of the iridium cationic complexes is provided by the behavior of the propenylbenzene derivatives. The ¹H NMR spectra of the *trans*-propenylbenzene complex (11) indicated that the complex was in equilibrium with free *trans*-propenylbenzene and the acetone complex. However, acetone solutions of the *cis*-propenylbenzene complex contained free *cis*-propenylbenzene and the acetone complex, as well as small but spectroscopically detectable amounts of 11.

Solutions of the allylbenzene complex (12) had no free allylbenzene but did contain 11 as well as a small amount of the acetone complex. Allowing acetone solutions of the *cis*-propenyl- and allylbenzene complexes to stand at room temperature resulted in complete conversion to the *trans*-propenylbenzene complex. Since the acetone complex itself was found to react with allylbenzene to give 11 (within 2 h at room temperature),⁷⁵ a mechanism for this reaction can be proposed in which the acetone complex isomerizes the arene by a 1,3-hydrogen shift mechanism.⁷⁶ Equilibration between the newly formed *trans*-propenylbenzene (by far the most stable isomer⁷⁷)

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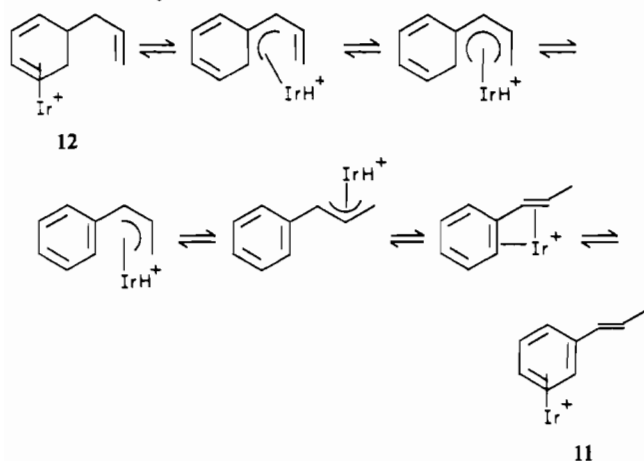
(75) The acetone complex also isomerized 1-hexene in acetone at room temperature.^{71b} After 30 h of reaction all possible hexene isomers were observed by gas chromatography. At longer reaction times, 3-hexene isomers became the major products. Green has shown that $[\text{M}(\eta^4\text{-COD})(\text{CH}_3\text{CN})_2]^+$ (M = Rh, Ir) complexes are hexene isomerization catalysts: M. Green and T. A. Kuc, *Ger. Offen., GER. OFFEN.*, **2,153,314** (1972); *Chem. Abstr.*, **77**, P37216r (1972).

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Scheme I. Proposed Intramolecular Isomerization of Coordinated Allylbenzene



and the starting arene complex would eventually result in total conversion to **11**. Sherman has recently presented evidence for a 1,3-hydrogen shift mechanism in the isomerization of allylbenzene by $\{\text{Ru}(\pi\text{-C}_6\text{H}_5)_3\}(\text{CH}_3\text{CN})$.⁷⁸

Chloroform solutions of the allylbenzene complex isomerized to the *trans*-propenylbenzene complex at the same rate observed in acetone solutions ($k_{\text{obsd}} = \text{ca. } 2 \times 10^{-5} \text{ s}^{-1}$; see Figure 5). The reactions proceeded in a first-order fashion although some curvature in the rate plot was observed at higher concentrations and long reaction times. The *cis*-propenylbenzene complex also isomerized in chloroform solution. Since arene-exchange rates have been shown to be much slower in chloroform than in acetone, it seems clear that arene dissociation is not rate determining. Scheme I presents a plausible mechanism for the allylbenzene \rightarrow *trans*-propenylbenzene conversion.

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Grant to the Department of Chemistry, University of California at Berkeley, for purchase of a 180-MHz NMR spectrometer. In addition, we thank Professor J. R. Shapley for helpful discussions.

Registry No. 1, 75751-41-6; 3, 75751-42-7; 6, 75751-43-8; 7, 75751-45-0; 8, 75751-47-2; 11, 75800-61-2; 12, 75751-49-4; $[\text{Ir}(\eta^6\text{-C}_6\text{H}_5\text{C}_6\text{H}_5)(\eta^4\text{-COD})^+(\text{BF}_4^-)]$, 75751-51-8; $[\text{Ir}(\eta^4\text{-COD})(\text{CH}_3\text{CN})_2]^+(\text{BF}_4^-)$, 32679-03-1; $[\text{Ir}(\eta^6\text{-C}_6\text{H}_6)(\eta^4\text{-COD})^+(\text{OSO}_2\text{CF}_3)]$, 75751-52-9; $[\text{Ir}(\eta^6\text{-1,4-C}_6\text{H}_4(\text{CH}_3)_2)(\eta^4\text{-COD})^+(\text{OSO}_2\text{CF}_3)]$, 75751-53-0; $[\text{Ir}(\eta^6\text{-1,4-C}_6\text{H}_4(\text{CH}_3)_2)(\eta^4\text{-COD})^+(\text{PF}_6^-)]$, 75751-54-1; $[\text{Ir}(\eta^6\text{-1,4-C}_6\text{H}_4(\text{CH}_3)_2)(\eta^4\text{-COD})^+(\text{B}_{12}\text{Cl}_{12}^{2-})_{1/2}]$, 75751-55-2; $[\text{Ir}(\eta^6\text{-C}_6\text{H}_6)(\eta^4\text{-COD})^+(\text{BF}_4^-)]$, 74238-34-9; $[\text{Ir}(\eta^6\text{-1,3-C}_6\text{H}_4(\text{CH}_3)_2)(\eta^4\text{-COD})^+(\text{BF}_4^-)]$, 74238-40-7; $[\text{Ir}(\eta^6\text{-1,2,3-C}_6\text{H}_3(\text{CH}_3)_3)(\eta^4\text{-COD})^+(\text{BF}_4^-)]$, 75751-57-4; $[\text{Ir}(\eta^6\text{-1,2,4-C}_6\text{H}_3(\text{CH}_3)_3)(\eta^4\text{-COD})^+(\text{BF}_4^-)]$, 74238-44-1; $[\text{Ir}(\eta^6\text{-1,2,3,4-C}_6\text{H}_2(\text{CH}_3)_4)(\eta^4\text{-COD})^+(\text{BF}_4^-)]$, 74238-46-3; $[\text{Ir}(\eta^6\text{-1,2,3,5-C}_6\text{H}_2(\text{CH}_3)_4)(\eta^4\text{-COD})^+(\text{BF}_4^-)]$, 74238-48-5; $[\text{Ir}(\eta^6\text{-1,2,4,5-C}_6\text{H}_2(\text{CH}_3)_4)(\eta^4\text{-COD})^+(\text{BF}_4^-)]$, 74238-48-5; $[\text{Ir}(\eta^6\text{-1,2-C}_6\text{H}_4(\text{CH}_3)_2)(\eta^4\text{-COD})^+(\text{BF}_4^-)]$, 74238-38-3; $[\text{Ir}(\eta^6\text{-cis-C}_6\text{H}_5\text{CH}=\text{CHCH}_3)(\eta^4\text{-COD})^+(\text{BF}_4^-)]$, 75751-24-5; $[\text{Ir}(\eta^6\text{-C}_6\text{H}_5\text{OH})(\eta^4\text{-COD})^+(\text{BF}_4^-)]$, 75751-26-7; $[\text{Ir}(\eta^6\text{-tetralin})(\eta^4\text{-COD})^+(\text{BF}_4^-)]$, 75751-28-9; $[\text{Ir}(\eta^6\text{-naphthalene})(\eta^4\text{-COD})^+(\text{BF}_4^-)]$, 75751-30-3; $[\text{Ir}(\eta^6\text{-9,10-dihydroanthracene})(\eta^4\text{-COD})^+(\text{BF}_4^-)]$, 75751-32-5; $[\text{Ir}(\eta^6\text{-indene})(\eta^4\text{-COD})^+(\text{BF}_4^-)]$, 75751-34-7; $[\text{Ir}(\eta^6\text{-C}_6(\text{CH}_3)_6)(\eta^4\text{-COD})^+(\text{BF}_4^-)]$, 74238-50-9; $[\text{Ir}(\eta^6\text{-C}_6\text{H}_5\text{CH}_3)(\eta^4\text{-COD})^+(\text{BF}_4^-)]$, 74238-36-1; $[\text{Ir}(\eta^6\text{-1,4-C}_6\text{H}_4(\text{CH}_3)_2)(\eta^4\text{-COD})^+(\text{BF}_4^-)]$, 74238-42-9; $[\text{Ir}(\eta^4\text{-COD})\text{HCl}_2]$, 12148-12-8; $[\text{Ir}(\eta^4\text{-COD})(\mu\text{-OCH}_3)_2]$, 33087-83-1; $[\text{Ir}(\eta^4\text{-COD})\text{Cl}_2]$, 12112-67-3; $[\text{Ir}(\eta^4\text{-COD})(\text{acac})]$, 12154-84-6; $[\text{Ir}(\eta^6\text{-C}_6\text{D}_6)(\eta^4\text{-COD})^+(\text{BF}_4^-)]$, 75751-36-9; $[\text{Ir}(\eta^6\text{-1,4-C}_6\text{D}_4(\text{CD}_3)_2)(\eta^4\text{-COD})^+(\text{BF}_4^-)]$, 75751-38-1; $[\text{Ir}(\eta^4\text{-COD})(\text{S}(\text{C}_2\text{H}_5)_2)^+(\text{BF}_4^-)]$, 75751-40-5; C_6H_6 , 71-43-2; $1,2\text{-C}_6\text{H}_4(\text{CH}_3)_2$, 95-47-6; $1,3\text{-C}_6\text{H}_4(\text{CH}_3)_2$, 108-38-3; $1,2,3\text{-C}_6\text{H}_3(\text{CH}_3)_3$, 526-73-8; $1,2,4\text{-C}_6\text{H}_3(\text{CH}_3)_3$, 95-63-6; $1,3,5\text{-C}_6\text{H}_3(\text{CH}_3)_3$, 108-67-8; $1,2,3,4\text{-C}_6\text{H}_2(\text{CH}_3)_4$, 488-23-3; $1,2,3,5\text{-C}_6\text{H}_2(\text{CH}_3)_4$, 527-53-7; $1,2,4,5\text{-C}_6\text{H}_2(\text{CH}_3)_4$, 95-93-2; $\text{C}_6\text{H}_5\text{OH}$, 108-95-2; $\text{C}_6\text{H}_5\text{C}_6\text{H}_5$, 92-52-4; $\text{C}_6\text{H}_5\text{CH}_2\text{CH}=\text{CH}_2$, 300-57-2; *cis*- $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_3$, 766-90-5; *trans*- $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_3$, 873-66-5; tetralin, 119-64-2; naphthalene, 91-20-3; 9,10-dihydroanthracene, 613-31-0; anthracene, 120-12-7; indene, 95-13-6.

Supplementary Material Available: Tables I-VIII (arene-exchange data), Table IX (kinetic data for isomerization of coordinated allylbenzene), and Table XV (¹H chemical shifts for iridium(I) *p*-toluenesulfonato complexes and salts) (14 pages). Ordering information is given on any current masthead page.

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Synthesis of Poorly Crystallized Platinum Metal Dichalcogenides

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Poorly crystallized RuS_2 , OsS_2 , PtS_2 , and PdS_2 were prepared by the reaction of the anhydrous hexachlorometallate(IV) with hydrogen sulfide at various temperatures. Magnetic susceptibility measurements were obtained for the poorly crystallized materials as well as their annealed crystalline analogues. The magnetic susceptibility data indicate that the dichalcogenides are diamagnetic in both the poorly crystallized and crystalline phases. Powder X-ray diffraction analysis of the annealed materials indicates that RuS_2 and OsS_2 crystallize with the pyrite structure ($a = 5.610$ and $a = 5.620$ Å, respectively). PdS_2 crystallizes with an orthorhombic, distorted-pyrite structure ($a = 5.457$, $b = 5.532$, $c = 7.524$ Å). PtS_2 crystallizes in the hexagonal CdI_2 structure ($a = 3.544$, $c = 5.029$ Å).

Introduction

There has been recent interest in the "amorphous" or poorly crystallized transition-metal dichalcogenides, especially in the areas of electrochemistry and catalysis.¹⁻⁶ [X-ray diffraction

patterns of these compounds resemble those obtained for materials which might be classified as being almost amorphous. The presence of only a small degree of short-range order, as evidenced by the shape of the X-ray diffraction pattern ob-

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