species. Well-ordered supports are more selective than less ordered supports, and their structures influence reaction pathways.

Cracking Experiments. Pore sizes, surface area, and acidity also control the activity and cracked product selectivities of these catalysts when used in upgrading gas oil to transportation and heating fuels. Because of their lack of surface acidity, low (40–90 m^2/g) surface area, and small pore opening, natural clays are not active cracking catalysts. Similarly, UO$_2^{2+}$-exchanged bentonite (with 9.91% UO$_2^{2+}$), because of its small ($\sim$4.6 Å) pore height, cannot sorb or crack the high molecular weight hydrocarbons present in gas oil; therefore (like zeolites with 4–6-Å pore openings), it is inactive, Table IV. Introduction of oxycations of aluminum and dehydroxylation (in air at 300 °C/4 h) generates a microporous structure with 392 m^2/g of BET surface area and a pore height of $\sim$8.2 Å capable of sorbing C$_6$–C$_{10}$ normal paraffins and branched aromatics;[23,24] the ACH–(UO$_2^{2+}$–bentonite) contains 0.33% UO$_2$.

The presence of 2.96% UO$_2$ as in (UO$_2^{2+}$,ACH)–bentonite does not significantly affect activity nor product selectivity; these properties depend mainly on the area generated by pillaring and on the nature of the silicate layer.[20]

Pillared clays (after a mild thermal aging) are as active as commercially available fluid cracking catalysts containing a zeolite (of the faujasite type) with an effective pore opening of 8.2 Å;[16] see Table IV. However, commercial FCC are more carbon selective and hydrothermally stable to temperatures at which pillared clays collapse with loss of surface and catalytic properties.

Conclusion

Pillared clays can bridge the gap between small pore zeolites and larger pore amorphous aluminosilicates and mixed oxide catalysts. Photochemical selectivity can be controlled by choosing a support with different pore sizes. In general, the order of increased selectivity for the photooxidation reactions reported here is clay < pillared clay ≤ zeolite. Photochemical selectivity (as well as product selectivity for gas oil cracking) is controlled by the catalysts' pore sizes and surface area.

Acknowledgment. S.L.S. and J.F.T. acknowledge the generous support of the National Science Foundation under Grants NSF-CHE 8204417 and NSF-CPE-8317876 for this work. Special thanks go to Prof. James M. Bobbitt for discussions concerning the mechanisms proposed in this work.

Registry No. UO$_2^{2+}$, 16637-16-4; H$_3$CCH$_2$OCH$_2$CH$_3$, 60-29-7; H$_3$CCHO, 75-07-0; H$_3$CCH$_2$OH, 64-17-5; H$_3$CCH(OCH$_2$CH$_3$)$_2$, 105-57-7; ACH, 1327-41-9; hectorite, 12173-47-6.

Mechanisms of Arene Exchange in (Arene)tricarbonylchromium Compounds: Intermolecular and Intramolecular Exchanges in Complexes of Propenylbenzene, Stilbenes, and 1,1-Diphenylethylene

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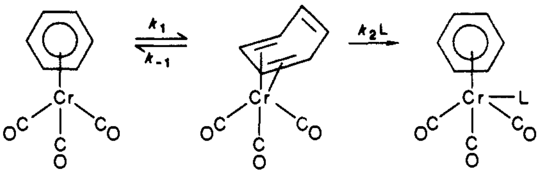
Contribution from the Department of Chemistry, D-006, University of California, San Diego, La Jolla, California 92093. *Received May 2, 1986*

Abstract: Kinetic studies of arene exchange of (*trans*-propenylbenzene)tricarbonylchromium with benzene reveal intramolecular and intermolecular participation by the propenyl substituent. Intramolecular participation via direct bonding of Cr(CO)$_3$ to the alkene portion of the ligand is supported by the observed "internal" exchange in Cr(CO)$_3$ complexes of the three isomers of diphenylethene. The magnitudes of the internal exchange rate constants and the effect of added donor catalysts on internal exchange indicate that the geometry of the unsaturated hydrocarbon influences the movement of Cr(CO)$_3$ along π systems.

Our first report on arene exchange reactions of (arene)tricarbonylchromium complexes[1] confirmed and expanded upon the earlier results[2-4] and clarified the mechanisms of arene exchange of benzene with alkyl-substituted benzene complexes. The significant elementary step of the proposed mechanism for arene complex reaction, with any of the ligands investigated, is a reduction in coordination of the arene ligand, eq 1. The first-order dependence upon ligand concentration is ascribed to unsuccessful competition for the vacant coordination site by attacking ligand compared to the "uncoordinated" ene of the arene ligand ($k_{-1} \gg k_2[\mathrm{L}]$). Studies of arene exchange in polycyclic aromatic complexes by Strohmeier,[5] Cais,[6] and others[7,8] have indicated an increase in rate of exchange compared to benzene derivatives. Coordinated naphthalene is more labile than coordinated benzene, exchanging [^{14}C]naphthalene primarily via a unimolecular process.[5] This could result from a stabilization of the tetrahapto intermediate as shown in eq 2. Tricarbonylchromium also moves from ring-to-ring in naphthalene and substituted naphthalene Cr(CO)$_3$ complexes.[7] These migrations occur readily only in coordinating solvents, implying intermolecular dissociative exchange via (solvent)$_3$Cr(CO)$_3$ intermediates. A theoretical



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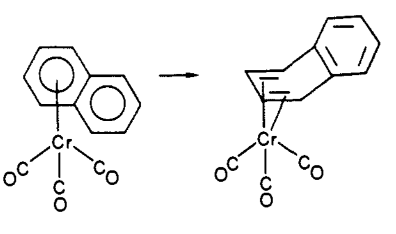

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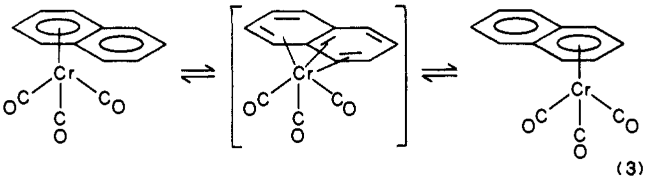
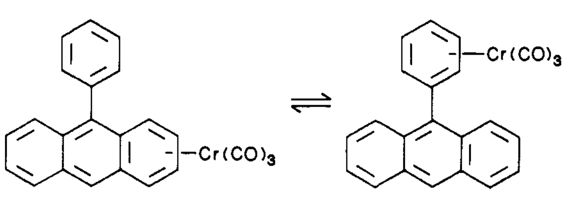
treatment of "haptotropic" rearrangements focused on intramolecular migration of $M(CO)_3$ between rings of naphthalene.[8] The study revealed the minimum energy pathway to be circuitous, eq 3, therefore permitting dissociative intermolecular reaction with



(3)

donor ligands, via movement of $Cr(CO)_3$ away from the ring junction, to compete with intramolecular exchange. Experimental evidence has been provided for this process.[7b] Similarly, the migration from benzene ring to anthracene ring in (9-phenylanthracene)tricarbonylchromium, eq 4, occurs readily in ether



(4)

solvent and is believed to transpire via an intermolecular dissociative process.[9]

Herein we report the effects of extending the π system at one position of an arene ring on arene exchange reactivity. The reactivity of (*trans*-propenylbenzene)tricarbonylchromium toward benzene as well as the internal and external exchange reactivities of $Cr(CO)_3$ complexes of the three diphenylethylene isomers were investigated. Examples of intramolecular migrations of $Cr(CO)_3$ between identical binding sites are provided, and the effects of arene structure and added catalyst on "internal" arene exchange provide evidence concerning the nature of the unsaturated chromium species in solution.

Experimental Section

General. Methods. Proton NMR spectra were recorded on both a Varian EM-390 90-MHz spectrometer and a fabricated ^{1}H NMR spectrometer equipped with a Nicolet 1180E computer operating at 360 MHz. Infrared spectra were recorded on either a Pye-Unicam 3-200 or Nicolet 7199 infrared spectrometer. Mass spectra were recorded on a VG-ZAB 1F high resolution mass spectrometer by using 20 eV ionizing energy, an accelerator voltage of 8000 eV and with a resolution of 2000. Solvents and liquid reactants were handled by using either Precision Sampling Corp. pressure-lok syringes or Popper and Sons, Inc. Perfektum glass syringes. Syringes were weighed before and after addition with concentrations being calculated by weight. ^{1}H NMR tubes were of 9-in. length and 5 mm o.d. model 507-PP from the Wilmad Glass Co.

Reagents and Materials. Deuterated solvents, benzene-d_6 (99.5% atom %), cyclohexane-d_{12} (99.5% atom %), acetone-d_6 (99.5% atom %) and *p*-dioxane-d_8 (98.5% atom %) were used as purchased in sealed ampules from either Aldrich or Sigma. Other reactants or solvents were purified according to literature methods[10] and distilled. α-Chloro-*p*-xylene, α-bromo-*p*-xylene, triphenylphosphine, potassium carbonate, Mg turnings, ammonium chloride, benzil, *trans*-propenylbenzene, cyclopropylbenzene, deuterium oxide, and phenyltrimethylsilane were used as purchased. *p*-Tolualdehyde was distilled before using. *p*-Bromotoluene was recrystallized from ethanol before use. Ehtyl acetate was dried over anhydrous K_2CO_3 for 2 days before using. Sodium hydride was washed with hexanes, dried in vacuo, and stored as a powder in a dessicated container.

Methods: Syntheses

(4-Methylbenzyl)triphenylphosphonium Bromide. Triphenylphosphine (28 g, 0.11 mol) and α-chloro-*p*-xylene (20.5 g, 0.11 mol) were refluxed in toluene (250 mL) for 18 h. The reaction mixture was then cooled and filtered. The white solid was washed with cold ethyl acetate and dried to yield 28.2 g (66% yield): ^{1}H NMR (360 MHz, $CDCl_3$, Me_4Si) s, 2.24, 3 H; d, 5.20, 2 H, J = 14 Hz; br s, 6.91, 4 H; m, 7.71, 15 H.

***trans*- and *cis*-4,4′-Dimethylstilbene.** A phase transfer Wittig reaction[11] between (4-methylbenzyl)triphenylphosphonium chloride or bromide (26.5 g, 0.07 mol) and *p*-tolualdehyde (8.0 g, 0.07 mol) using K_2CO_3 (9.2 g, 0.07 mol) as base in wet *p*-dioxane was used. Chromatography of the crude product on silica gel, hexane eluent, first provided *cis*-4,4′-dimethylstilbene (2.5 g, 18% yield) as clear liquid and then *trans*-4,4′-dimethylstilbene (7.0 g, 51% yield) as white flaky crystals for an overall yield of 69%: *cis*-4,4′-dimethylstilbene IR ($CHCl_3$, CaF_2) 3016 (s), 2923 (w), 1516 (ms), 1509 (ms); ^{1}H NMR (360 MHz, $C_6D_6$8, Me_4Si) s, 2.04, 6 H; s, 6.51, 2 H; d, 6.87, 4 H, J = 8 Hz; d, 7.25, 4 H, J = 8 Hz. *trans*-4,4′-Dimethylstilbene mp 182–183 °C; ^{1}H NMR (360 MHz, C_6D_6, Me_4Si) s, 2.15, 6 H; d, 7.00, 4 H, J = 8; s, 7.02, 2 H; d, 7.30, 4 H, J = 8; IR ($CHCl_3$, CaF_2) 3027 (m), 3016 (ms), 3012 (ms), 2922 (ms), 1516 (s).

***trans*- to *cis*-4,4′-Dimethylstilbene Photoisomerization.** The trans isomer was isomerized to the cis isomer according to a literature method[12] by using a photolysis mixture of *trans*-4,4′-dimethylstilbene to triplet sensitizer, benzil, of 5:1 in benzene solvent. *cis*-4,4′-Dimethylstilbene (80% yield), containing a small amount of trans isomers, was isolated from the photolysis mixture (40 h) after solvent removal and chromatography on silica gel. Rigorous separation of the cis and trans hydrocarbons was never necessary, as the monotricarbonylchromium complexes were easily separated by chromatography.

1,1-Di-*p*-tolylethylene. The method for synthesis of diphenylethylene was used.[13] Two equivalents of *p*-tolylmagnesium bromide were reacted with 1 equiv of ethyl acetate. The intermediate, 1,1-di-*p*-tolylethan-1-ol, liberated by hydrolysis, was dehydrated to the olefin, in situ, to provide, after extraction and chromatography, a 60% isolated yield of the clear liquid. The product contained a small amount of di-*p*-tolyl which was easily removed after complex synthesis by chromatography: IR (neat, NaCl) 3050 (m), 3024 (m), 2950 (s), 2860 (s), 1510 (m), 1500 (m), 1450 (m), 1110 (m), 900 (m), 820 (s), 800 (s); ^{1}H NMR (360 MHz, C_6D_6, Me_4Si) s, 2.26, 6 H; s, 5.38, 2 H; d, 7.13, 4 H, J = 8 Hz; d, 7.23, 4 H, J = 8 Hz.

(Arene)tricarbonylchromium Complexes. The majority of complexes were synthesized by using the method of Mahaffy and Pauson.[14] A few complexes were available from Strem Chemical Co. The complexes were very amenable to purification by column chromatography on silica gel, eluent/hexanes to 9:1 hexanes/ethylacetate. The unreacted hydrocarbon, used in excess of $Cr(CO)_6$, eluted much more rapidly than the mono complexes. Bis complexes did not move from the origin until the eluent was richer in ethyl acetate. The complexes were then either vacuum sublimed or recrystallized from hexanes as final purification. The complexes are yellow to orange-yellow crystalline solids. The physical data on the complexes[1c] are in agreement with those previously published.[15-18]

Deuteration of (Di-*p*-tolylethylene)$Cr(CO)_3$ Isomers. The complexes were deuterated in the manner of Trahanovsky and Card[19] except that sodium hydride was used as base to generate the deuteriomethylsulfinyl carbanion[20] and the complexes were dissolved in THF or THF–Me_2SO-d solution for introduction into the reaction vessel. Control of reaction conditions was important as side reactions of the benzylic tricarbonylchromium anion can become competitive with deuterium exchange. The most prevalent side reactions of the anions were isomerization of the cis isomer anion to the trans isomer and apparent nucleophilic addition of the anion of the 1,1-isomer to the terminal olefin of another complex[21]

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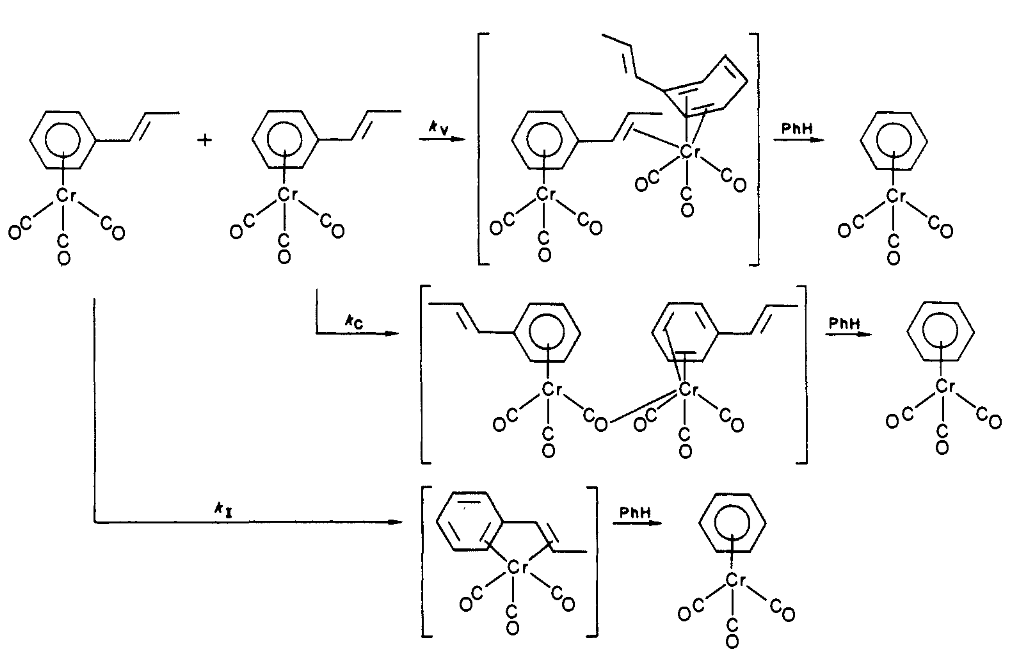


(6)

(7)

(8)

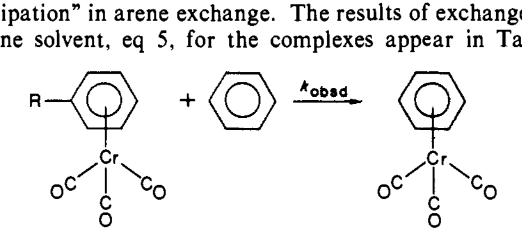
to produce a more stable benzhydryl anion and therefore oligomers upon quenching with D_2O. The cis-to-trans isomerization was minimized by shortening the reaction times and lowering the temperature. Enough trans deuterated complex was produced from the isomerization that deuteration of the trans complex was never necessary. Reducing the initial concentration of anion, lowering the temperature, and lengthening the reaction time lead to efficient deuteration of the 1,1-isomer. The physical properties of the deuterated complexes are the same as the proto derivatives except the upfield methyl resonance, 1.4–1.6 ppm, in the ^1H NMR is reduced to a small broad resonance and the ions in the MS reflect the isotopic substitution. The free hydrocarbon ions were used to calculate the percent deuterium incorporation rather than the parent ions. The parent ions were less intense due to fragmentation, even at low EI, and the different Cr isotopes complicated the analysis: *trans*-$C_{19}D_3H_{13}O_3Cr$ 95% atom %, ^1H NMR; 91% atom %, MS. *cis*-$C_{19}D_3H_{13}O_3Cr$ 92% atom %, ^1H NMR; 93% atom %, MS. 1,1-$C_{19}D_3H_{13}O_3Cr$ no. 1, 69% atom %, ^1H NMR; 65% atom %, MS; no. 2, 98% atom %, ^1H NMR; 98% atom % MS.

Kinetic Studies. Exchange reactions were observed by NMR methods as previously described.[1a] Typical rate plots are shown in Figure 1.

Equilibrium Constant Determinations. The ^1H NMR tube was charged with equimolar amounts of complexed arene and free arene (and vice versa). A half of a milliliter of *p*-dioxane-d_8 was added, and the tube was sealed under vacuum as in the procedure for preparing kinetics samples. The reaction mixture was permitted to equilibrate for 24 h at 142 °C. The ^1H NMR spectrum was recorded and resonances integrated several times. Initial experiments showed that further heating was unnecessary and equilibrium was established in a day. (Toluene)tricarbonylchromium (and toluene) usually were used with another arene (arene complex) in an experiment so the free and complexed methyl protons could be used to evaluate the equilibrium position. Equilibrium constants were calculated as the ratio of the square of the mol fractions of free and complexed toluene.

Results and Discussion

External Exchange. A few substituted (arene)tricarbonylchromium complexes were investigated for "intramolecular participation" in arene exchange. The results of exchange with benzene solvent, eq 5, for the complexes appear in Table I.



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(*trans*-Propenylbenzene)tricarbonylchromium exhibited the fastest rate of exchange. (Styrene)tricarbonylchromium could not be studied quantitatively due to polymerization of the liberated styrene at the high temperatures necessary to observe exchange. An earlier report[3] showed that olefins catalyze arene exchange; therefore, any intermolecular contributions to the k_{obsd} value needed to be evaluated and considered separately. This was accomplished by determining first-order rate constants at four different initial complex concentrations. The first-order kinetics plots, Figure 1, are all linear within experimental error. The slope of a plot of these rate constants vs. complex concentration, 170 M^{-1} s^{-1}, evaluates intermolecular participation of the propenyl substituent (k_V) plus the usual complex catalysis (k_C), while the *y*-intercept, 50×10^{-7} s^{-1}, measures the intramolecular participation of the propenyl substituent (k_I) (eq 6, 7, and 8). It is not possible to evaluate k_V and k_C separately. We have shown elsewhere[1b] that eq 7 actually proceeds through a bridged species, which might take the form shown below. This species would derive simultaneous and perhaps synergistic catalysis from both carbonyl and alkene substituents. However, comparison of k_V + k_C with k_C for benzene (2×10^{-6} M^{-1} s^{-1}) indicates that the

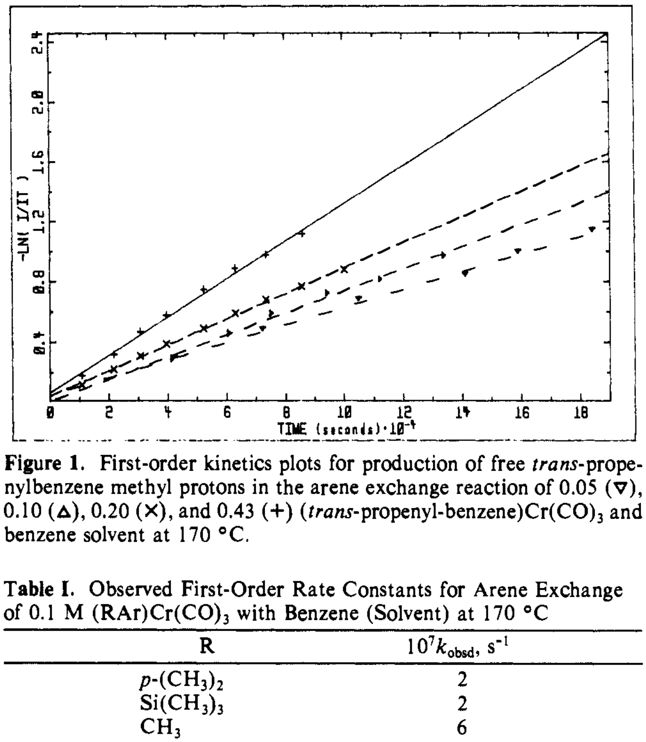
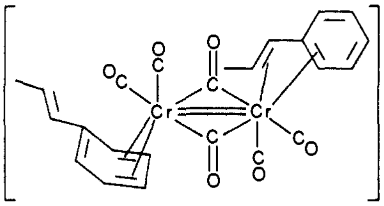


Figure 1. First-order kinetics plots for production of free *trans*-propenylbenzene methyl protons in the arene exchange reaction of 0.05 (▽), 0.10 (△), 0.20 (×), and 0.43 (+) (*trans*-propenyl-benzene)$Cr(CO)_3$ and benzene solvent at 170 °C.

Table I. Observed First-Order Rate Constants for Arene Exchange of 0.1 M $(RAr)Cr(CO)_3$ with Benzene (Solvent) at 170 °C

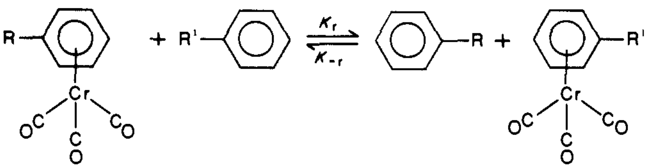
R	10^7k_{obsd}, s^{-1}
p-$(CH_3)_2$	2
$Si(CH_3)_3$	2
CH_3	6
cyclopropyl	7
$N(CH_3)_2$	26
trans-propenyl	73



alkene is involved in the intermolecular catalysis as well as the intramolecular acceleration (k_1).

A similar treatment for *N,N*-dimethylaniline complex, requiring a more complicated kinetic analysis due to the thermodynamic stability of the aniline complex, indicated the enhanced exchange rate is due to intermolecular interactions.

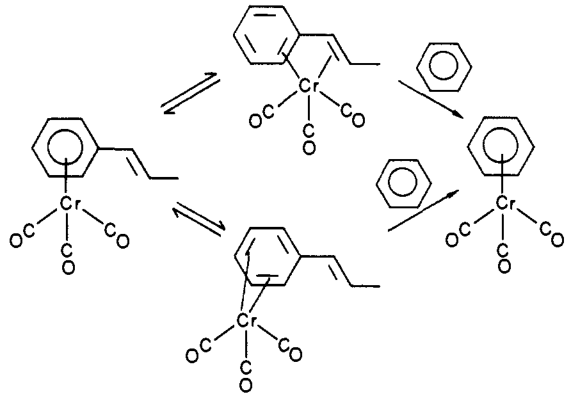
Equilibrium constants, Table II, determined according to eq 9 for the toluene, benzene, and *trans*-propenylbenzene complexes, indicate the propenyl substituent does not significantly destabilize the complex relative to toluene and benzenetricarbonylchromium. The accelerations of exchanges by the propenyl substituent are therefore kinetic rather than thermodynamic effects.



(9)

The accelerated exchange of (*trans*-propenylbenzene)Cr(CO)$_3$ is anticipated since a decrease in coordination of the arene is important in arene exchange.[1,22] Partial or complete localization of a diene fragment from the π system in styrene requires less energy than in benzene.[23] The reactivity of (naphthalene)Cr(CO)$_3$ in exchange with naphthalene[5] indicated that stabilization of the lower coordination (η^4), by stabilizing the uncoordinated "ene", causes the kinetics to change from second order (first order in attacking arene and complex) to first order, independent of attacking arene. Attempts to determine the dependence of the rate of *trans*-propenylbenzene complex exchange on attacking benzene concentration, cyclohexane solvent, were frustrated by plating of Cr metal on the walls of the NMR tube. The rate appears to depend upon benzene concentration, but a precise concentration dependence could not be determined.

The necessary reduction in coordination of arene, hexahepta to tetrahapto, can occur in two different ways for a styrene complex, eq (10). The rearrangement producing the "internal"



(10)

η^4-intermediate requires less energy than the rearrangement to the "external" η^4-intermediate.[23] The reactivity of the intermediates toward external ligand attack probably differs significantly. The chromium of the "external" η^4-intermediate appears to be open to ligand attack, reducing the unfavorable interactions normally encountered by the ligand when the chromium of the unsaturated intermediate is complexed only to carbon atoms of the arene ring.[22,24]

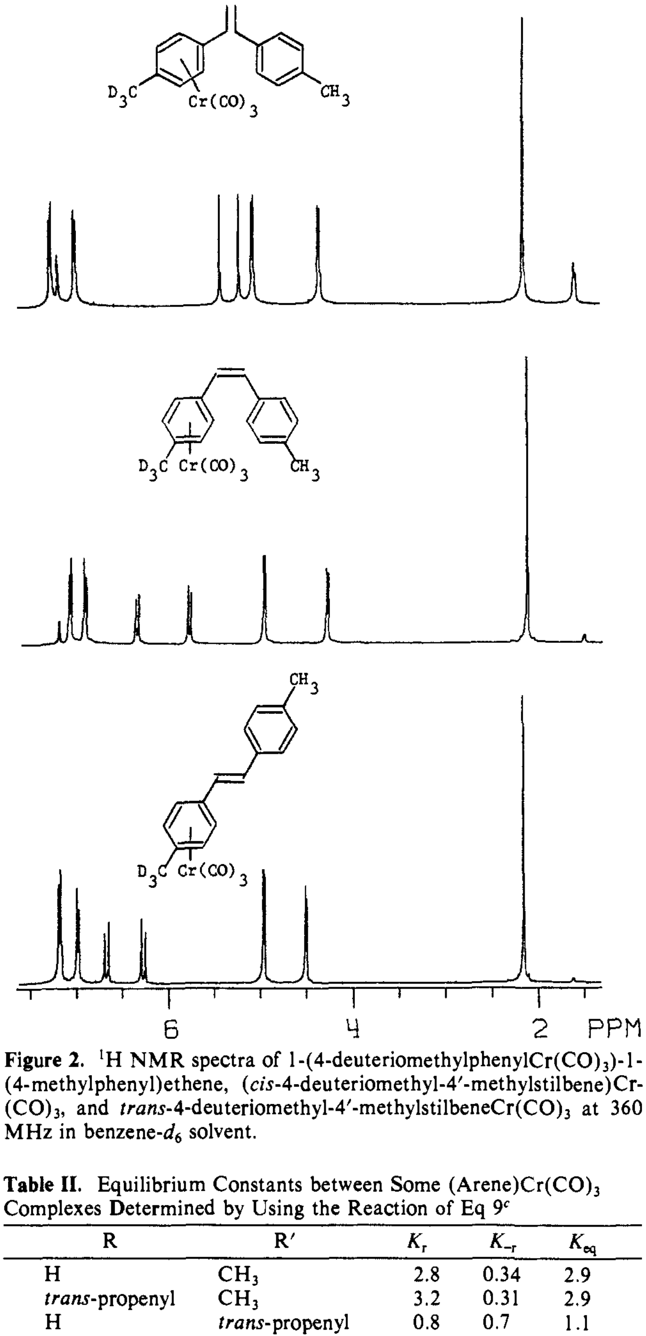


Figure 2. ^{1}H NMR spectra of 1-(4-deuteriomethylphenylCr(CO)$_3$)-1-(4-methylphenyl)ethene, (*cis*-4-deuteriomethyl-4'-methylstilbene)Cr(CO)$_3$, and *trans*-4-deuteriomethyl-4'-methylstilbeneCr(CO)$_3$ at 360 MHz in benzene-d_6 solvent.

Table II. Equilibrium Constants between Some (Arene)Cr(CO)$_3$ Complexes Determined by Using the Reaction of Eq 9[c]

R	R'	K_r	K_{-r}	K_{eq}
H	CH_3	2.8	0.34	2.9
trans-propenyl	CH_3	3.2	0.31	2.9
H	*trans*-propenyl	0.8	0.7	1.1
H	*p*-$(CH_3)_2$	7.3	0.12	7.7[a]
H	*E* isomer[b]	~2		
H	*Z* isomer[b]	~4		
H	1,1-isomer[b]	~2		

[a] From ref 3. [b] The R'Ph was the isomeric ditolylethene indicated. [c] Ratios of uncomplexed and complexed methyl and olefin protons were used to determine the equilibrium position.

The molecular orbitals of cyclopropane[25] suggested that (phenylcyclopropane)tricarbonylchromium might exhibit reactivity similar to the *trans*-propenylbenzene complex. The exchange reactivity, however, was very similar to that of the toluene complex. The orbital energies of the C–C bonds in cyclopropane lie intermediate between the normal C–C σ orbitals and the π molecular orbitals of ethylene.[25] Either these energy differences or differences

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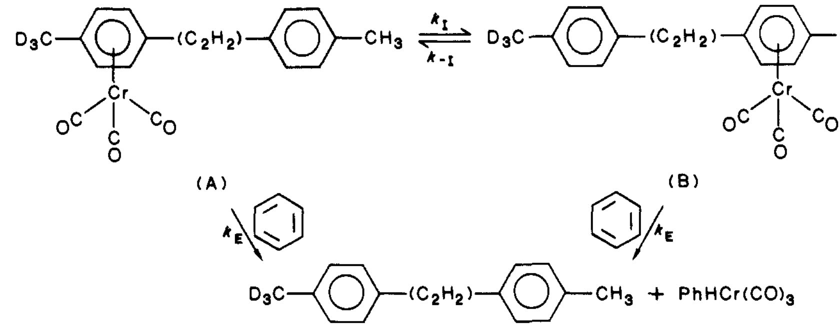
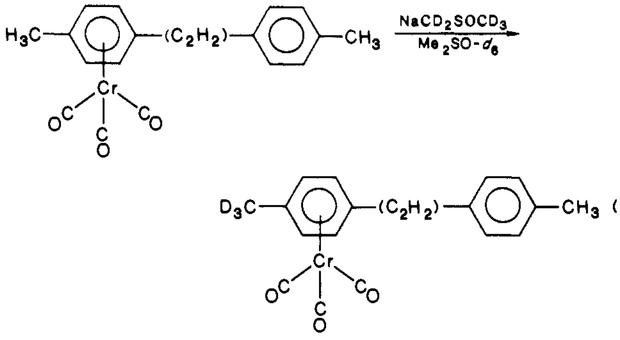
Scheme I



in orbital symmetry could account for the absence of the bent bond interaction.

Internal and External Exchange in Diphenylethane Isomers. Participation of the alkene by direct bonding to the chromium may be determined by measuring "internal" and external arene exchange of 1,2-diphenyletheneCr(CO)$_3$. If the tricarbonylchromium group complexes the olefin of styrene in a partially coordinated intermediate, it should slide from ring to ring in *trans*-stilbene. Disubstitution of the alkene permitted examining the effect of isomerism on internal and external arene exchange. The ratios of rate constants for internal exchange, movement of Cr(CO)$_3$ from ring to ring in stilbene, and external exchange onto arene solvent evaluate the capacity of Cr(CO)$_3$ to utilize extensions of the π system in exchange reactions. The three isomers of bis(4-methylphenyl)ethene were synthesized readily and complexed with 1 equiv of tricarbonylchromium. Methyl substitution on the rings was necessary to follow the internal arene exchange, and para substitution afforded simplified ^{1}H NMR spectra in the complexed aromatic and aromatic proton regions. The ability to selectively deuterate the complexed ring methyl protons[19] and the upfield shift of complexed ring methyl protons permits quantitative evaluation of rate constants for internal exchange. Figure 2 shows the ^{1}H NMR spectra of the three deuterated isomer complexes, 1,1, *Z*, and *E*, at 360 MHz in benzene-d_6 solvent. The proton impurity in the deuteriomethyl group is visible at ~1.6 ppm in all three spectra. Characteristic of the geometries are the 16 and 12 Hz coupling constants of the olefin protons for the *E* and *Z* isomers, respectively, and the terminal olefin protons of the 1,1-isomer between 5.0–5.5 ppm.



(11)

The reaction scheme for arene exchange of these complexes appears in Scheme I. The equilibrium constant of unity between the species A and B simplifies the kinetics considerably. The kinetics of internal and external exchange are analyzed separately when $k_I \gg k_E$. k_I is determined from the first-order approach to equilibrium disappearance of species A methyl protons relative to total methyl protons. The k_E value is calculated as before,[1] from the first-order appearance of free hydrocarbon or benzene complex. The kinetics eq, 12 and 13, are plotted to provide $(2k_I$

$$-\ln (A_t - B_t) = (2k_I + k_E)t + C \qquad (12)$$

$$-\ln (A_t + B_t) = k_E t + C \qquad (13)$$

$+ k_E)$ and k_E as the slopes when internal and external exchange rates are comparable. The methyl resonances of the starting complex, *A*, and free hydrocarbon have similar chemical shifts and cannot be integrated separately. A separate measure of external exchange, production of free olefin protons, for example, is necessary to evaluate the fraction of starting complex, *A*, at time, *t*. The A_t values then are used in both equations to permit evaluation of k_I and k_E.

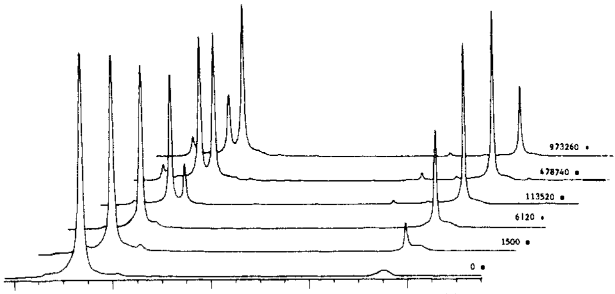


Figure 3. Methyl region in the ^{1}H NMR (360-MHz) of 0.1 M (*cis*-4-deuteriomethyl-4′-methylstilbene)Cr(CO)$_3$ in benzene-d_6 (solvent) at various reaction times at 170 °C. Resonances are CH$_3$ of free hydrocarbon (2.03 ppm), CH$_3$ of starting complex (A) (2.07 ppm), and CH$_3$ of internal exchange product (B) (1.47 ppm).

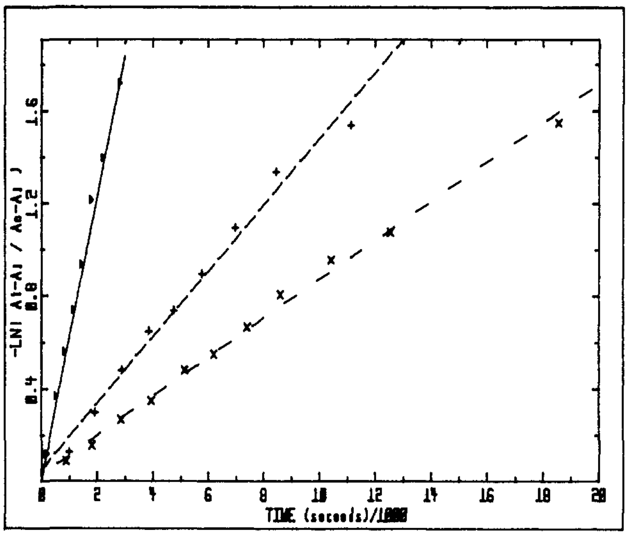


Figure 4. First-order approach to equilibrium kinetics plots for internal exchange of the three di-*p*-tolylethylene isomer complexes: *E*, (×--); *Z*, (+--), and 1,1 (△—).

The methyl region in the ^{1}H NMR spectrum of one complex at various reaction times in benzene-d_6 at 170 °C is shown in Figure 3. Internal exchange is faster than external exchange for all three isomers so the rate constants are evaluated separately as in the first case discussed. The first-order approach to equilibrium kinetics plots for the isomers are illustrated in Figure 4. The rate constants for internal and external exchange of the three isomer complexes in benzene or benzene-d_6 are summarized in Table III. . The order of reactivity for "uncatalyzed" internal exchange is 1;1 > *Z* > *E* and for external exchange it is *E* > 1,1 > *Z*. The 1,1- and *E* isomers usually exhibited oxidative decomposition approaching the first half-life of external exchange

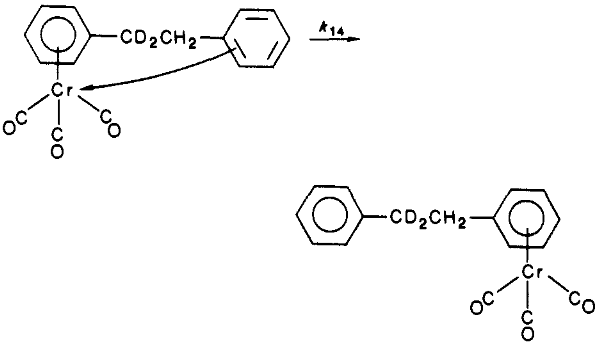
Table III. Observed First-Order Rate Constants for Internal and External Exchange of the Three (Di-*p*-tolylethylene)tricarbonylchromium Complexes (0.1 M) in Benzene-d_6 or Benzene at 170 °C

isomer	$k \times 10^7$ s^{-1}	
	k_I	k_E
E	420 ± 10	18 ± 1
E	420 ± 20	16 ± 1
Z	695 ± 30	
Z	670 ± 35	6.6 ± 0.3
Z	715 ± 35	5.9 ± 0.4
1,1	3160 ± 130	14.0 ± 0.7
1,1	2710 ± 220	
1,1	3060 ± 90	10.4 ± 0.8

and, therefore, were monitored only to 40% external arene exchange with benzene.

Internal Alkene Catalysis of External Exchange. The increased rates of external exchange of all the ditolylethene isomeric complexes (Table III) can be seen by comparing the second-order rate constants (k_E/complex concentration) with those for the toluene or xylene complexes shown in Table I. Although the rate constants for the *E*, *Z*, and 1,1-isomers, 17×10^{-6}, 6×10^{-6}, and 12×10^{-6} M^{-1} s^{-1}, respectively, do not equal that of the propenylbenzene complex (73×10^{-6} M^{-1} s^{-1}), they are larger than that of the logical reference compounds, *p*-xylenechromium tricarbonyl (2×10^{-6} M^{-1} s^{-1}). The thermodynamic stabilities of the isomeric ethene complexes are similar to that of xylene complex (Table II). Therefore the accelerated external exchange rates, albeit with small accelerations, are kinetic and reflect an "internal alkene catalysis" of the type shown for the propenylbenzene complex in eq 8. The somewhat faster reactions of the *Z* and 1,1-isomers are consistent with a steric effect toward attack on the *E* isomer.

Alkene-Mediated Internal Exchange. Table III clearly demonstrates extraordinary rates of internal exchange for all three alkene isomers. A comparison of internal exchange with the attack by benzene can be made by calculating the concentration of benzene required (assuming first-order in benzene) to make the external rate equal to the internal exchange. This would require about 270, 1300, and 2700 M benzene for the *E*, *Z*, and 1,1-isomers, respectively. This large acceleration might be due to simple internal attack of arene such as we have observed elsewhere.[26] However, the first-order rate constant for this process is 6×10^{-8} M^{-1} s^{-1}. Thus the *E* and *Z* ethene isomers exchange 700 and 1000 times faster than the saturated analogue. In addition, such a direct process is sterically prevented in the *E* isomer.

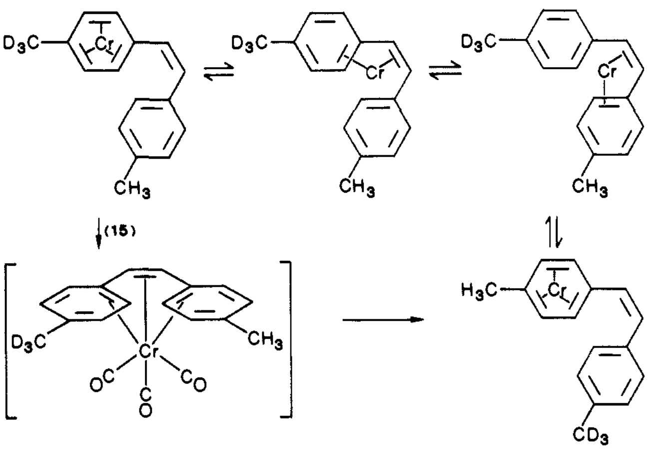


(14)

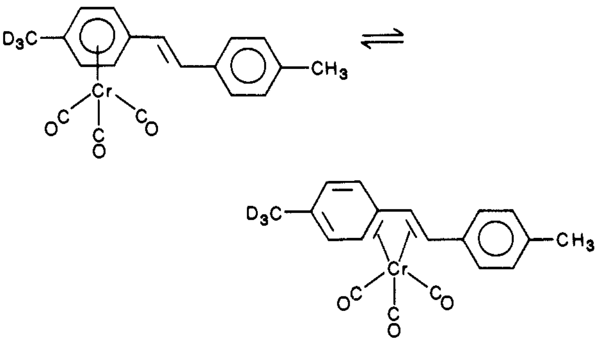
It is therefore established that the Cr(CO)$_3$ group moves across the alkene in each case. Similarly, the 1,1-isomer exchanges internally 40 times faster than does the reference compound, (ditolylmethane)tricarbonylchromium.[26]

The migration in the *Z*- or 1,1-isomers could be visualized as either a three-step process, by using the analogy of reaction 8, or a two-step process with simultaneous involvement of the ethene and arene groups.

Although the metal saturated complex along the pathway of eq 15 should be more stabilized than the unsaturated intermediates, the small increase in rate in changing from the *E* to *Z* isomer indicates that this preference is small, perhaps a result of the steric interference of the two arene rings. Taken together these rearrangements provide additional evidence for the η^6 to η^4 rearrangements of (arene)tricarbonylchromium complexes.



The facile migration in the (*E*)-ditolylethene complex is especially informative with regard to the η^4 complex involving the alkene ligand. In this case the η^4 complex external to the ring must be transgressed and there is essentially no driving force available from the second ring. The logical transition state for this migration is essentially an η^2 complex because the distances to the two arene rings is rather large. This suggests that the *E* isomer has a more unsaturated transition state than do the *Z* or 1,1-isomers, a conclusion further documented below.



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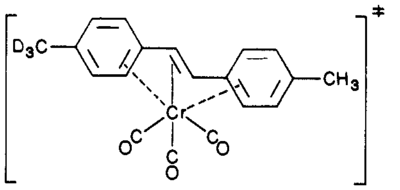

Catalyses of Internal and External Exchange by Ketones and Ethers. The effect of a catalyst on internal and external exchange was examined initially for the *E* and *Z* isomers. The successive NMR spectra show that the resonance of the rearranged product and of free hydrocarbon appear at comparable rates. Internal and external exchange are competitive, and eq 12 and 13 are plotted in Figure 5 for the *Z* isomer to evaluate k_I and k_E. These values appear in the top entries of Table IV. The rate constants indicate that for the *E* isomer both internal and external exchange are accelerated by catalyst. Only external exchange is accelerated by catalyst in the *Z* complex.

To compare the behavior of the 1,2-diphenylethene isomers with that of the 1,1-isomer, the temperature was reduced to 160 °C, and *p*-dioxane was substituted as catalyst. Internal and external exchanges were measured at 0, 0.1, and 0.4 molar *p*-dioxane. Internal exchange was more rapid than external exchange, even at the highest *p*-dioxane concentration, and this permitted separate analysis of internal and external exchange to determine the rate

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[26] Traylor, T. G.; Goldberg, M. J., unpublished results.

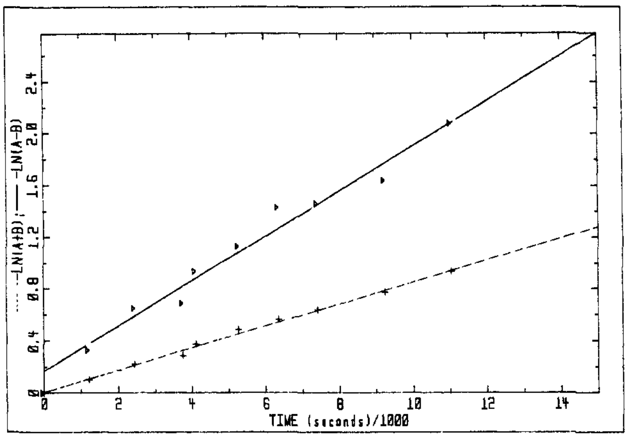
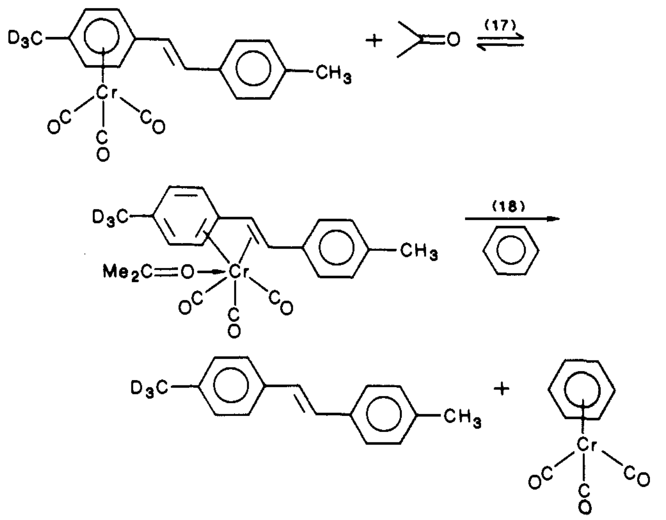


Figure 5. Plots of eq 11 (---) and 12 (—) for arene exchange of *Z* isomer complex in benzene-d_6 with 0.37 M acetone-d_6 at 170 °C.

constants. These rate constants appear in Table IV.

The effect of catalyst on internal exchange is best illustrated graphically as shown in Figure 6. Only the internal exchange of the *E* isomer is accelerated by the catalyst as evidence by the E line (x---) of the three plots. The slope of this line increases notably progressing from benzene to 0.4 M *p*-dioxane, bypassing the *Z* isomer at 0.1 M *p*-dioxane and the 1,1-isomer at 0.4 M *p*-dioxane. The external exchange is accelerated by catalyst, as expected, for all three isomers.

Synergistic Catalysis of External Exchange. Since the acetone catalyzed external exchange rate constants (k_E) exceed the uncatalyzed rate constants by about a factor of 100 and because such catalyzed exchanges were shown to be independent of arene concentration,[1] we can calculate a second-order rate constant $k_E{}^{\text{acetone}} = 7 \times 10^{-4}$ M^{-1} s^{-1} for the *E* isomer complex and $k_E{}^{\text{acetone}} = 2.3 \times 10^{-4}$ M^{-1} s^{-1} for the *Z* isomer. These rate constants should be smaller than the value of $k_E{}^{\text{acetone}} = 5 \times 10^{-5}$ M^{-1} s^{-1} for the benzene complex[1] because the alkene complexes are thermodynamically more stable. The 12 times greater rate for the *E* isomer suggests that the acetone and internal alkene catalyses act in concert. Therefore it appears that two catalyst donors (alkene and ketone) and one arene can occur in the transition state. The intermediate shown above would then react rapidly with arene. All three ditolylethene isomer complexes show catalysis of external exchange, but it is not clear from the data that the outer (arene–alkene) complex is involved in the cases of the *Z* and 1,1-isomers.



Catalysis of Internal Exchange. Perhaps the most striking observation in this work is the effect of acetone or dioxane on the rates of internal exchanges of the *E*, *Z*, and 1,1-isomers seen in Table IV and illustrated in Figure 6. The *Z* and 1,1-isomer complexes, which react faster than does the *E* isomer in the absence of catalyst, are essentially unaffected by the presence of

Table IV. Observed First-Order Rate Constants for Internal and External Exchange of the Three Di-*p*-tolylethylene Complex Isomers (0.1 M) in Benzene or Benzene-d_6 at 170 °C in the Presence of Dilute Catalyst, Acetone-d_6, or *p*-Dioxane

isomer	catalyst	(cat.), M	*T* °C	k_I	k_ϵ
E			170	420 ± 10	18 ± 1
E	acetone-d_6	0.23	170	2630 ± 210	1670 ± 60
Z			170	670 ± 30	7 ± 0.3
Z	acetone-d_6	0.37	170	440 ± 30	850 ± 20
E[a]			160	115 ± 6	
E			160	145 ± 6	
E	*p*-dioxane	0.1	160	510 ± 15	40 ± 2
E	*p*-dioxane	0.4	160	1330 ± 30	137 ± 6
Z			160	290 ± 5	
Z	*p*-dioxane	0.1	160	305 ± 10	23 ± 1
Z	*p*-dioxane	0.4	160	380 ± 20	65 ± 1
1,1			160	1280 ± 40	
1,1	*p*-dioxane	0.1	160	1220 ± 60	43 ± 2
1,1	*p*-dioxane	0.4	160	1100 ± 40	133 ± 4

[a] 1:1 benzene-d_6/cyclohexane-d_{12}.

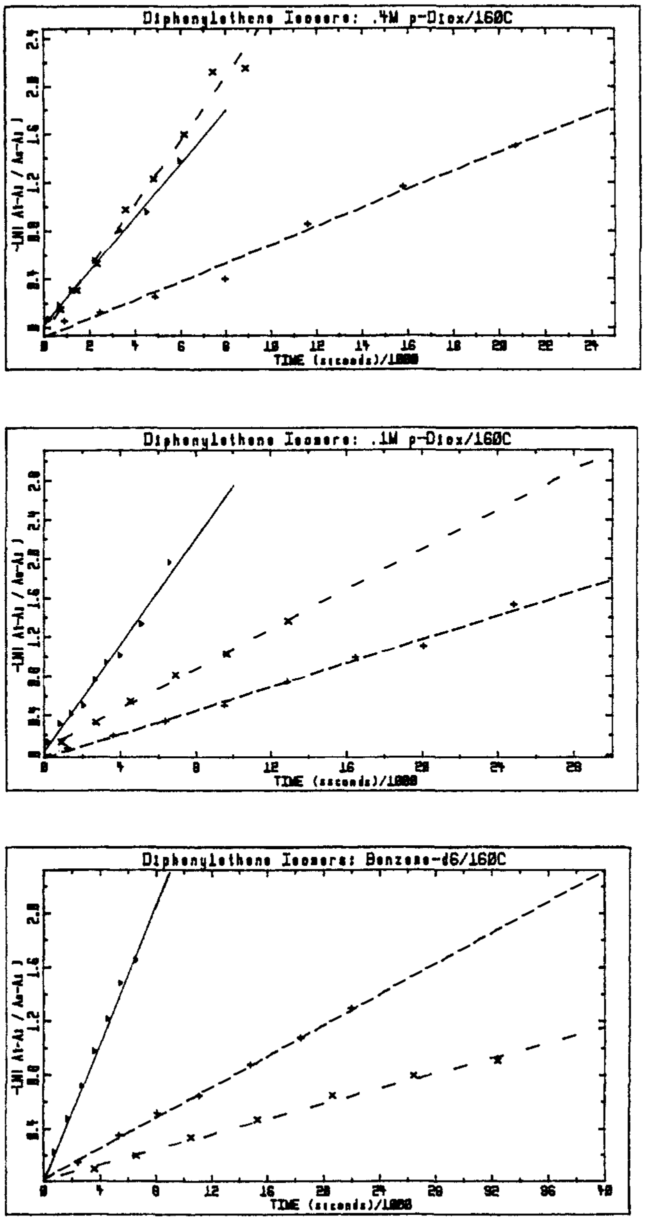


Figure 6. First-order approach to equilibrium kinetics plots for internal exchange of 1-(4-$CD_3PhCr(CO)_3$)-1-(4-CH_3Ph)ethylene (▲), (*cis*-4-deuteriomethyl-4-methylstilbene)$Cr(CO)_3$ (+) and (*trans*-4-deuteriomethyl-4-methylstilbene)$Cr(CO)_3$ (×) at 160 °C. From bottom to top: benzene-d_6 solvent, 0.1 M *p*-dioxane/benzene-d_6 solvent, and 0.4 M *p*-dioxane/benzene-d_6 solvent.

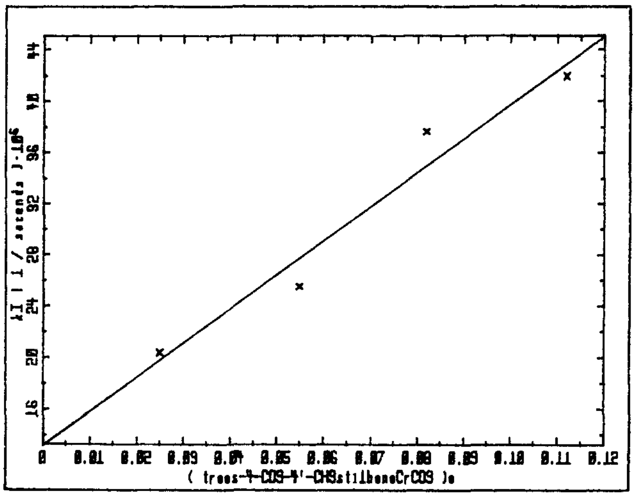
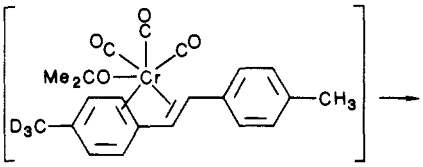
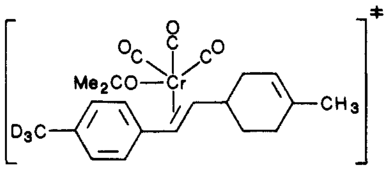


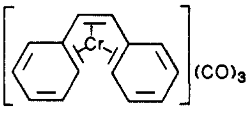
Figure 7. First-order rate constants for internal exchange of E complex at 170 °C vs. complex concentration (M).

0.1 or 0.4 M dioxane while the *E* isomer is accelerated. Similarly acetone accelerates internal exchange of the *E* but not the *Z* isomer. The simplest explanation of this result is the greater unsaturation of the intermediate species in the internal exchange of the *E* than of the other isomers as illustrated with the intermediate below.

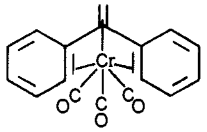


E complex intermediate





Z complex intermediate

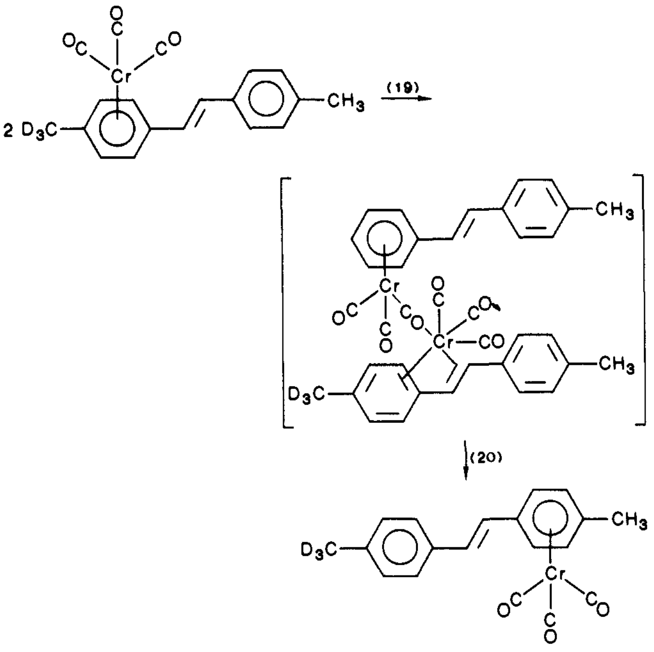


1,1-complex intermediate

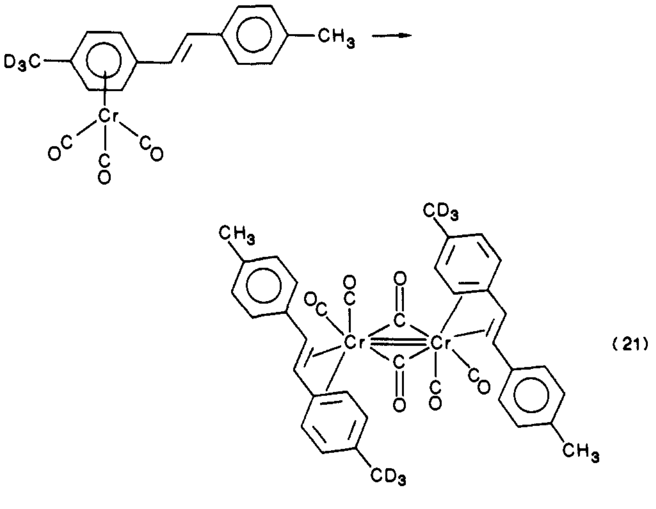
Both the *Z* and 1,1-isomeric complexes can remain saturated at chromium throughout the migration process by interacting simultaneously with the alkene and arene groups in a manner which is well-documented for simple triene complexes.[27-31] Thus, in these cases, an η^6 to η^6 migration occurs. Such processes would compete with rather than be assisted by acetone attack. Furthermore this arrangement provides steric hindrance against ligand attack.[22,24]

On the other hand, the *E* isomer would derive considerable stabilization from acetone complexation at the transition state. This transition state is necessarily very unsaturated. This scheme is also consistent with the proposed synergistic internal and external catalysis of the *E* isomer, eq 17 and 18.

The sensitivity of the *E* isomer toward catalysis of internal exchange was also demonstrated by plotting the rate of internal exchange as a function of complex concentration in Figure 7. The slope of the line, although inaccurate, reveals a second-order rate constants of 4 × 10^{-4} M^{-1} s^{-1} for the complex–complex catalysis of the internal exchange, shown in eq 19 and 20. The complex



catalysis constant for internal exchange is only 2 to 3 times smaller than the acetone catalysis constant (10^{-3} M^{-1} s^{-1}) for the same process. This ratio for the benzene complex is about ten. This result suggests the intriguing possibility that bridged species, demonstrated for benzene exchange,[1b] might occur here as well and that the rearrangement occurs within the dimer structure.



It is important to note that the acetone catalysis does not have the same rate-limiting step for the internal exchange as for external arene exchange (see eq 1) because the catalyzed internal exchange is much too fast. The step shown in reaction 22 is much slower than reaction 17. This is an additional indication that the outer η^4 intermediate (eq 16) is more stable than the internal one (eq 1).

Migrations of Metals along π Systems. Although the migration from one arene ring along a π system to a second ring has not previously been observed, there are other examples of apparently less energetic migrations. In particular the migration of metal groups in a polynuclear hydrocarbon are well-documented.[8,27] The rearrangement of a chromiumtricarbonyl group from the arene

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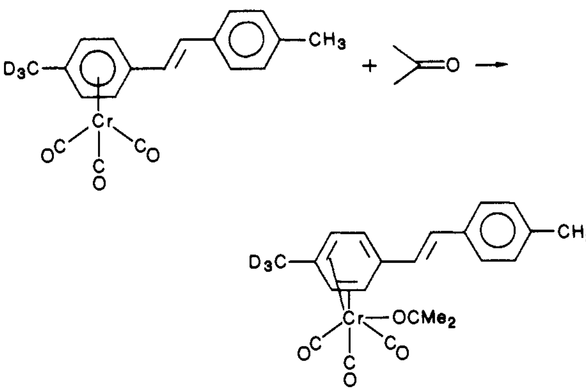
(27) See references In Deganello, G. *Transition Metal Complexes of Cyclic Polyolefins*; Academic Press: New York, 1979.

(28) Nicholas, K. M.; Kerber, R. C.; Stiefel, E. I. *Inorg. Chem.* **1971**, *10*, 1519.

(29) King, R. G.; Stone, F. G. A. *J. Am. Chem. Soc.* **1960**, *82*, 4557. King, R. B.; Stone, F. G. A. *J. Am. Chem. Soc.* **1961**, *83*, 3590.

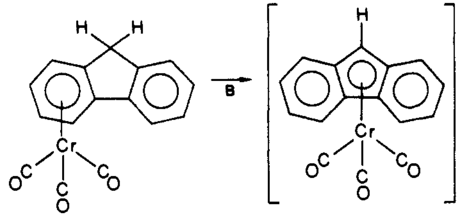
(30) Salzer, A. *J. Organomet. Chem.* **1976**, *107*, 79. Salzer, A. *J. Organomet. Chem.* **1976**, *117*, 245.

(31) Yalpani, M.; Benn, R.; Goddard, R.; Wilke, G. *J. Organomet. Chem.* **1982**, *240*, 49.



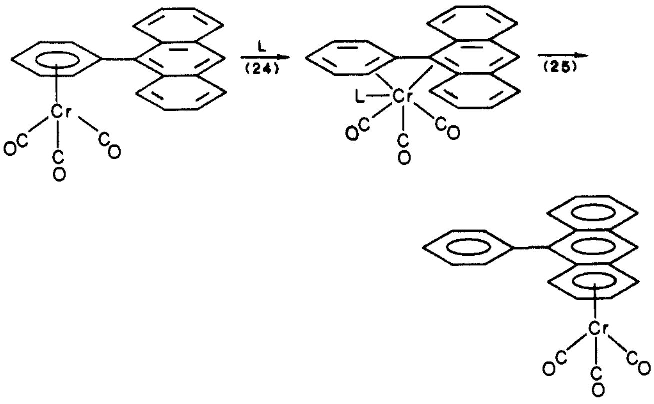
(22)

in fluorene or indene[28] to the five-membered ring upon deprotonation is well-known.



(23)

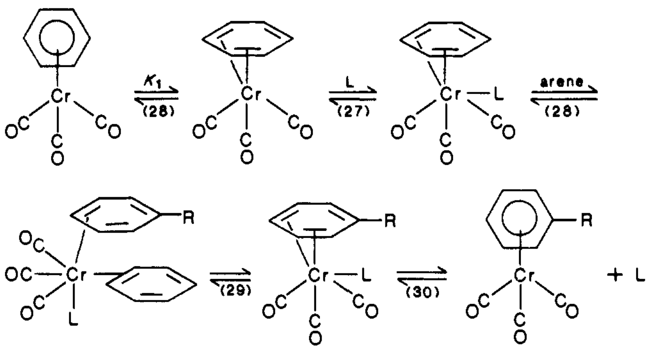
Other examples are migration in complexes of naphthalene and 9-phenylanthracene mentioned earlier (eq 3 and 4). Although the migration of eq 4 was suggested to proceed by a dissociative (catalyzed) process, the present results make a direct migration more likely.



Mechanistic Conclusions

The catalyzed internal exchanges provide convincing evidence for the nature of nucleophilic catalysis of exchange in general. It is not necessary that the $Cr(CO)_3$ group be removed as $L_3Cr(CO)_3$.[32] This group is made more subject to a second nucleophilic attack by the attachment of the first nucleophile, presumably resulting from the decreased bond strength per electron pair as the arene decreases its hapticity.

The general mechanistic scheme which arises from this work involves a sensitivity of (arene)tricarbonylchromium species to two electron donors, perhaps through $\eta^6 \rightleftharpoons \eta^4$ preequilibria. The further η^4 to η^2 migration is then much more facile and more easily brought about by nucleophiles than is the $\eta^6 \rightleftharpoons \eta^4$ change. Finally, η^2 ligands dissociate whether they are arenes or other nucleophiles. The catalytic ligand L can be any two-electron Lewis base, including ketones, nitriles, carbonyl groups (M—C≡O), alkenes, or even another arene.[27]



Acknowledgment. We are grateful to the National Science Foundation (Grant CHE-20612) for support of this research and to Professor Martin Semmelhack for helpful discussions.

Registry No. (p-$(CH_3)_2C_6H_4$)$Cr(CO)_3$, 12129-27-0; ($PhSi(CH_3)_3$)$Cr(CO)_3$, 33248-13-4; ($PhCH_3$)$Cr(CO)_3$, 12083-24-8; (PhB)$Cr(CO)_3$ (B = cyclopropyl), 104337-77-1; ($PhN(CH_3)_2$)$Cr(CO)_3$, 12109-10-3; (PhB)$Cr(CO)_3$ (B = *trans*-propenyl), 98169-43-8; (PhH)$Cr(CO)_3$, 12082-08-5; (B)$Cr(CO)_3$ (B = *trans*-4,4′-dimethylstilbene), 104337-78-2; (B)$Cr(CO)_3$ (B = *cis*-4,4′-dimethylstilbene), 104419-22-9; (B)$Cr(CO)_3$ (B = 1,1-di(p-tolyl)ethylene), 104337-79-3; Ph_3P, 603-35-0; (4-methylbenzyl)triphenylphosphonium bromide, 2378-86-1; *trans*-4,4′-dimethylstilbene, 18869-29-9; *cis*-4,4′-dimethylstilbene, 2510-76-1; 1,1-di(p-tolyl)ethylene, 2919-20-2; α-chloro-p-xylene, 104-82-5; p-tolualdehyde, 104-87-0; toluene, 108-88-3; *trans*-propenylbenzene, 873-66-5; p-xylene, 106-42-3.

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(32) See: Casey C.; O'Connor, J. *Chem. Rev.* **1986**, in press, for a review of direct and catalyzed ring slippage processes.