

Stereoelectronic Effects in Arene Exchange of (Arene)tricarbonylchromium Complexes: Internal Arene Exchange and Internal Arene Catalysis of External Arene Exchange

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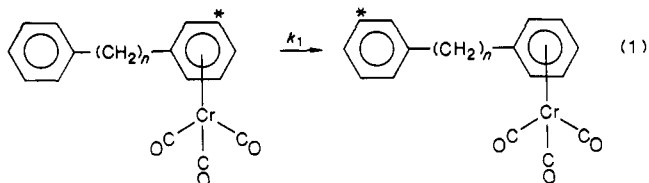
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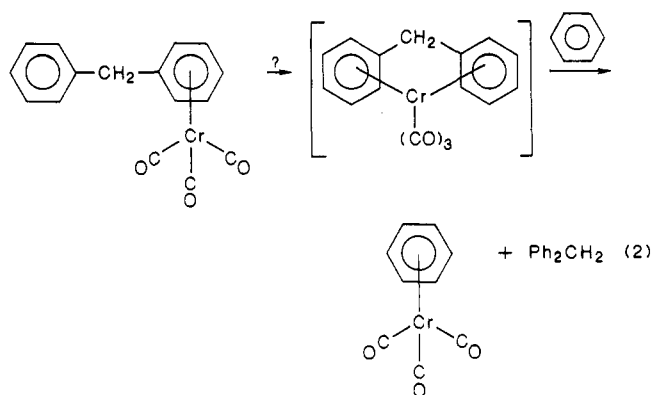
Kinetics of internal and external arene exchanges in benzene as solvent have been studied with tricarbonylchromium complexes of ditolylmethane, ditolylcyclopropane, dimesitylmethane, and dibenzobicyclo[2.2.2]octadienes. These studies define the stereoelectronic requirements for arene exchange and document the stepwise process in which the bonding in the displaced arene proceeds from η^6 to η^4 to η^2 . A new intermediate, (arene)₃Cr(CO)₃, is indicated by the catalyzed exchange reactions of some of these compounds.

Introduction

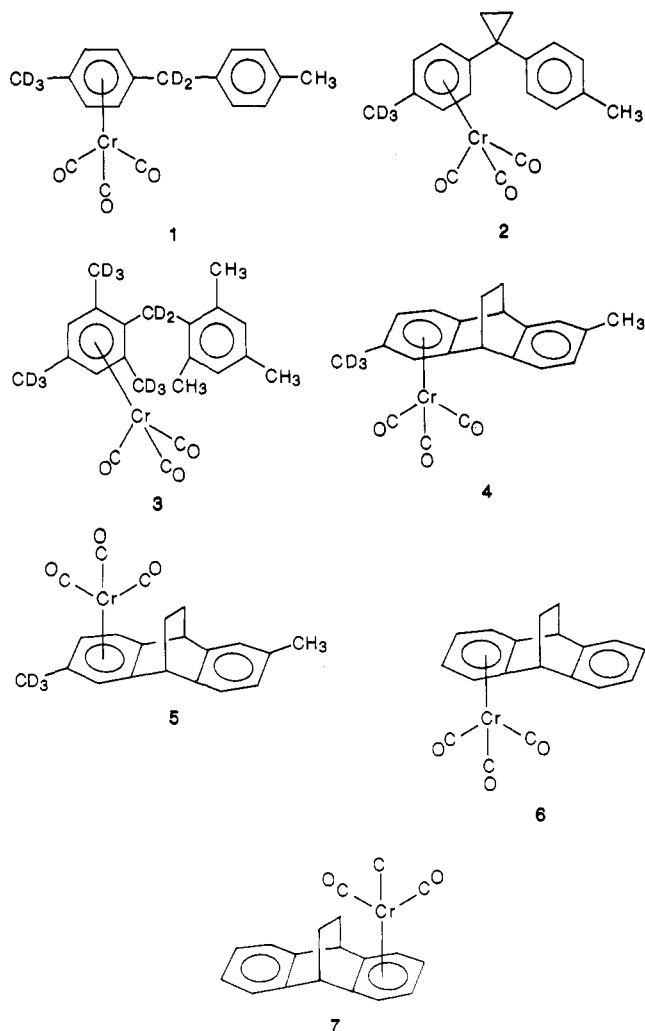
In a previous study¹ of neighboring group participation² in arene exchange reactions of (arene)tricarbonylchromium complexes, we made two observations that seemed to require further investigation. First, the internal exchange in diarylalkanes is dependent upon chain length (k_1 in eq 1 depends upon n) implying some stereoelectronic pref-



erence in the transition state for exchange. Second, the external exchange rate for the diphenylmethane complex appeared to be faster than that of the toluene complex, suggesting some catalytic behavior of the appended arene ring (eq 2.)



In order to further probe the geometrical requirements for arene exchange³ and to amplify any possible internal catalytic effect, we have prepared additional complexes having the appended arene in an ideal arrangement for the formation of η^2 - η^2 complex and others designed deliberately to destabilize this conformation. Complexes 1-7 are shown below.



Experimental Section

General. ¹H NMR, FTIR, and mass spectra were recorded as previously described. The NMR determination of rates has also been described in detail elsewhere.^{1,3}

Cyclohexane and di-*n*-butyl ether were distilled from sodium metal. Tetrahydrofuran (THF) was dried over potassium-benzophenone and distilled. Dimethyl-*d*₆ sulfoxide (Sigma), cyclohexane-*d*₁₂ (Aldrich), and benzene-*d*₆ (Aldrich) were used as received, with a fresh ampule being used for each kinetic run. Diiodomethane was purchased from Alfa Chemical Co. Hexacarbonylchromium (Alfa) was used without purification, as was 2,2',4,4',6,6'-hexamethyldiphenylmethane (dimesitylmethane)

(1) Traylor, T. G.; Goldberg, M. J. *J. Am. Chem. Soc.* 1987, 109, 3968.
 (2) (a) Capon, B.; McManus, S. P. *Neighboring Group Participation*; Plenum: New York, 1976; Vol. 1. (b) Hutchins, R. O.; Rua, L. *J. Org. Chem.* 1975, 40, 2567.
 (3) Traylor, T. G.; Stewart, K. J.; Goldberg, M. J. *J. Am. Chem. Soc.* 1984, 106, 4445.

(Alfa) and zinc-copper couple (Alfa). Carbon-13 carbon monoxide was 90% carbon-13 (Merck, Sharp, and Dohme), and ethylene was 99.5% minimum (Matheson).

Preparation of Complexes. Synthesis of [4-(trideuteriomethyl)-4'-methyl- α,α -dideuteriodiphenylmethane]tricarboxylchromium (1) has been described elsewhere.¹ [2,4,6-Tris(trideuteriomethyl)-2',4',6'-trimethyl- α,α -dideuteriodiphenylmethane]tricarboxylchromium was synthesized and deuterated by standard methods detailed previously:¹ ¹H NMR (CDCl₃, 90 MHz) δ 6.8 (s, 2 H), 4.9 (s, 2 H), 2.25 (s, 6 H), 2.0 (br s, 4 H). (2,2'-4,4'-6,6'-Hexamethyldiphenylmethane)tricarboxylchromium: mp 127–130 °C (lit.⁴ 126–130.5 °C); ¹H NMR (CDCl₃, 90 MHz): δ 6.8 (s, 2 H), 4.9 (s, 2 H), 3.9 (s, 2 H), 2.27 (s, 6 H), 2.18 (s, 3 H), 2.15 (s, 3 H), 2.08 (s, 6 H).⁴

[4-(Trideuteriomethyl)-4'-methyl-1,1-diphenylcyclopropane]tricarboxylchromium (2). The alkene 1,1-ditolylethene, prepared from tolyl Grignard reagent and ethyl acetate followed by acid dehydration, was converted to the cyclopropane by the Simmons-Smith procedure. It contained some bitolyl which was not separated. The chromium complex was synthesized as previously described.¹ Chromatography on silica gel separated the bitolyl complex and yielded 1.6 g (31%) of (4,4'-dimethyl-1,1-diphenylcyclopropane)tricarboxylchromium: mp 109–110 °C; ¹H NMR (CDCl₃, 90 MHz) δ 7.2–7.0 (A₂B₂, 4 H), 5.2–4.9 (A₂B₂, 4 H), 2.3 (br s, 3 H), 2.1 (s, 3 H), 1.2 (s, 4 H). The complex was deuterated in the usual manner,¹ with the yield of deuterated material being lower than usual (25%). Chromatography yielded 0.4 g of [4-(trideuteriomethyl)-4'-methyl-1,1-diphenylcyclopropane]tricarboxylchromium: mp 109–110 °C; ¹H NMR (CDCl₃, 90 MHz): δ 7.2–7.0 (A₂B₂, 4 H), 5.2–4.9 (A₂B₂, 4 H), 2.3 (br s, 3 H), 1.2 (s, 4 H); IR (CaF₂, CDCl₃) ν (CO) 1960, 1883 cm⁻¹.

exo- and endo-Tricarboxylchromium Complexes of Dibenzobicyclo[2.2.2]octadiene.⁵ Dibenzobicyclo[2.2.2]octadiene⁶ (1.4 g, 6.8 mmol) and 0.76 g (3.5 mmol) of hexacarboxylchromium were added to 5 mL of THF in 55 mL of di-*n*-butyl ether and refluxed (120 °C) for 90 h under argon. After the solution was cooled, 2 g of silica gel was added and the solvent removed in vacuo. Chromatography from a hexanes-packed column using hexanes as eluent gave recovered starting hydrocarbon. Upon changing to 90:10 hexanes/ethyl acetate, two yellow bands were isolated, separated by approximately *R_f* 0.1. The first band off the column was identified as the *exo*-tricarboxylchromium isomer 7 (0.28 g, 11% yield): mp 178–179 °C; ¹H NMR (C₆D₆, 90 MHz) δ 7.0 (s, 4 H), 4.85–4.75 (m, 2 H), 4.45–4.3 (m, 2 H), 3.45 (s, 2 H), 2.2–2.0 (m, 2 H), 1.4–1.2 (m, 2 H); IR (CaF₂, CDCl₃) ν (CO) 1960, 1885 cm⁻¹. The second band was found to be the corresponding *endo*-tricarboxylchromium isomer 6 (0.73 g, 31% yield): mp 177–178 °C; ¹H NMR (C₆D₆, 90 MHz) δ 7.3 (s, 4 H), 5.1–4.9 (m, 2 H), 4.6–4.45 (m, 2 H), 3.6 (s, 2 H), 1.5–1.2 (A₂B₂, 4 H); IR (CaF₂, CDCl₃) ν (CO) 1965, 1888 cm⁻¹; mass spectra (DI, 70 eV), *m/e* (% RA) 343 (14.7), 342 (49.9), 286 (65.8), 260 (33.1), 259 (100), 143 (16.4). A third yellow band was isolated by using 50:50 hexanes/ethyl acetate and identified as the bis(tricarboxylchromium) adduct having one Cr(CO)₃ group *exo* and the other *endo* by comparison with the individual mono(tricarboxylchromium) complexes (0.88 g, 37% yield): ¹H NMR (C₆D₆, 90 MHz) δ 5.1–4.9 (m, 2 H), 4.7–4.5 (m, 4 H), 4.35–4.2 (m, 2 H), 2.8 (s, 2 H), 2.1–1.85 (m, 2 H), 1.1–0.9 (m, 2 H).

endo-Tricarboxylchromium 2-(Trideuteriomethyl)-6-methyldibenzobicyclo[2.2.2]octadiene (4). 2,6-Dimethylanthracene was synthesized by the method of Morgan and co-workers:⁷ mp 242–244 °C (lit. 250 °C); ¹H NMR (CDCl₃, 90 MHz) δ 8.3 (s, H₉, H₁₀), 7.9–7.7 (ABC, H₁, H₄, H₅, H₈), 7.3–7.15 (m, H₃, H₇), 2.45 (s, 6 H). The remaining product of the thermolysis step leading to 2,6-dimethylanthracene was identified as the 2 + 2

Table I. Equilibria between Various Complexes and Their Respective Arenes According to Eq 3^a

reagents		K	ref
A'	C		
benzene	4	0.055	this work
toluene	PhHCr(CO) ₃	3	8
<i>p</i> -xylene	PhHCr(CO) ₃	7	8
mesitylene	PhHCr(CO) ₃	28 (calcd)	
mesitylene	(<i>p</i> -xylene)Cr(CO) ₃	4	8, 9
benzene	5	300 (estd)	this work

$$^a K = (C')(A)/(C)(A')$$

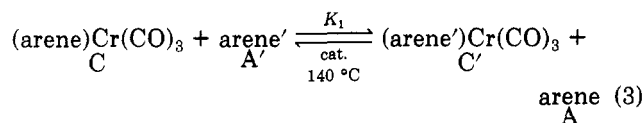
cyclodimer of two anthracene molecules: ¹H NMR (CDCl₃, 90 MHz) δ 8.3–8.0 (m, 4 H), 7.3–7.1 (m, 8 H), 4.2 (s, 4 H), 2.4 (s, 12 H). Diels-Alder bomb reaction with ethylene in the same manner as that described above for anthracene, followed by recrystallization from ethanol, yielded 1.7 g (95%) of 2,6-dimethyldibenzobicyclo[2.2.2]octadiene: ¹H NMR (CDCl₃, 90 MHz) δ 7.1–6.8 (m, 6 H), 4.15 (s, 2 H), 2.25 (s, 6 H), 1.65 (s, 4 H). Reaction with hexacarboxylchromium also paralleled that outlined above for dibenzobicyclo[2.2.2]octadiene, with the reaction being refluxed for only 48 h to minimize formation of the bis-Cr(CO)₃ adduct. Despite repeated chromatography with a variety of hexane/ethyl acetate mixtures, separation of the *exo* complex could not be achieved. The yield of the isomeric mixture of complexes was 50%. A solvent mixture of 50:50 hexanes/ethyl acetate eluted the bis complex, which had one Cr(CO)₃ moiety *endo* and the other *exo* in 10% yield: ¹H NMR (CDCl₃, 90 MHz) δ 5.7–5.35 (m, 4 H), 5.15–4.95 (m, 2 H), 3.75 (br s, 2 H), 2.15 (d, 6 H), 2.4–2.2 (m, 2 H), 1.75–1.55 (m, 2 H). Chromatography of the *exo-endo* mixture of mono(tricarboxylchromium) complexes using 98:2 hexanes/ethyl acetate as eluent and taking 15–25 mL cuts yielded pure *endo*-tricarboxylchromium 2,6-dimethyldibenzobicyclo[2.2.2]octadiene: ¹H NMR (CDCl₃, 90 MHz) δ 7.2–6.9 (m, 3 H), 5.7–5.45 (m, 2 H), 5.1–4.9 (m, 1 H), 4.0 (d, 2 H), 2.4 (s, 3 H), 2.2 (s, 3 H), 1.75 (s, 4 H). This NMR identifies the compound as an analogue of 6 whose crystal structure has been determined. Deuteration in the usual manner gave the desired *endo*-tricarboxylchromium 2-(trideuteriomethyl)-6-methyldibenzobicyclo[2.2.2]octadiene (4): ¹H NMR (CDCl₃, 90 MHz) δ 7.2–6.9 (m, 3 H), 5.7–5.5 (m, 2 H), 5.1–4.9 (m, 1 H), 4.0 (d, 2 H), 2.4 (s, 3 H), 1.8 (s, 4 H).

Equilibrium Studies. Equimolar amounts of 2,6-dimethyldibenzobicyclo[2.2.2]octadiene and (benzene)tricarboxylchromium were weighed into an NMR tube, and 500 μ L of dioxane was syringed in. After three to five freeze-pump-thaw cycles the tube was sealed and its NMR spectrum recorded prior to heating in an oil bath thermostated at 142 \pm 0.2 °C. After the mixture was heated for 24 h, the NMR spectrum was recorded and the equilibrium constant determined by multiple integrations of the appropriate chemical shifts. Another spectrum was taken after heating for an additional 10 h to ensure that equilibrium had been achieved in 24 h. The equilibrium constant for 4 reacting with benzene was found to be 35.2 in favor of 4, which, for our purposes, must be statistically corrected to 17.6.

Results and Discussion

Variations in rates of arene exchange could result either from differences in thermodynamic complex stabilities or from differences which develop at the transition state. Among the compounds studied, only the *exo* isomer 7 showed unusual instability.

Equilibration of one complex with a second arene afforded equilibrium constants shown, along with published values, in Table I for reaction 3. In the case of equi-



(8) Mahaffy, C. A. L.; Pauson, P. L. *J. Chem. Res., Miniprint* 1979, 1752.

(4) Trahanovsky, W. S.; Kowalski, D. J.; Avery, N. J. *J. Am. Chem. Soc.* 1974, 96, 1502. ¹H NMR of (2,2',4,4',6,6'-hexamethyldiphenylmethane)tricarboxylchromium (100 MHz, CDCl₃, -45 °C): δ 6.89 (s, 2 H), 5.02 (s, 2 H), 3.89 (s, 2 H), 2.42 (s, 6 H), 2.26 (s, 3 H), 2.16 (s, 3 H), 2.06 (s, 6 H).

(5) Traylor, T. G.; Goldberg, M. J.; Mikszal, A. R.; Strouse, C. E., submitted for publication in *Organometallics*. Crystal structures of 6 and 7 are reported here.

(6) Thomas, C. L. (to Universal Oil Products Co.), U.S. Patent 2406 245, 1946.

(7) Morgan, G. T.; Coulson, E. A. *J. Chem. Soc.* 1929, 2203.

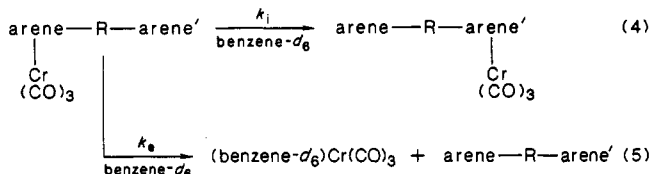
Table II. First-Order Internal (k_i) and External (k_e) Arene Exchange Rate Constants for the Reaction of Various (Diarylalkane)Cr(CO)₃ Complexes at 170 °C^a Along with Calculated Neighboring Group Participation (NGP) Values^b

complex	$10^7 k_i, \text{s}^{-1}$	$10^7 k_e, \text{s}^{-1}$	NGP, M
1	63.5 ± 4.2	5.7 ± 0.3	126
2	226 ± 9	3.0 ± 0.1	850
3	0.5 ^c	0.9 ± 0.1	6.3
4	9400 ± 460	12.4 ± 0.2	8600

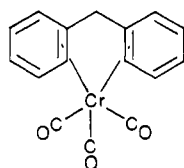
^a0.2 M complex in neat C₆D₆. ^bNGP = $k_i/(k_e/11.3 \text{ M})$. ^cMaximum rate assuming 2% would go undetected by NMR.

bration of dimethyldibenzobicyclo[2.2.2]octadiene with the (benzene)tricarbonylchromium complex to get equilibrium between this complex 4 and its exo isomer 5, none of the latter could be detected. Setting the limits of our detection at 5% of the other complexes, we estimate that the equilibrium $5 \rightleftharpoons 4$ favors the endo complex by at least 20. This makes 5 unstable toward the benzene complex by a factor of at least 300 in the equilibrium constants. By contrast, the equilibrium constant for 4 and the benzene complex is 18 compared to about 30 for mesitylene, a trisubstituted arene complex which is a good electronic model for 4. Therefore the endo complex 4 should behave about like the mesitylene complex toward displacement and the exo complex should be greatly accelerated. These findings are in agreement with the conclusions reached from the crystal structures which show 6 to be undistorted and 7 to be highly distorted as compared to the (benzene)tricarbonylchromium complex.⁵

The rate constants for internal and external exchange (eq 4 and 5) for complexes 1–4 are given as first-order constants in Table II.

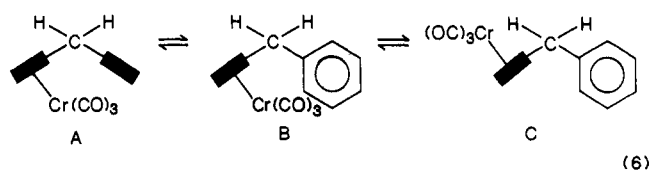


Internal Migrations. We had already discovered that the internal reaction varies with the length of the chain separating arene and arene' in the order (64, 0.62, 3.1, and $<0.1) \times 10^{-7} \text{ s}^{-1}$ for $n = 1, 2, 3,$ and $4,$ respectively, where $\text{R} = (\text{CH}_2)_n$.¹ Therefore, in this series the best geometry for neighboring group participation is provided by diphenylmethane, perhaps in a pseudopentadiene conformation.

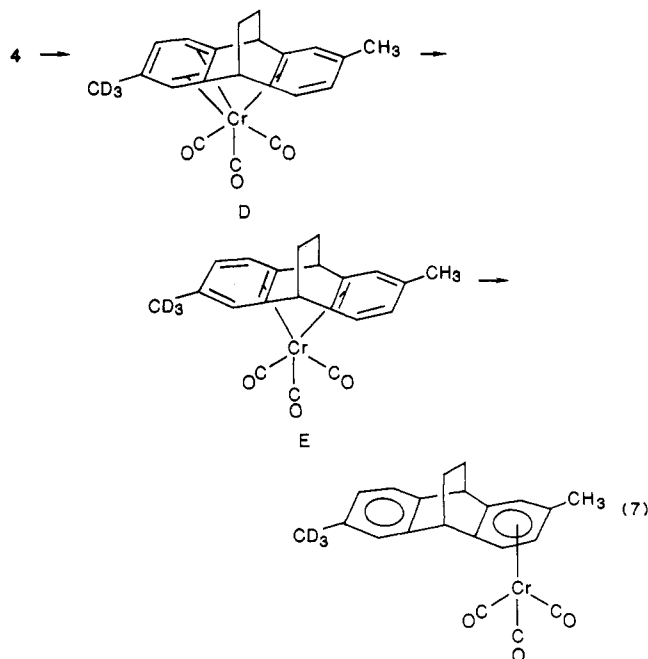


The first three entries in Table II, in which various steric restraints are placed upon the diphenylmethane type complexes, indicate a requirement for some optimum geometry for neighboring group participation. Comparing the dimesitylmethane complex 3 with the diphenylmethane complex 1, it is clear that in the displacement close approach of the second phenyl ring is required. The mesityl complex would, according to Trahanovsky,⁴ have much more strain in the "planar" form A required for optimum overlap of the incoming π orbitals. The stable conformer of 3 is C. This results in a 100-fold reduction

in internal migration for 3.

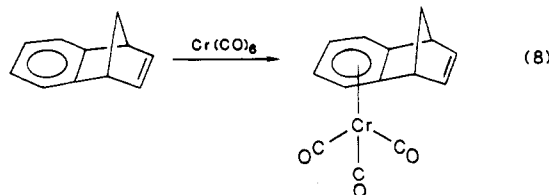


The probe for direct η^2 orbital overlap in the internal exchange is shown in the exchange of 4. The internal migration rate constant for 4 is $9.4 \times 10^{-4} \text{ s}^{-1}$, 150 times larger than that for 1. This rate is 8600 times faster than the bimolecular rate at an equivalent concentration of benzene, indicating an extraordinary neighboring group participation for this kind of reaction. This result indicates that the orientation of the attacking arene in the geometry of 4 is preferred and strongly supports the $\eta^4 + \eta^2$ interaction shown in eq 7, leading to the symmetrical η^4 in-



termediate or transition state. During the time required for this process to reach equilibrium, there is no CO exchange with either external CO or the CO ligands on another complex.¹⁰ Therefore the reaction is a true internal migration.

There are several other examples which show, in a more qualitative way, the participation of a π bond in the transfer of the tricarbonylchromium group to an arene. The exclusive formation of the product shown in eq 8, even though it is not thermodynamically favored, is a case in point.¹¹



Arene Catalysis of Arene Exchange Reactions. Perhaps the most striking results in this study are the

(10) Traylor, T. G.; Stewart, K. J.; Goldberg, M. J. *Organometallics* 1986, 5, 2062.

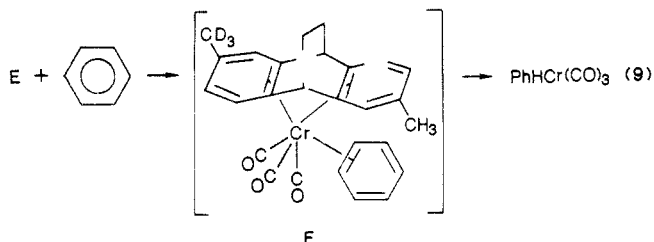
(11) (a) Bly, R. S.; Maier, T. L. *J. Org. Chem.* 1978, 43, 614. (b) Wege, D.; Wilkinson, S. P. *J. Chem. Soc., Chem. Commun.* 1972, 1335. (c) Wege, D.; Wilkinson, S. P. *Aust. J. Chem.* 1973, 25, 1751. (d) Wilkinson, S. P. Ph.D. Thesis, University of Western Australia, 1974.

Table III. First-Order External (k_e) Arene Exchange Rate Constants for the Reactions of *exo*-Cr(CO)₃ and *endo*-Cr(CO)₃ Isomers of Dibenzobicyclo[2.2.2]octadiene in C₆D₆/C₆D₁₂ Mixtures at 170 °C^a

	[C ₆ D ₆], M	10 ⁷ k_e , s ⁻¹
<i>endo</i> -Cr(CO) ₃ (6)	11.3	57.5 ± 1.9
<i>endo</i> -Cr(CO) ₃ (6)	5.6	27.8 ± 3.2
<i>exo</i> -Cr(CO) ₃ (7)	11.3	254 ± 8
<i>exo</i> -Cr(CO) ₃ (7)	5.6	75.0 ± 2.5
toluene	11.3	6 ^b
xylene	11.3	2 ^b
mesitylene	11.3	1

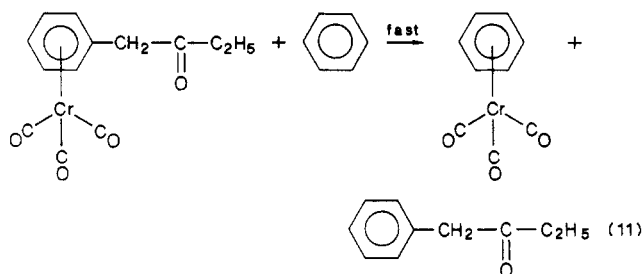
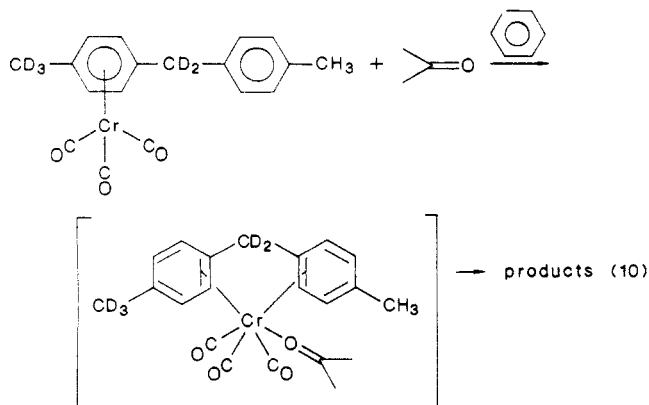
^a0.2 M complex. ^bReference 8.

accelerated rates of external exchange of the *endo* complexes 4 and 6 with benzene. Table III compares the rates of several similarly substituted (arene)tricarbonylchromium complexes with benzene as solvent and reactant. Since 6 and 4 are di- and trisubstituted benzene complexes, their external arene exchange rates are compared with those of xylene and mesitylene, respectively. The rate of external exchange of 4 is 12 times faster than that of the mesitylene complex (Tables II and III), and that for 6 is about 30 times faster than the exchange for the *p*-xylene complex (Table III). Since the differences in the equilibrium constants for tricarbonylchromium transfer from 4 and from mesitylene differ by less than a factor of 2, we expect even less difference in their rates to derive from thermodynamic differences (Table I). We therefore suggest that the external exchange of 4 is catalyzed by the neighboring arene group to the extent of at least a factor of 15. Although the intermediate containing three bound arene groups could be reached through two different sequences of events, it is appealing to visualize the following process, referring to eq 7.

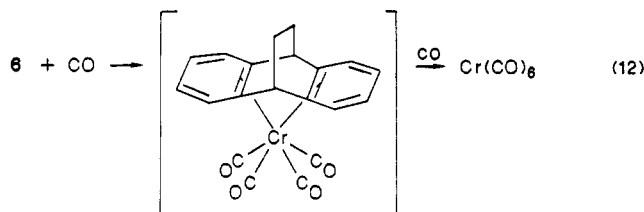


The intermediate F could decompose to yield starting material, rearranged product, or the indicated (benzene)tricarbonylchromium complex.

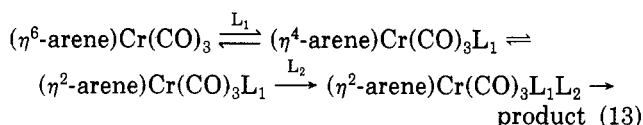
This mechanism is consistent with other observations. Thus both internal and external exchange in 1 are catalyzed by acetone.¹³ In the external exchange, the catalyzed reaction (eq 10) is 5 times faster than that of the toluene complex, implicating arene catalysis.¹ Furthermore, attached ketones have been shown to accelerate external exchange (eq 11),¹² another example of internal catalysis.



A further indication of internal arene catalysis in 6 is revealed by the production of hexacarbonylchromium reported previously.¹⁰ Under 1 atm of CO at 170 °C 6 affords 10% hexacarbonylchromium in 1300 min while (benzene)tricarbonylchromium produces 33% Cr(CO)₆ in 14000 min (eq 12). This indicates about a 40-fold faster reaction of 6 although it should be slower on thermodynamic grounds. This reaction can also be described with reference to eq 7.



These observations allow the following general arene exchange reaction to be written with some confidence.



The products can be Cr(CO)₆, or complexes of L₁ or L₂. We have demonstrated this process for L₁ and/or L₂ being CO, ketones, ethers, alkenes, or other Cr(CO)₃ complexes and, with the present results, arenes as well. In all cases except L = CO, the attacking reagents can act as arene exchange catalysts; i.e., L₂ = arene and L₁ = catalyst.

Conclusion. Using a rigidly held neighboring arene in the *endo*-tricarbonylchromium complex of dibenzobicyclo[2.2.2]octadiene 6 (or 4), we have probed the geometrical requirements for neighboring group participation in (arene)tricarbonylchromium exchange reactions and have provided strong evidence that an intermediate containing three η²-bound arenes [(arene)₃Cr(CO)₃] is formed during some of these exchange reactions.

Acknowledgment. We are grateful to the National Science Foundation, Grant CHE84-20612, for support of this research and to Professor Charles L. Perrin for helpful discussions. We thank Eric Rosenzweig and Era Lewis for synthesis and kinetics of some of the compounds described herein.

Registry No. 1-*d*₅, 108295-88-1; 2, 109908-71-6; 2-*d*₃, 109908-72-7; 3, 52346-22-2; 3-*d*₁₁, 109908-70-5; 4, 109908-67-0; 4-*d*₃, 109908-69-2; 4 (*exo*-Cr(CO)₃ adduct), 109908-68-1; 5, 109908-66-9; 5-*d*₃, 109958-13-6; 6, 109958-12-5; 6 (*exo*-Cr(CO)₃ adduct), 109908-65-8; 7, 51286-78-3; C₆D₆, 1076-43-3; dibenzobicyclo[2.2.2]octadiene, 5675-64-9; hexacarbonylchromium, 13007-92-6; 2,6-dimethylantracene, 613-26-3; 2,6-dimethyldibenzobicyclo[2.2.2]octadiene, 109908-64-7; 1,1-ditolyethene, 2919-20-2; 1,1-bis(*p*-methylphenyl)cyclopropane, 56860-31-2; mesitylene, 108-67-8; benzene, 71-43-2; (benzene)tricarbonylchromium, 12082-08-5.