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Supplementary Material Available: Tables of bond lengths, bond angles, anisotropic thermal parameters, and H-atom coordinates (6 pages); a listing of structure factor amplitudes (26 pages). Ordering information is given on any current masthead page.

Neighboring Group Participation in Organometallic Chemistry: Anchimeric Assistance in Catalyzed Arene Exchange Reactions of (Diarylalkane)tricarbonylchromium Complexes

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Nucleophilic catalysis of the migration of a tricarbonylchromium group from one ring to the other in diarylalkane tricarbonyl derivatives has been observed and compared with catalysis of external exchange. Internal catalysis by a neighboring tricarbonylchromium is also being reported. These results demonstrate the intermediacy of a chromium complex having three carbonyl groups, ketone, and two η^2 -bound arenes. The consequences of this result for metal exchange reactions are discussed.

Introduction

The study of solvent effects in systems involving neighboring group participation has provided important information regarding reaction mechanisms and transition-state geometries, particularly in systems involving direct solvent participation.¹ In arene exchange reactions of (arene)tricarbonylchromium complexes, the addition of nucleophiles such as ketones, ethers, and nitriles enhances the rate of arene exchange by orders of magnitude. This also leads to a change in mechanism of the reaction from one which is first order in both complex and attacking arene to one which is first order in complex and nucleophile and independent of attacking arene.² We have proposed a single mechanism for both of these processes involving either rate-limiting attack of arene or nucleophile followed by rapid collapse to product.^{2a}

As a further extension of our earlier work on neighboring group assistance in the arene exchange reactions of a series of (diarylalkane)tricarbonylchromium complexes, we report the effect of the addition of ketones and ethers on the rates, mechanism, and degree of internal arene participation in these systems. Such an investigation provides information regarding the existence of species of the types (η^4 -arene) $\text{Cr}(\text{CO})_3\text{L}$, (η^2 -arene) $\text{Cr}(\text{CO})_3\text{L}_2$, or $\text{L}_3\text{Cr}(\text{CO})_3$ (L = nucleophile) prior to trapping by arene, through reactivity selectivity relationships involving internal vs. external arene exchange.

Catalysis can also be accomplished by a second mole of (arene)tricarbonylchromium complex. Mechanisms proposed for this reaction include an $\text{S}_{\text{N}}2$ displacement from a sandwich-like structure of two complexes,³ use of a bound carbonyl ligand as a nucleophile,^{2a,c} and formation of a bridging carbonyl complex.⁴ This process has been in-

Table I. Internal (k_i) and External (k_e) Arene Exchange Rate Constants for the Reaction of (1,3-Diphenylpropane)tricarbonylchromium (6) in $\text{C}_6\text{H}_6/\text{C}_6\text{D}_{12}$ Mixtures Catalyzed by Acetone- d_6 or Dioxane- d_8 at 170 °C^a Along with NGP Values^b

cat.	$[\text{C}_6\text{H}_6]$, M	$10^7 k_i^{\text{obsd}}$, s ⁻¹	$10^7 k_e^{\text{obsd}}$, s ⁻¹	NGP, M
none	11.3	3.1 ± 0.3	5.7 ± 0.3	6
acetone- d_6 , 0.05 M	1.0	24.7 ± 1.3	19.2 ± 1.9	1.6
acetone- d_6 , 0.05 M	2.8	9.5 ± 0.5	28.3 ± 2.3	0.8
acetone- d_6 , 0.05 M	5.6		28.0 ± 2.2	
acetone- d_6 , 0.5 M	2.8		289 ± 9	
acetone- d_6 , 0.5 M	5.6		349 ± 20	
dioxane- d_8 , 4.0 M	1.0		313 ± 21	
dioxane- d_8 , 4.0 M	2.8		332 ± 55	
dioxane- d_8 , 4.0 M	5.6		371 ± 26	

^a 0.2 M complex ^b Calculated according to eq 5-7.

Table II. Rates of Internal (k_i) and External (k_e) Arene Exchange Reactions of (Di-*p*-tolylmethane)tricarbonylchromium (5) Catalyzed by Acetone- d_6 or THF- d_8 at 170 °C^a Along with NGP Values^b

cat.	$10^7 k_i^{\text{obsd}}$, s ⁻¹	$10^7 k_e^{\text{obsd}}$, s ⁻¹	NGP, M
none	63.5 ± 4.2	5.7 ± 0.3	126
acetone- d_6 , 0.2 M	146 ± 8	103 ± 5	9
acetone- d_6 , 0.5 M	248 ± 10	336 ± 23	6
acetone- d_6 , 1.0 M	488 ± 18	840 ± 24	6
THF- d_8 , 0.2 M	99.5 ± 2.1	83.3 ± 1.6	5
THF- d_8 , 0.5 M	110 ± 4	149 ± 2	3
THF- d_8 , 1.0 M	167 ± 9	371 ± 18	3

^a 0.2 M complex in neat C_6D_6 . ^b Calculated as in Table I.

vestigated by using bis(tricarbonylchromium) adducts of the same diarylalkanes to address these possible pathways, which should have different geometrical requirements for catalysis.

Experimental Section

General Data. All solvents were purified by published procedures.⁵ Cyclohexane- d_{12} , benzene- d_6 , acetone- d_6 , dioxane- d_8 ,

(5) Perrin, D. D.; Armarego, w. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon: Oxford, 1966.

(1) Capon, B.; McManus, S. P. *Neighboring Group Participation*; Plenum: New York, 1976; Vol. 1.

(2) (a) Traylor, T. G.; Stewart, K. J.; Goldberg, M. J. *J. Am. Chem. Soc.* 1984, 106, 4445. (b) Zimmerman, C. L.; Shaner, S. L.; Roth, S. A.; Willeford, B. A. *J. Chem. Res., Miniprint* 1980, 1289. (c) Traylor, T. G.; Stewart, K. J. *Organometallics* 1984, 3, 325.

(3) Strohmeier, W.; Mittnacht, H. *Z. Phys. Chem. (Wiesbaden)* 1961, 29, 339.

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

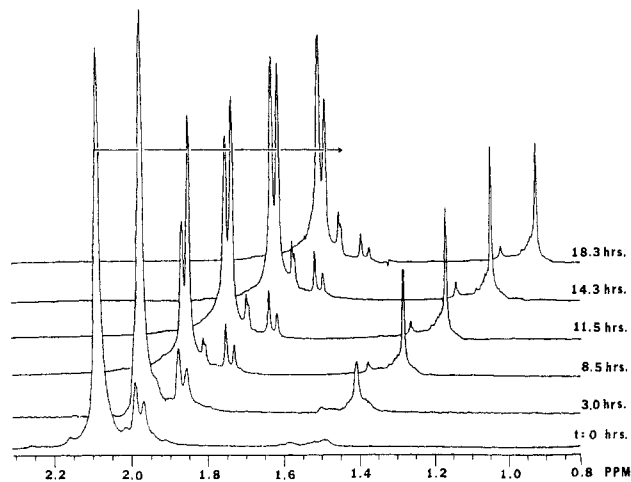


Figure 1. Stacked plots showing changes in the methyl region of the ^1H NMR (360 MHz) spectrum during the arene exchange reactions of **5** in C_6D_6 at 170°C , catalyzed by 0.2 M acetone- d_6 .

and THF- d_8 were purchased from Aldrich Chemical Co. in sealed ampules with a fresh ampule being used for each kinetic run.

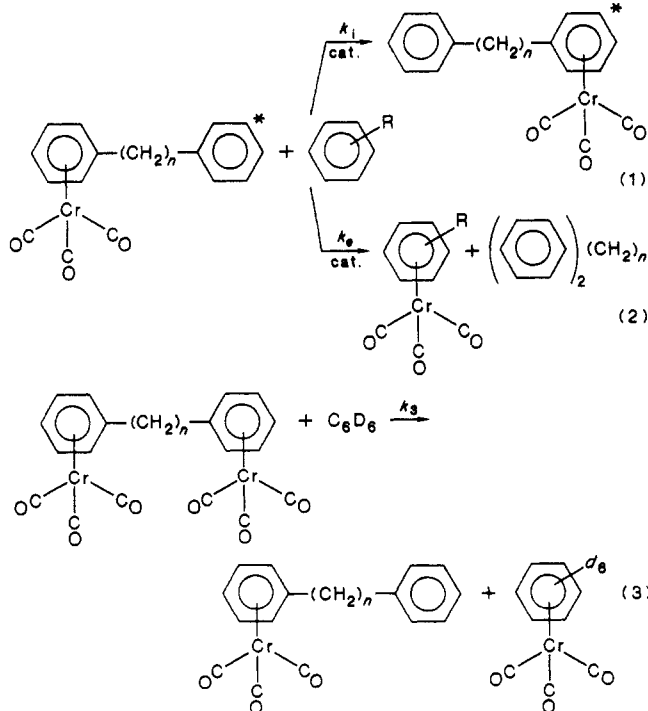
^1H NMR spectra were recorded on either a Varian EM-390 90 MHz spectrometer or an assembled spectrometer using Nicolet software operating at 360 MHz.^{2a}

Preparation of Complexes. Synthesis of all complexes used in this study has been described in detail elsewhere,^{6,7} except for **1**, whose structure was identified with a known bis complex of diphenylmethane by its NMR spectrum.⁸

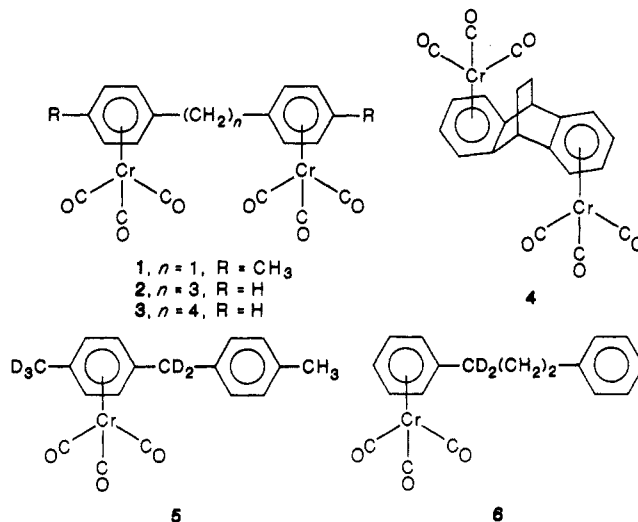
NMR Determination of Rates. Sample preparation and rate determination by NMR methods is the same as that described previously.^{4,6}

Results

Complexes **1–6** used in this study are shown below. Internal (k_i) and external (k_e , k_g) exchange rate constants were determined in the usual way by ^1H NMR analysis of reaction mixtures (eq 1–3).⁶ Rate constants for exchange



of the tricarbonylchromium complexes of 4-(trideuterio-



methyl)-4'-methyl- α,α -dideuteriodiphenylmethane (**5**) and 1,1-dideuterio-1,3-diphenylpropane (**6**) under varying catalyst and benzene or benzene- d_6 concentrations are given in Tables I and II, compared with the same values in the absence of added catalyst. Figure 1 shows the changes in the ^1H NMR spectra for the arene exchange reactions of **5** with benzene- d_6 (11 M) catalyzed by 0.2 M acetone- d_6 . Neighboring group participation (NGP) factors were calculated in the usual way⁶ with eq 4 or 5, where k_e

$$\text{NGP} = \frac{k_i}{k_e / [\text{C}_6\text{H}_6]} \quad (4)$$

$$\text{NGP}^{\text{cat.}} = \frac{k_i^{\text{cat.}}}{k_e^{\text{cat.}} / [\text{C}_6\text{H}_6]} \quad (5)$$

or k_i and $k_e^{\text{cat.}}$ or $k_i^{\text{cat.}}$ refer to external or internal uncatalyzed or external or internal catalyzed reactions, respectively. Since $k_{\text{obsd}}^{\text{cat.}}$ for both external and internal processes is a sum of catalyzed ($k_e^{\text{cat.}}$ or $k_i^{\text{cat.}}$) reactions, the uncatalyzed rate constant must be subtracted, eq 6 and 7, before NGP can be calculated.

$$k_i^{\text{cat.}} = k_{i,\text{obsd}} - k_i \quad (6)$$

$$k_e^{\text{cat.}} = k_{e,\text{obsd}} - k_e \quad (7)$$

Table I shows that the addition of a ketone such as acetone increases internal and external rates over their values in neat benzene. The last three entries of Table I address the dependence of the dioxane- d_8 catalyzed process on arene concentration, where the rate constant for external exchange changes negligibly over a 5- to 6-fold change in benzene concentration.

Table II (Figure 2) addresses the effect of varying catalyst concentration (acetone- d_6 or THF- d_8) on the rates of internal and external exchange, again compared with the corresponding uncatalyzed values.

Table III concerns the involvement of neighboring group participation in the (arene)tricarbonylchromium catalysis of arene exchange^{2c} depicted in eq 3. The bis- $\text{Cr}(\text{CO})_3$ complexes of di-*p*-tolylmethane (**1**), 1,3-diphenylpropane (**2**), 1,4-diphenylbutane (**3**), and dibenzobicyclo[2.2.2]octadiene (**4**) were heated in neat benzene- d_6 , and the rate of external arene exchange was determined. The k_e values listed in the table are corrected for the first-order external arene exchange rates of the corresponding mono- $\text{Cr}(\text{CO})_3$ complexes, listed elsewhere.^{6,7} Unlike eq 4 and 5 where internal and external processes lead to different products (eq 1 and 2), the direct exchange and internal catalysis of eq 3 are competitive. Therefore the rate constant for direct

(6) Traylor, T. G.; Goldberg, M. J. *J. Am. Chem. Soc.* 1987, 109, 3968.

(7) Traylor, T. G.; Goldberg, M. J. *Organometallics*, in press.

(8) Reinke, H.; Oehme, G. *J. Prakt. Chem.* 1978, 320, 967.

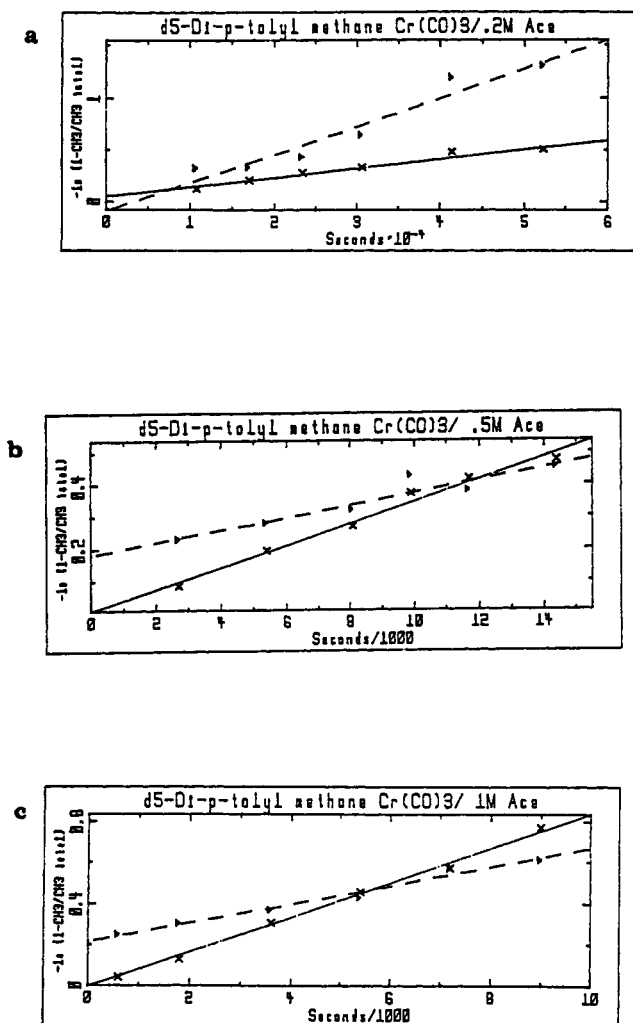


Figure 2. First-order kinetic plots for catalyzed internal (---) and external (—) arene exchange of **5** in C₆D₆ at 170 °C at acetone-d₆ concentrations of 0.2 M (a), 0.5 M (b), and 1.0 M (c).

Table III. Observed (k_o) and Corrected^a (k_e) External Arene Exchange Rate Constants for the Reaction of Various (Diarylalkane)bis(tricarbonylchromium) Complexes at 170 °C^b

complex	$10^7 k_o, s^{-1}$	$10^7 k_e, s^{-1}$
1 ^c	14.8 ± 1.1	9.1
2 ^d	49.7 ± 2.4	44.0
3 ^e	19.5 ± 1.7	14.2
4 ^f	218 ± 10	0

^a Corrected for external arene exchange rate of the corresponding mono-Cr(CO)₃ complex, $k_e = k_o^{bis} - k_o^{mono}$, where the mono- and bis-Cr(CO)₃ complexes of the same structure are used.^g ^b 0.1 M complexes in C₆D₆. ^c (4,4'-Dimethyldiphenylmethane)bis(tricarbonylchromium). ^d (1,3-Diphenylpropane)bis(tricarbonylchromium). ^e (1,4-Diphenylbutane)bis(tricarbonylchromium). ^f (*endo,exo*-Dibenzobicyclo[2.2.2]octadiene)bis(tricarbonylchromium).

exchange must be subtracted from the observed rate constant to get the internal catalysis rate constant. The acceleration due to internal catalysis by the tricarbonylchromium group is given by eq 8. This enhancement of

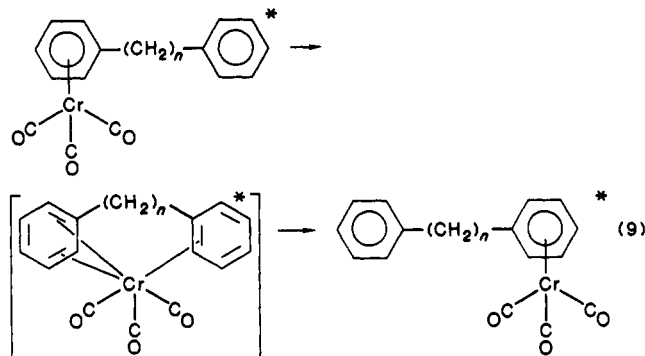
$$k_{ic} = \frac{k_{obsd} - k_{direct}}{k_{direct}} \quad (8)$$

external arene exchange for the bis- versus mono-Cr(CO)₃ complexes varies from a maximum of 7 for (1,3-diphenylpropane)bis(tricarbonylchromium) to zero, or no enhancement, for (dibenzobicyclo[2.2.2]octadiene)bis-

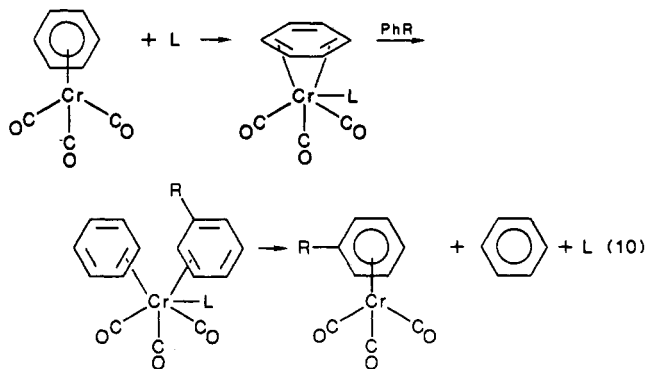
(tricarbonylchromium) (**4**) in which direct catalysis is geometrically forbidden. Here the concentration of complexes was 0.1 M, to maintain a chromium concentration of 0.2 M, equal to that used in our earlier neighboring group study.⁶

Discussion

Neighboring group participation in (arene)tricarbonylchromium compounds, indicating an η^4, η^2 transition state, was established in the previous paper (eq 9).⁶ The NGP



values (eq 4) for such reactions are 130 M for $n = 1$, 1 M for $n = 2$, 6 M for $n = 3$, and very small for $n = 4$, competing with attack of pure benzene which is 11 M. Thus, for $n = 1$ neighboring group participation accelerates the rate 130 times that for 1 M benzene as an external nucleophile. We^{2a,4} and others^{2b,3} have also demonstrated that nucleophiles such as acetone or tetrahydrofuran and also a second molecule of (arene)tricarbonylchromium complex catalyze the exchange reaction. Thus these catalyzed reactions are first order in catalyst and zero order in attacking arene, a result which is inconsistent with a simple solvent effect. Preliminary observations also seemed to suggest the possibility that an arene could act as catalyst for the attack of a second arene. These findings lead to the conclusion that several types of intermediates could be involved, some of which have simultaneous attachment of three different η^2 groups (eq 10). In order to demon-

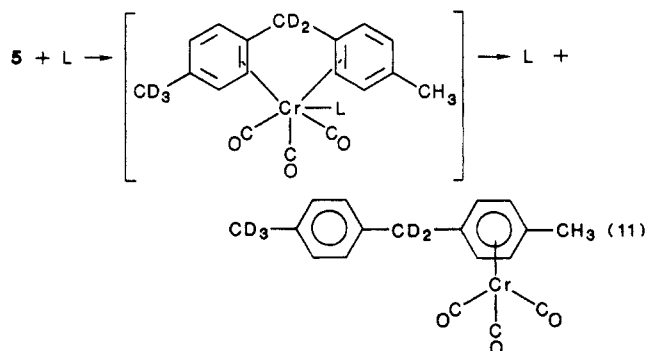


strate that the catalyzed exchange proceeds with only one molecule of catalyst rather than through L₃Cr(CO)₃ and to further define the stoichiometry and geometry of the intermediate, we have combined these two effects of catalysis and neighboring group participation.

Two novel and interrelated aspects of neighboring group participation in (arene)tricarbonylchromium complexes are revealed in Tables I–III: (1) the acceleration of neighboring group participation by external catalysts and (2) the internal catalysis of external (bimolecular) exchange.

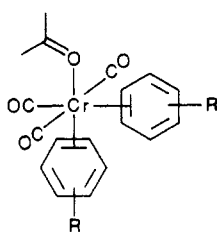
Nucleophilic Catalysis of Internal Exchange. Catalysis of internal exchange is clearly demonstrated in both Tables I and II where the k_i is increased by a factor of 6 upon addition of 0.05 M acetone in the reaction of **6** and

by a factor of over 7 upon addition of 1.0 M acetone to a solution of 5. Tetrahydrofuran also catalyzes internal exchange of 5 (Table II) whereas dioxane catalyzes only external exchange of 6. It is particularly clear in Table II that acetone and tetrahydrofuran accelerate the internal exchange in 5. This eliminates the possibility of $L_3Cr(CO)_3$ formation which would give only external exchange due to the high concentration of benzene and requires that both arenes and the catalyst are attached to the chromium at the transition state; i.e., both neighboring arene and catalyst contribute to the rate increase (eq 11). The ap-



proximate first-order dependence upon acetone concentration suggests that a single acetone molecule is involved. Similar conclusions regarding this transition state are indicated for the reaction of 6 at low acetone concentration.

However, we have previously shown^{2a} that ketone-catalyzed exchange occurs without external CO exchange, showing that the $Cr(CO)_3$ group migrates intact. This result, coupled with the present finding of catalyzed internal exchange, requires that a species containing two arenes, three carbonyl groups, and at least one catalyst molecule must be transgressed. We extrapolate this internal exchange to general catalyzed exchange and conclude that such exchanges involve the *cis* η^2, η^2 acetone species shown below.



This species allows saturation at chromium throughout the reaction.

Mechanism of Catalyzed Exchange. Further details of the catalysis are available from a comparison of external and internal exchange in the compounds 5 and 6. Table I indicates that increasing the concentration of benzene

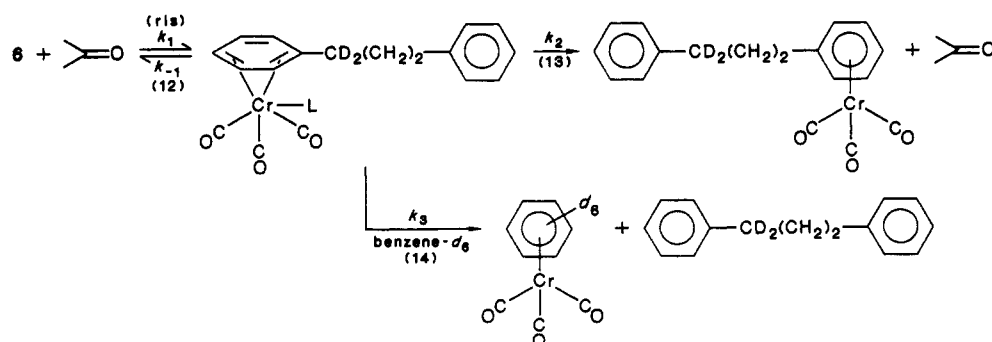
decreases the internal exchange, k_i , and in fact decreases the total rate of disappearance of starting material, 6. While the decrease in total rate might be a solvent effect, the decrease in rate and final disappearance of the internal exchange as benzene concentration increases is best explained by rate-limiting attack of acetone (or dioxane) followed by rapid competitive trapping by internal and external arene (Scheme I). The modest anchimeric assistance in 6 results in the failure to compete with high concentrations of external benzene. Since the external ketone-catalyzed rate has been shown to be independent of arene concentration, indicating $k_3(C_6H_6) \gg k_{-1}$, then the rate constant calculated from the acetone data in Table I is about $6 \times 10^{-5} M^{-1} s^{-1}$ and the total rate ($k_e + k_i$) should be about $3 \times 10^{-6} s^{-1}$ at 0.05 M acetone. The slightly higher value of $4 \times 10^{-6} s^{-1}$ cannot be taken as evidence for anchimeric assistance in the catalyzed system. Therefore, k_1 is rate-limiting.

A different situation arises with 5 in which anchimeric assistance is much greater (i.e., $k_1 = 63 \times 10^{-7} s^{-1}$ versus $3 \times 10^{-7} s^{-1}$ for 6). In this case the bimolecular rate constant for the reaction of acetone with (xylene)tricarboxylchromium, an unassisted model for 5, is estimated from our earlier determinations^{2a,c} and those of Willeford^{2b} to be about $2 \times 10^{-5} M^{-1} s^{-1}$. A plot of k_i versus acetone concentration from Table II reveals a slope of $4 \times 10^{-5} M^{-1} s^{-1}$ for this catalyzed internal exchange. This suggests that the attack by internal arene occurs at the transition state for external exchange. Similarly, the external exchange rate is also greater than that in the absence of the second arene ring. Thus both internal and external catalyzed exchange are anchimerically assisted. This can be illustrated with a plot of $k_e + k_i$ versus acetone concentration from Table II. The slope of $14 \times 10^{-5} M^{-1} s^{-1}$ is seven times larger than that in the absence of the second arene. Since increased internal attack in the scheme presented for 6, i.e., increasing k_2 , would leave the rate-limiting step and the rate unchanged, an alternative proposal is required. We suggest Scheme II. This indicates that the intermediate B not only leads to catalytically and anchimerically accelerated internal exchange, but it is also subject to external attack either by arene or another ketone. This suggests that B is a true intermediate.

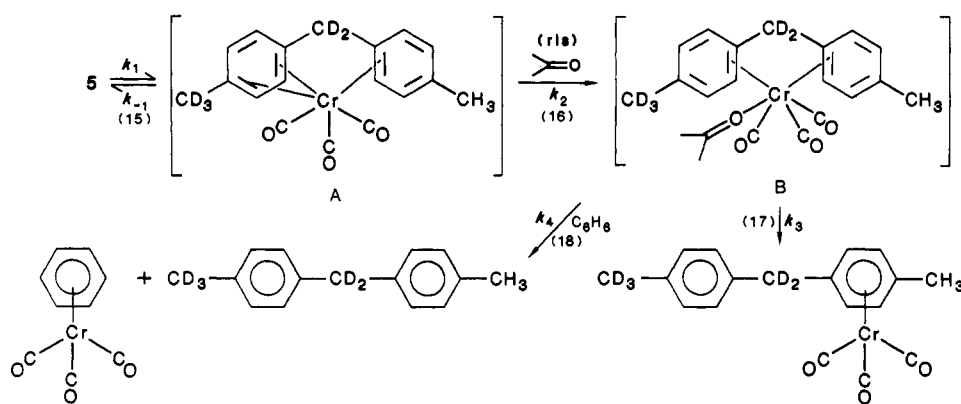
While the increases in the internal catalyzed rates are small, they are sufficiently interesting to prompt further studies in other systems related to possible intermediacy of B which will be reported elsewhere.⁷

Selectivity for Internal Exchange. In either of the schemes above the anchimeric assistance, as indicated by the NGP value, is expected to be higher for the uncatalyzed process, since higher selectivity is generally associated with higher activation energies.¹ The NGP value, determined by k_2/k_3 in Scheme II, should be independent of acetone or benzene concentrations. Table II shows that

Scheme I



Scheme II



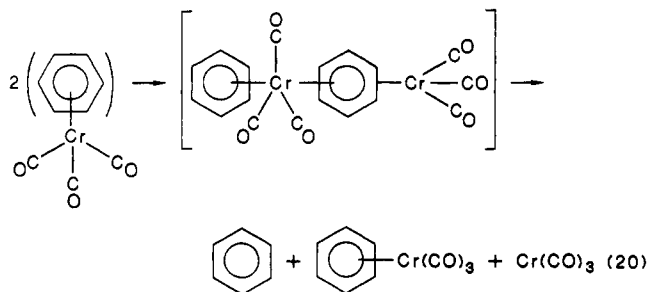
this value is decreased with catalysis and that it is approximately independent of acetone concentration. The limited data in Table I are inconclusive but still consistent with Scheme I.

We conclude that external arene cannot compete with acetone for attack on (arene)tricarbonylchromium complexes, even at 11 M in pure benzene. However, internal exchange equivalent to 120 M benzene begins to compete with acetone attack, leading to one transition state for catalyzed external or slow internal exchange (Scheme I) and a different transition state for highly anchimerically assisted exchange reactions (Scheme II).

Internal (Arene)tricarbonylchromium Catalysis. The catalysis of arene exchange by a second (arene)tricarbonylchromium complex was first observed by Strohmeier and co-workers³ for the self-exchange of various arene complexes with their corresponding ¹⁴C-labeled arenes. This was based upon his rate law for arene exchange which contained a term which was second-order in complex (eq 19) where C and Ar are starting complex and [¹⁴C]-

$$v = k_I[C]^2 + k_{II}[C][Ar] \quad (19)$$

arene, respectively, and k_I is approximately a factor of 10 greater than k_{II} . For this term he proposed a mechanism (eq 20) that has received much criticism based upon the



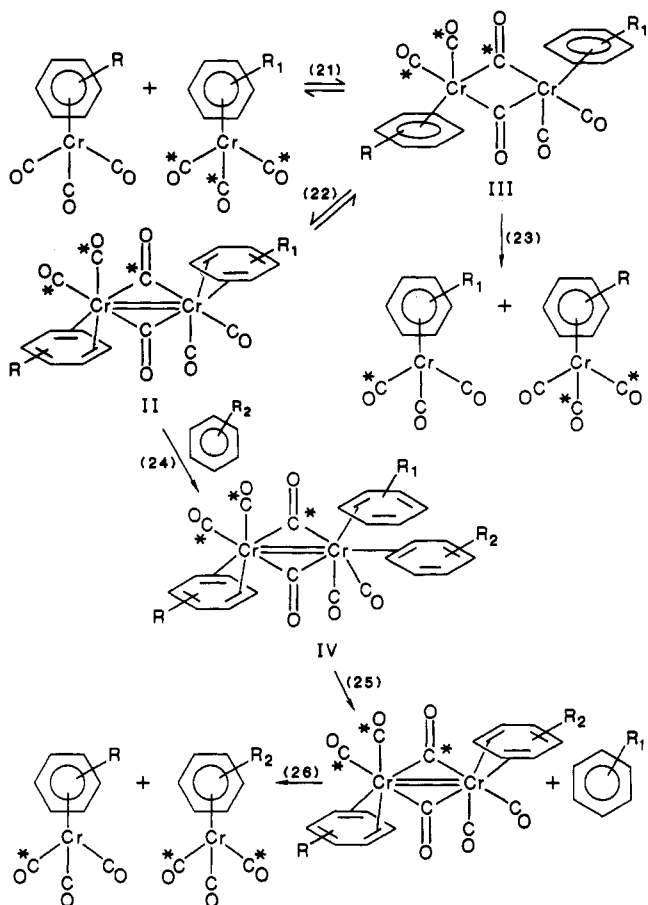
work of Jackson and others,⁹⁻¹¹ whose own work is inconclusive, as discussed in detail in a previous publication.^{2a} We have studied this reaction in detail and find that the first term of eq 19 is more accurately written as $k_I[C][\text{total arene complex}]$.^{2c} On the basis of the results of arene exchange of a mixture of unlabeled and ¹³CO-labeled

(9) Gracey, D. E. F.; Jackson, W. R.; McMullen, C. H.; Thompson, N. *J. Chem. Soc. B* 1969, 1197. The authors reported that (*cis*- or *trans*-1-methylindan)tricarbonylchromium did not isomerize when heated at 170 °C in decalin for 21 h. This experiment, however, is not definitive since arene exchange would proceed only 1.5% under these conditions.

(10) Mahaffy, C. A. L.; Pauson, P. L. *J. Chem. Res., Miniprint* 1979, 1752. In this study the authors observed no isomerization of (*trans*-1-methylindan)tricarbonylchromium after heating with mesitylene in acetone-*d*₆ at 142 °C. Under these conditions, however, acetone-*d*₆ catalysis of arene exchange would dominate the rate law.

(11) Cais, M.; Rejoan, A. *Inorg. Chim. Acta* 1970, 4, 509.

Scheme III

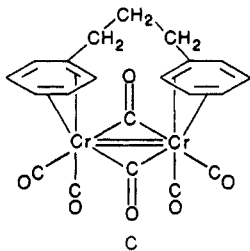


complexes, we recently proposed a mechanism for (arene)tricarbonylchromium catalysis of arene exchange (Scheme III).⁴ The arenes in the intermediates are shown in a *trans* arrangement, but the *cis* form is equally valid.

To further define the direction of approach of the two complexes, we have prepared and studied the rates of exchange of compounds 1-4. Compound 4 is incapable of neighboring nucleophilic attack or bridging as shown in Scheme III but is arranged so that the Strohmeier mechanism (eq 16) is possible. The absence of acceleration in this compound, $k_{ex} = 0$, shown in Table III, is evidence against this mechanism. By contrast, compounds 1-3, having free rotation, all display internal catalysis of external exchange. This is consistent with an attack *cis* to each arene and eliminates the Strohmeier mechanism from further consideration.

The geometry of this bridged intermediate is indicated in C. This structure appears to achieve greatest stability

with three CH₂ groups, in contrast to the internal attack of another arene in which the most anchimerically assisted system is with one CH₂ unit. (See Table III.) Part of this



difference could be due to the preference for trans geometry in 1, as demonstrated by Reinke and Oehme.⁸ However, it seems clear from the structure C that, if approximately octahedral geometry is maintained, the arene rings are held quite far apart by the bonds which are cis to both linear and bridged CO groups indicated in C. This requires a longer connecting chain.

Conclusions. We have demonstrated that both external and internal arene exchange in tricarbonylchromium complexes of bis(1,*n*-diarylalkanes) are catalyzed by nucleophiles and derive anchimeric assistance from the internal arene. We also show that the tricarbonylchromium group can catalyze arene exchange by neighboring group participation in bis(arene)tricarbonylchromium compounds.

Taken together, these results tend to confirm the general mechanism for arene exchange in which the bound arene progresses from η^6 to η^4 to η^2 bonding under the influence of attacking nucleophiles such as ketones, arenes, or (arene)tricarbonylchromium groups.

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Registry No. 1, 110434-23-6; 2, 108319-36-4; 3, 108319-37-5; 4, 109908-65-8; 5, 108319-38-6; 6, 82066-92-0; THF-*d*₈, 1693-74-9; acetone-*d*₆, 666-52-4; dioxane-*d*₈, 17647-74-4.

UV-PE Spectra and DV-X α Calculations of Some Phosphido-Bridged Dimers

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Phosphido-bridged transition-metal complexes of the type [(CO)₄M(μ -PR₂)₂] (M = V, Cr, Mo, W, Mn) have been investigated by means of gas-phase ultraviolet (UV)-photoelectron (PE) spectroscopy and first-principle DV-X α quantum mechanical calculations. The attention was focused on the variation of the metal-metal bond multiplicity along the series and on the changes in the whole electronic structure, with particular emphasis on the metal-bridge interactions. The increase in the metal-metal distance observed on going from the V to the Mn complex reflects the progressive occupation of antibonding metal-metal MOs. In agreement with such considerations, difference density maps for the V and Mn complexes show an evident charge accumulation between the two V atoms in contrast with a saddle point along the Mn-Mn axis. However, the large M-M lengthening observed on passing from Cr to Mn is more easily understood if the occupation of a M-bridge antibonding orbital is also taken into account. The UV-PE data and the theoretical results both demonstrate the existence of through-space interactions between the phosphorus bridging atoms, maximized in the Mn complex where the P-P distance takes the minimum value.

Introduction

Phosphido-bridged transition-metal complexes represent an interesting class of polynuclear compounds, in that they maintain their nuclearity in both substitution² and redox reactions,³ so enabling, in principle, unusual reactivities via cooperative effect of the adjacent metals.⁴ In this

context, most of the very extensive studies has been mainly concerned so far with their synthesis and reactivity.^{2,5}

The dinuclear-bridged complexes of the type [(CO)₄M(μ -PR₂)₂] were first prepared in the late 1964 by Chatt⁶ and by Hayter.⁷ On the basis of NMR studies, Hayter proposed a planar structure for the M₂(μ -PR₂)₂ ring (see below) and this was later confirmed by several X-ray diffraction analyses which revealed centrosymmetrical structures.⁸

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