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Neighboring Group Participation in Organometallic Chemistry: Internal Exchange in (Diarylalkane)tricarbonylchromium Complexes

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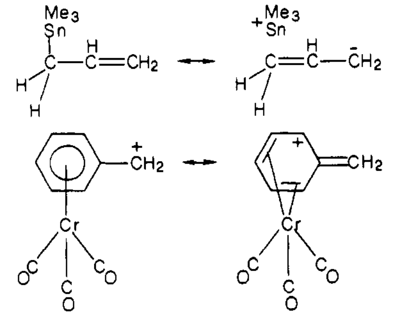
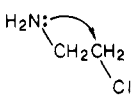
Abstract: The rates of internal and external exchange of (diarylalkane)tricarbonylchromium complexes in benzene/cyclohexane mixtures have been determined. Neighboring group participation is demonstrated in all complexes and follows an order with respect to ring size in the transition state similar to that found in classical neighboring group participation. External exchange rates are unexceptional except for the di-*p*-tolylmethane complex where there seems to be some indication of neighboring group catalysis of external exchange.

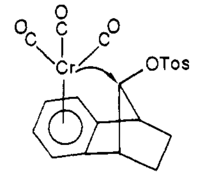
The formation of rings by internal reaction has been used in organic synthesis for almost a century. The process of ring closure (neighboring group participation) and its kinetic expression (anchimeric assistance) were put on a quantitative and firm theoretical basis by Winstein and his contemporaries in the period from 1950 to 1965.[1] The ideas developed at that time have been very useful in the understanding of a wide variety of organic and biochemical reactions.

Although considerable use of proximity effects and conformational control have recently been employed in organometallic chemistry[2] and neighboring group participation used to explain certain ring-forming organometallic reactions,[3] kinetic investigations of this phenomenon in organometallic chemistry are lacking. The β-metal effect,[4] sometimes referred to as neighboring group participation,[5] has been shown to derive its rate-accelerating affect from σ–π conjugation of the carbon–metal bond.[6] This kind of resonance phenomenon, because it is displayed in both spectroscopic and chemical properties, has been called "vertical stabilization".[6]

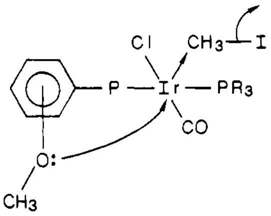


This contrasts the ring-forming reactions in which a lone pair on the neighboring group acts as an internal nucleophile.[1h] Although the (benzene)tricarbonylchromium group displays σ–π conjugation effects, there is no evidence for NGP by the chromium in, e.g., the bicyclic compound A shown above.[7] However, a strong case for neighboring group participation in oxidative addition to metals has been made for the iridium compound B in which the *o*-anisyldimethylphosphine causes the bimolecular addition to proceed about 100 times faster than does the *p*-anisyldimethylphosphine.[8] With regard to the effects of neighboring nucleophiles assisting metal ligand processes by internal trans effects, many other examples might be cited; among them are myoglobin and the chelated heme models[9] and vitamin B_{12} and chelated models for that species.[10] However, NGP in purely organometallic reactions such as carbonyl migrations, π-exchanges, etc. has not been studied in any detail.



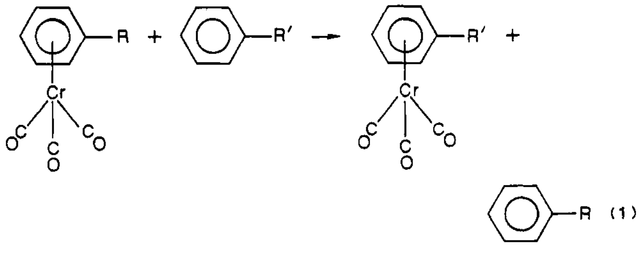


A



B

Since π-bond displacements in transition-metal complexes have been shown to sometimes occur by associative processes (e.g., eq 1),[11,12] it is probable that such associative processes would occur internally. This, in itself, would not be surprising, but, in contrast



(1)

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to the bimolecular exchange, the use of internal or NGP exchange affords the means of probing geometries of the transition state for π-exchanges. Thus, if the Strohmeier mechanism[11] for reaction 1, in which the displacing arene attacks trans to the bound arene, were correct, the neighboring group participation in arene exchanges of this type would be very unlikely and would be impossible for arenes connected by short chains.

In order to probe the geometry for π-attack in this particular reaction and to extend the kinetic (steric and stereoelectronic) consequences of anchimeric assistance to organometallic reactions in general, we have initiated studies of anchimeric assistance in arene exchange reactions of (arene)tricarbonylchromium compounds.

Experimental Section

General Data. Infrared spectra were recorded on a Pye Unican 3-200 spectrophotometer. Proton NMR were taken on a Varian EM-390 90-MHz spectrometer. Chemical shifts are given in parts per million relative to Me_4Si. NMR tubes used in kinetic studies were 9 in. 507-PP purchased from Wilmad Glass Co.

Reagents and Materials. Solvents were purified just prior to use, either by small scale distillation or use of a solvent still. All drying followed published procedures.[13] Dimethyl-d_6 sulfoxide (Aldrich), cyclohexane-d_{12} (Aldrich), benzene-d_6 (Sigma), and acetone-d_6 (Sigma) were purchased in sealed ampules (1- or 5-g size), with a fresh ampule being used for each kinetic run. Ethyl acetate and hexanes used for chromatography were supplied by Mallinkrodt and simply degassed with Ar prior to use. Hexacarbonylchromium was used without purification (Alfa Chemical Co.). 1,3-Diphenylpropane was either supplied by Pfaltz and Bauer Chemical Co. or prepared from chalcone (benzylideneacetophenone) as described elsewhere.[14] 1,4-Diphenylbutadiene (Aldrich) was hydrogenated to produce 1,4-diphenylbutane. Di-*p*-tolylmethane (Pfaltz and Bauer Inc.) and 1,2-diphenylethane (Aldrich) were used as recieved. (Toluene)tricarbonylchromium was purchased from Strem Chemical Co.

Preparation of Complexes. All tricarbonylchromium complexes were synthesized by using the method of Pauson and Mahaffy, except where noted.[15]

(1,1-Dideuterio-1,2-diphenylethane)tricarbonylchromium (2). Bibenzyl (27 g, 148 mmol) and hexacarbonylchromium (2.5 g, 11.4 mmol) were refluxed for 42 h in a solvent mixture containing 7 mL of THF in 84 mL of di-*n*-butyl ether under argon.[16] Reaction progress was followed by thin-layer chromatography on silica, using 90:10 hexanes/ethyl acetate, to minimize production of bis(tricarbonylchromium) species during the reaction. The mixture was cooled to room temperature and 5 g of silica gel added prior to solvent removal (in vaccuo). Subsequent chromatography from a dry-packed column afforded recovery of unreacted starting materials and desired product using neat hexanes and 90:10 hexanes/ethyl acetate mixture as respective eluents. Solvent removal under vacuum yielded 3.4 g (94% yield) of (1,2-diphenylethane)tricarbonylchromium: mp 97–100 °C (lit.[17a] 98–100 °C); ^{1}H NMR ($CDCl_3$, 25 °C) δ 7.15 (br s, 5 H), 5.15 (m, 5 H), 2.80 (AA′BB′, 4 H);[17,18] IR (CCl_4) ν(CO) 1895, 1970 cm^{-1}; TLC (90:10 hexanes/ethyl acetate, silica) R_f 0.3. This complex was used without purification.

Deuteriation. After being washed with hexanes to remove packing oil, a sample of NaH (0.68 g, 28.2 mmol) was degassed with argon. Upon addition of Me_2SO-d_6, anion formation is accompanied by a change in solution color to muddy yellow, as well as a production of HD gas.[19] After the solution was heated for 1 h at 70 °C and cooled to room temperature, addition of 3.4 (12.3 mmol) of (1,2-diphenylethane)tricarbonylchromium in 28 mL (364 mmol) of degassed Me_2SO-d_6 resulted in a color change from yellow to bright red. After 10 h of stirring, the mixture was quenched with D_2O, neutralized with saturated ammonium chloride, and extracted with ether. Addition of silica gel, followed by solvent removal, chromatography (as described above), and recrystallization from hexane gave 1.6 g (47% yield)[20] of (1,1-dideuterio-1,2-diphenylethane)tricarbonylchromium: mp 99–101 °C; ^{1}H NMR ($CDCl_3$) δ 7.2 (br s, 5 H), 5.2 (m, 5 H), 2.8 (s, 2 H); IR (CCl_4) ν(CO) 1890, 1975 cm^{-1}.

(1,1-Dideuterio-1,3-diphenylpropane)tricarbonylchromium (3). The method employed is the same as that outlined above for the ethane complex with a small modification. In this case, equimolar amounts of 1,3-diphenylpropane (6.8 g, 55 mmol) and hexacarbonylchromium (12.1 g, 55 mmol) were heated for 36 h in refluxing THF/di-*n*-butyl ether (20 mL:200 mL) under argon. Workup as above afforded 8.7 g (47% yield) of (1,3-diphenylpropane)tricarbonylchromium: mp 71–72.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.25 (m, 5 H), 5.0 (m, 5 H), 2.7 (t, 2 H), 2.4 (t, 2 H), 1.9 (p, 2 H); IR (CCl_4) ν(CO) 1975, 1890 cm^{-1}. Neat ethyl acetate eluted a yellow band containing 6.1 g (24% yield) of (1,3-diphenylpropane)bis(tricarbonylchromium): mp 125–128 °C; ^{1}H NMR ($CDCl_3$) δ 5.0 (m, 10 H), 2.5 (t, 4 H), 1.9 (m, 2 H); TLC (90:10 hexanes/ethyl acetate, silica) R_f 0.0. Deuteriation of 4.3 g (13 mmol) of the mono(tricarbonylchromium) complex using 0.33 g (14 mmol) of dry NaH in 25 mL of Me_2SO-d_6 gave 3.0 g (70% yield) of (1,1-dideuterio-1,3-diphenylpropane)tricarbonylchromium: mp 72–72 °C; ^{1}H NMR ($CDCl_3$) δ 7.2 (s, 5 H), 5.0 (m, 5 H), 2.7 (t, 2 H), 1.9 (t, 2 H); IR (CCl_4) ν(CO) 1970, 1890 cm^{-1}.

(1,1-Dideuterio-1,4-diphenylbutane)tricarbonylchromium (4). With use of the method described for the propane compound, 2.8 g (35% yield) of (1,4-diphenylbutane)tricarbonylchromium was obtained: mp 49–50 °C (lit.[21] 44.5–45 °C); ^{1}H NMR (acetone-d_6) δ 7.25 (m, 5 H), 5.6 (m, 5 H), 2.7 (br t, 2 H), 2.45 (br t, 2 H), 1.7 (m, 4 H). This preparation also afforded 1.9 g (18% yield) of (1,4-diphenylbutane)bis(tricarbonylchromium), eluted from the column with ethyl acetate: mp 179–180 °C; TLC (90/10 hexanes/ethyl acetate) R_f 0.0. Deuteriation in the usual manner with 0.22 g (9.2 mmol) of NaH and 2.0 g (5.8 mmol) (1,4-diphenylbutane)tricarbonylchromium in 14 mL of Me_2SO-d_6 afforded 1.1 g (53% yield) of (1,1-dideuterio-1,4-diphenylbutane)tricarbonylchromium: mp 49–50 °C; ^{1}H NMR ($CDCl_3$) δ 7.25 (m, 5 H), 5.3 (m, 5 H), 2.65 (t, 2 H), 1.65 (m, 4 H).

[(4-(Trideuteriomethyl)phenyl)(4-methylphenyl)dideuteriomethane]tricarbonylchromium (1). Di-*p*-tolylmethane (20 g, 102 mmol) and hexacarbonylchromium (1.9 g, 8.4 mmol) were heated for 41 h in refluxing THF/di-*n*-butyl ether (10 mL:100 mL) under argon atmosphere. Standard workup and recrystallization from 95:5 hexanes/ethyl acetate gave 1.5 g (54% yield) of the desired complex: ^{1}H NMR ($CDCl_3$) δ 7.1 (A_2B_2, 4 H), 5.1 (A_2B_2, 4 H), 3.6 (s, 2 H) 2.3 (s, 3 H), 2.1 (s, 3 H); IR ($CDCl_3$, 0.11 mm CaF_2) ν(CO) 1960, 1875 cm^{-1}. Deuteration of 0.5 g (1.5 mmol) was accomplished by using 0.05 g (2 mmol) of NaH in 7 mL of Me_2SO-d_6, followed by reaction quenching with D_2O. Extraction, chromatography, and recrystallization yielded 0.35 g (50% yield) of the desired deuteriated material: mp 133–134 °C; ^{1}H NMR ($CDCl_3$) δ 7.1 (A_2B_2, 4 H), 5.1 (A_2B_2, 4 H), 2.3 (s, 3 H); IR ($CDCl_3$, 0.11 mm of CaF_2) ν(CO) 1964, 1888 cm^{-1}; MS (DI, 70 eV), *m/e* 337 (6.2), 253 (37.7), 127 (24.5), 52 (100).

NMR Determination of Rates. All solvents employed were thoroughly degassed prior to addition to a weighed sample in an NMR tube. Sample preparation and rate measurememts were carried out as previously described by using appropriate resonances for internal and external changes.[12]

Results

Reactions were carried out in sealed NMR tubes at 170 °C with concentrations of products and reactants determined by multiple integrations of pertinent peaks at each time period. To monitor internal exchange, deuteriation of those protons benzylic to the complexed ring was accomplished by a variation of the method of Trahanovsky,[22] using sodium hydride as base[19] (eq 2).

Complexation of a phenyl group by a tricarbonyl chromium moiety causes an upfield shift in both aromatic ($\Delta\delta$ = 2 ppm) and benzylic protons ($\Delta\delta$ = 0.2–0.6 ppm) associated with the complexed ring, as well as a lowered acidity for these protons vs. their uncomplexed counterparts. This allows exclusive deuteriation α to the complexed ring in a series of diphenylalkanes. Figure 1

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[13] Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon: New York, 1966.

[14] Collins, C. J.; Raaen, V. F.; Benjamin, B. M.; Maupin, P. H.; Roark, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 5009. In our preparation the recovered carbinol was dehydrated in refluxing HMPA and the resulting olefin hydrogenated to give more 1,3-diphenylpropane.

[15] Pauson, P. L.; Mahaffy, C. F. *Inorg. Synth.* **1979**, *19*, 154.

[16] The apparatus is a combined air and water condenser. This results in THF efficiently recycling hexacarbonylchromium back to the reaction flask prior to its subliming in the water condenser.

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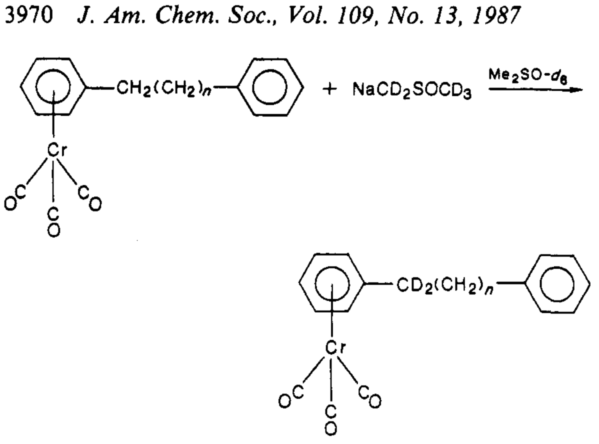
[18] Youngerman, E., unpublished results.

[19] Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1345.

[20] Low yield (47%) of deuteriation step is due to decomposition of complex during workup as well as some oxidative decomposition from heating during deuteriation procedure (to ensure complete solvation of the complex).

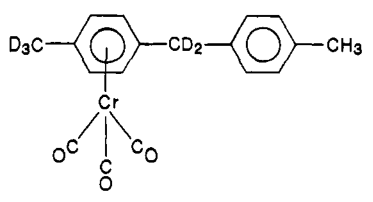
[21] See ref 3. (1,4-Diphenylbutane)tricarbonylchromium: ^{1}H NMR (CCl_4) δ 7.16 (m, 5 H), 5.10 (m, 5 H), 2.9–2.2 (m, 4 H), 1.66 (m, 4 H). 1,1-Dideuterio-1,4-diphenylbutane: ^{1}H NMR (CCl_4) δ 7.1 (s, 10 H), 2.6 (m, 2 H), 1.65 (m, 4 H).

[22] Trahanovsky, W. S.; Card, R. *J. Am. Chem. Soc.* **1972**, *94*, 2897.



(2)

2, *n* = 1
3, *n* = 2
4, *n* = 3



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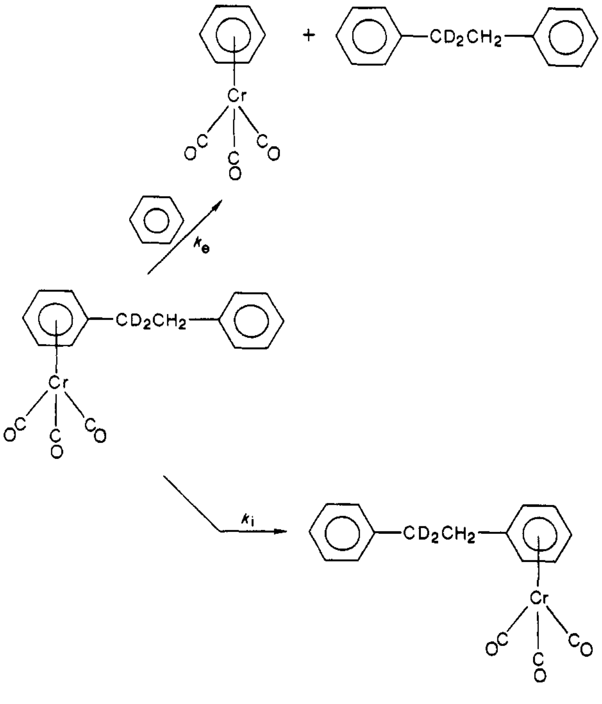
shows the NMR changes upon going from hydrocarbon (a) to mono-$Cr(CO)_3$ complex (b) and deuteriated complex (c) for the case of 1,2-diphenylethane. Complexation of one phenyl ring by a $Cr(CO)_3$ results in the appearance of a multiplet at 4.5 ppm, corresponding to aromatic protons associated with the complexed ring. Similarly, complexation results in a shift as well as a loss in the inherent degeneragy of the methylene protons α and β to the complexed ring, giving the observed pattern of two overlapping triplets centered at 2.5 and 2.3 ppm (Figure 1b). Deuteriation causes changes in only that region of the spectra containing methylene protons (Figure 1c), with removal of the upfield triplet and vicinal proton–proton coupling.

Upon heating of the complex in the appropriate solvent, internal exchange (k_i) was observed by a decrease in the peak at 2.5 ppm concomitant with the appearance of a singlet at 2.3 ppm and external exchange (k_e) was measured by the appearance of a singlet at 4.5 ppm, due to (benzene)tricarbonylchromium or the singlet at 2.8 ppm corresponding to the benzylic protons of 1,1-dideuterio-1,2-diphenylethane (eq 3; Figure 2).



(3)

Table I. First-Order Internal (k_i) and External (k_e) Arene Exchange Rate Constants for the Reaction of Various (Diarylalkane)tricarbonylchromium Complexes at 170 °C[a] along with Calculated Neighboring Group Participation (NGP) Values[b]

complex	$10^7\ k_i$ s^{-1}	$10^7\ k_e$, s^{-1}	NGP, M
1	63.5 ± 4.2	5.7 ± 0.3	126
2	0.62 ± 0.1	5.9 ± 0.9	1
3	3.1 ± 0.3	5.7 ± 0.3	6
4	<0.1[c]	5.3 ± 0.2	<0.2
5[d]		5.9 ± 0.2	

[a] 0.2 M complex in neat C_6H_6. [b] Calculated according to eq 4. [c] Maximum rate assuming 2% yield would go undetected. [d] (Toluene)-tricarbonylchromium.

Table II. First-Order Internal (k_i) and External (k_e) Arene Exchange Rate Constants for the Reaction of (Di-*p*-tolylmethane)tricarbonylchromium in C_6D_6/C_6D_{12} Mixtures at 170 °C[a]

$[C_6D_6]$, M	$10^7 k_i$, s^{-1}	$10^7 k_e$, s^{-1}
2.0	41.4 ± 6.7	0.9 ± 0.1
5.0	48.8 ± 1.4	2.2 ± 0.2
8.0	58.0 ± 2.3	2.8 ± 0.2
11.3	63.5 ± 4.2	5.7 ± 0.3

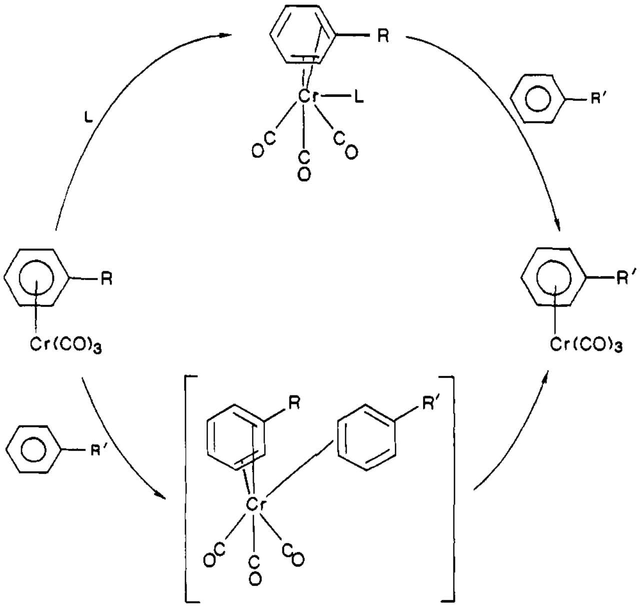
[a] 0.2 M complex.

Table III. Internal (k_i) Arene Exchange Rate Constants for the Reaction of Various (Diarylalkane)tricarbonylchromium Complexes[a] in C_6H_6 or C_6H_5Cl at 170 °C

complex	solv[b] (M)	$10^7\ k_i$, s^{-1}
2	C_6H_6 (5.6)	0.9 ± 0.2
	C_6H_5Cl (4.9)	1.8 ± 0.1
3	C_6H_6 (5.6)	1.7 ± 0.1
	C_6H_5Cl (4.9)	2.9 ± 0.1
4	C_6H_6 (5.6)	<0.1
	C_6H_5Cl (4.9)	0.2 ± 0.03

[a] 0.2 M complex. [b] The remaining solvent was C_6D_{12}. [c] Maximum rate assuming 2% yield would go undetected.

Scheme I



Integration of, for example, the peak at 2.3 ppm was compared with either the integration of an internal standard such as cyclohexane or total integration of benzylic protons. A plot of ln [1-(integration/total integration)] vs. time is shown in Figure 3. First-order rate constants for internal and external exchange of diphenylalkane complexes are listed in Table I. Table II shows the change in both internal and external exchange with varying

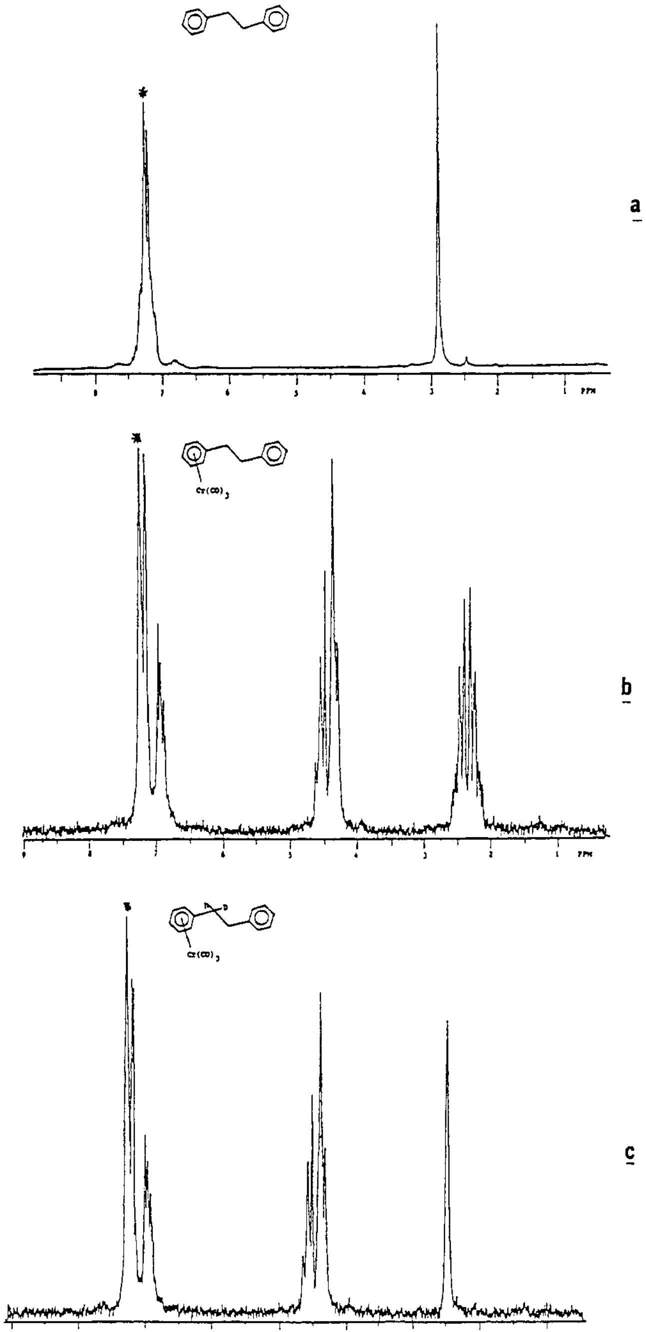


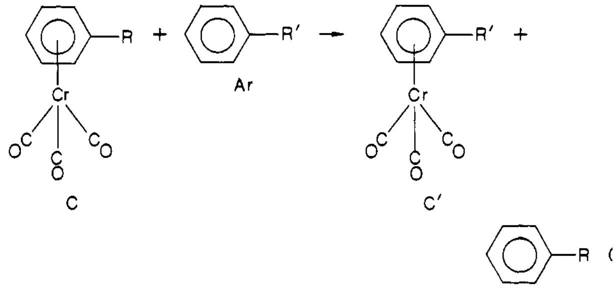
Figure 1. 90-MHz ^{1}H NMR spectra of 1,2-diphenylethane (a), (1,2-diphenylethane)tricarbonylchromium (b), and (1,1-dideuterio-1,2-diphenylethane)tricarbonylchromium (c) in benzene-d_6 at 28 °C. Peaks marked with an asterisk are benzene impurities.

benzene-d_6 concentration. The rate constants for internal exchange vary by a factor of 1.6 over a 5-fold difference in benzene-d_6 concentration, whereas those for external exchange show a 5–6 fold variation over the same range, yielding a second-order rate constant for external exchange of 4.9×10^{-8} M^{-1} s^{-1}. The influence of solvent polarity is addressed by the data in Table III where, for all complexes listed, the rate of internal exchange is increased upon going from 5.6 M benzene to 4.9 M chlorobenzene, both in cyclohexane. The right-hand column of Table I represents the neighboring group participation (NGP) factors that were determined by dividing the first-order internal rate constant by the second-order external rate constant, calculated from the observed first-order rate constant and benzene concentration of 11.3 M (eq 4).

$$NGP = k_i/(k_e/11.3\ M) \qquad (4)$$

Discussion

We have recently shown that the kinetics of exchange of a substituted (benzene)tricarbonylchromium complex (C) with a second arene (Ar) to give a second complex (C′), eq 5, are described by eq 6.[12] In the presence of a catalyst (L) such as



(5)

$$v = k_1[C][Ar] + k_2[C][C + C'] \qquad (6)$$

cyclohexanone, the reaction is greatly accelerated and the rate equation becomes[12]

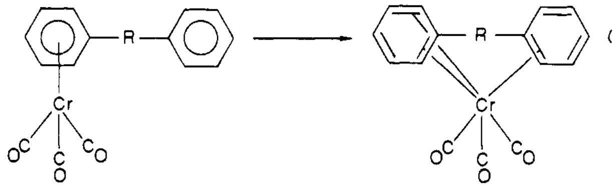
$$v = k_c[C][L] \qquad (7)$$

The reaction therefore results from either direct attack on the complex by the arene or attack by either a ketone or second molecule of complex acting as catalysts followed by rapid reaction with arene (Scheme I). When the exchanges of the diarylalkane complexes are carried out at high concentrations of free arene, we have eliminated the k_2 term of eq 6. Thus the kinetics of exchange of the diarylalkanes are described by eq 8.

$$v = k_i[C] + k_e[C][Ar] \qquad (8)$$

As expected, the k_e values are similar among complexes **1**–**4** and are also similar to that of (toluene)tricarbonylchromium, **5**. This demonstrates similar thermodynamic stabilities of all the complexes.

However, the internal exchange rate varies over a rather wide range of about 600 depending upon chain length. The anchimeric assistance, expressed as k_i/k_e (of eq 9), is greatest for the diphenylmethane derivative and least for the butane derivative. This is explicable in terms of better proximity of the second phenyl group in the former complex.[23] But we also note that the propane derivative exchanges internally faster than does the ethane derivative and much faster than the butane derivatives. Thus conformational effects are also important. It seems clear that the incoming arene has a definite regiospecific requirement. With use of space-filling Corey–Pauling–Koltun models, it appears that the incoming arene ring must be oriented to make an η^2-complex. In this configuration the 1,2-diphenylethane complex would have eclipsed methylene hydrogens whereas the propane derivative could have them in a skew configuration. The geometry of the diphenylmethane intermediate is such that no crowding is introduced in the intermediate. This is reflected in the very large value of k_i/k_e of 126. An interesting analogy can be drawn between the present results and the relative rates of ring closure during nucleophilic substitution. Figure 4 shows plots of relative rates of



(9)

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[23] Jencks, W. P. *Catalysis in Chemistry and Enzymology*; McGraw-Hill: New York, 1969; p 16.

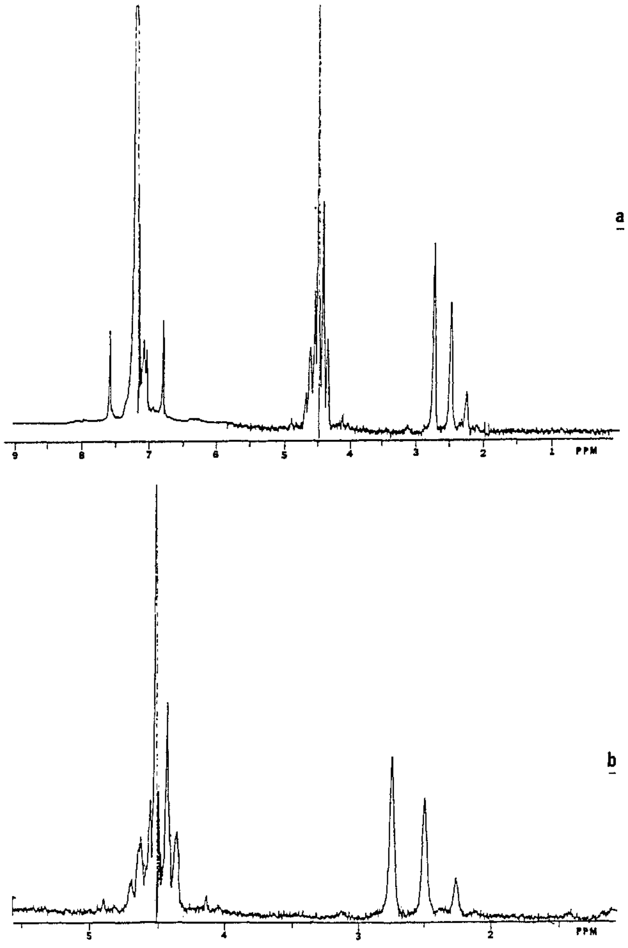


Figure 2. 10 ppm (a) and 5 ppm (b) sweep width ^{1}H NMR spectra (90 MHz) after heating (1,1-dideuterio-1,2-diphenylethane)tricarbonylchromium in benzene (170 °C).

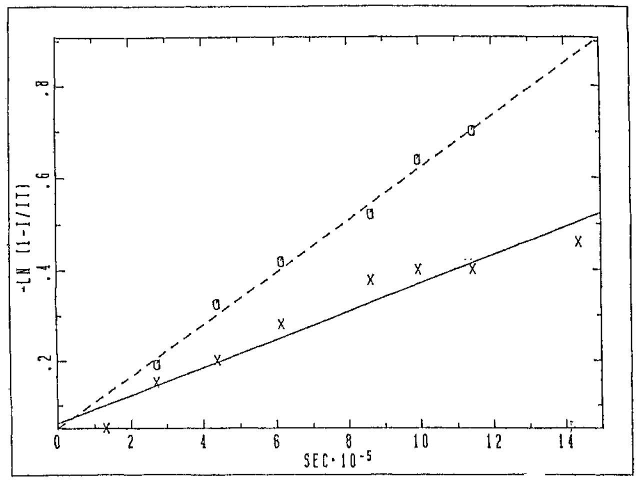
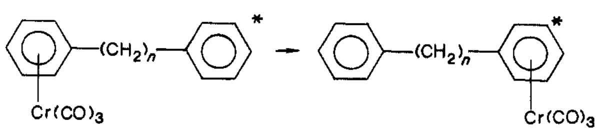
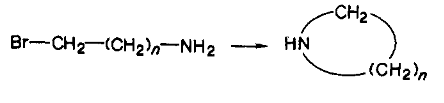


Figure 3. First-order plot showing rates of internal (–) and external (- - -) arene exchange for (1,1-dideuterio-1,3-diphenylpropane)tricarbonylchromium in neat benzene at 170 °C.

neighboring group participation vs. n, the number of CH_2 groups in reactions 10 and 11.



(10)



(11)

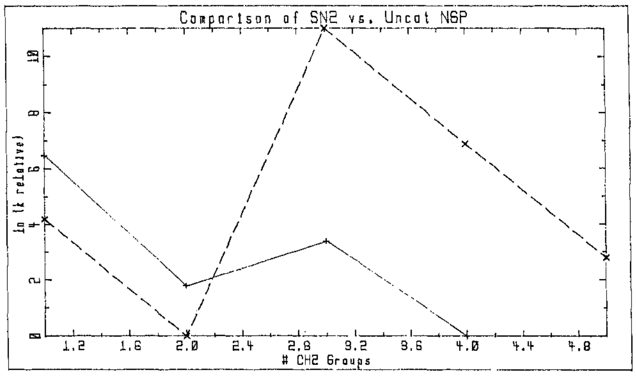
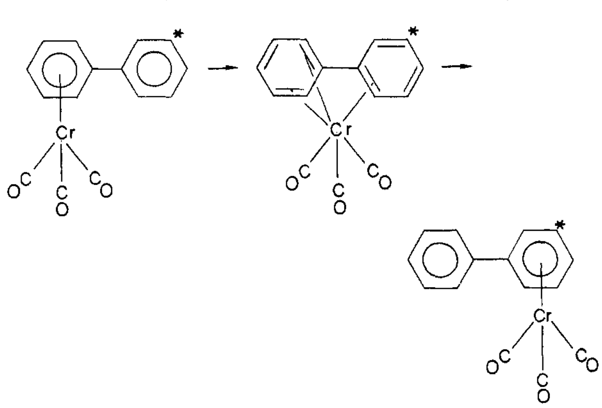


Figure 4. Plot showing the variation in first-order rate constants vs. chain length for internal arene exchange in (diphenylalkane)tricarbonylchromiuim complexes in benzene or benzene-d_6 at 170 °C (—) and cyclization of bromoalkyl amines in water at 25 °C (- - -).

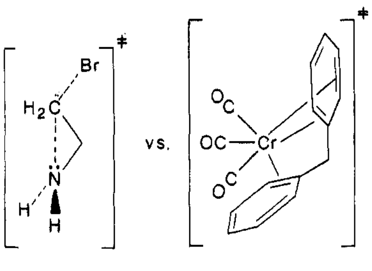
It is clear that, in both cases, the reaction should be much faster for $n = 0$ than for any other value.[24] These analogous processes partake of n–π and σ–π conjugation rather than neighboring group participation and will not be considered here (eq 12 and 13).[6]

$$Br—CH_2—NH_2 \rightarrow [CH_2{=}N^+H_2] \rightarrow CH_2 {=}NH \quad (12)$$



(13)

In the cases of $n = 1$ to 4, the analogy with other NGP processes seems to hold. This suggests that compound **1** ($n = 1$) behaves in analogy to the formation of three-membered carbon rings. The conformation in the transition state shown below is, for $n = 1$, a planar pentadienyl-type complex, and this makes the proper orientation for the η^6 binding for this compound.



It is in this sense that this transition state for internal exchange is analogous to that for internal S_N2 reactions. We conclude that neighboring group participation in organometallic chemistry has just as stringent stereoelectronic requirements as was found in the many studies of anchimerically assisted solvolysis reactions.

One observation in the exchange of the di-p-tolylmethane

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[24] (a) Hutchins, R. O.; Rua, L. *J. Org. Chem.* **1975**, *40*, 2567. (b) Nicholas, K. M.; Kerber, R. C.; Stiefel, E. *Inorg. Chem.* **1971**, *10*, 1519. (c) Ustynyuk, N. A.; Lokshin, B. V.; Oprunenko Yu. F.; Roznyatovsky, V. A.; Luzikov, Yu. N.; Ustynyuk, Yu. A. *J. Organomet. Chem.* **1980**, *202*, 279. The rate of internal migration in K^+ $^-$(flourenyl)tricarbonylchromium anion in THF is between 2×10^4 and 1×10^3 s^{-1} at 0 °C.

complex **1** suggests an anchimric assistance of external exchange. This derivative, being analogous to *p*-xylene rather than toluene, should exchange 6 times slower than the others. It exchanges externally at the same rate, and therefore k_e is accelerated. The slight increase in the internal rate of exchange of **1** with benzene concentration (Table II) could also result from benzene catalysis of internal exchange. However, this might be simple solvent polarity effect of the type shown in Table III. The cause of this intramolecular catalysis of external exchange will be discussed in a subsequent paper.[25]

Acknowledgment. We are grateful to the National Science Foundation, Grant CHE 20612, for support of this research.

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[25] Traylor, T. G.; Goldberg, M. J.; Strouse, C. E.; Miksztal, A. M., manuscript in preparation.

Platinacyclobutane Chemistry: Platinacyclobutanes from Bicyclo [*X*.1.0] Hydrocarbons

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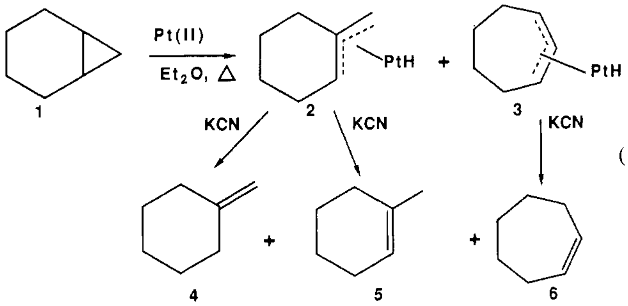
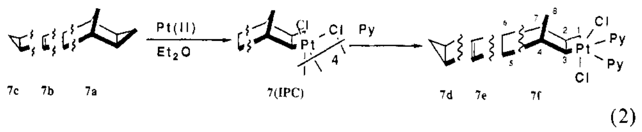
Abstract: Methodologies are now in place for the preparation, isolation, and characterization of platinacyclobutane complexes from ubiquitous substrates such as bicyclo [*X*.1.0] alkanes and alkenes (*X* equals 4 or 6). In the absence of strongly coordinating solvents, the 8-membered-ring complex rearranges to a hydrocarbon mixture containing 1-methylcyclooctene, the exocyclic methylene derivative, and cyclononene. Finally, the platinacyclobutane from bicyclo[6.1.0]nonane, in the presence of 2 equiv of pyridine, rearranges to methylidynylcyclooctane smoothly via an initial α-hydride transfer mechanism rather than a β-hydride transfer mechanism.

Prior to 1982, it was generally accepted that the preparation and isolation of platinacyclobutane complexes from the reaction of Pt(II) with cis-disubstituted cyclopropane derivatives was not possible. Instead, it was proposed that these reactions resulted in the formation of π allylic intermediates which further rearranged as shown in eq 1.[1,2] However, in 1982, we were able to show the cis-disubstituted cyclopropanes which were incorporated in norbornyl systems gave excellent yields of the platinacyclobutanes (eq 2).[3]



(1)



(2)

In this article, we report results on the preparation, isolation, and preliminary chemistry of platinacyclobutane complexes from more common cis-disubstituted cyclopropanes such as those found in bicyclo[*X*.1.0]hydrocarbons.

Results and Discussion

As shown in eq 2, the reaction of Zeise's dimer, Pt(II), with a cyclopropane derivative in ether yields a solid precipitate referred to as the IPC (initially precipitated complex). Previous work on the norbornyl and simple cyclopropane systems by CP/MAS NMR spectroscopy has shown that the hydrocarbon moiety of the IPC was bonded to platinum in the same way as that observed after reaction with pyridine.[4] Further, the IPC was very stable at room temperature. Thus, the strategy to be used for these presumably highly reactive substrates and products was to prepare the IPC, analyze it by solid-state NMR spectroscopy, and then attempt to prepare the mononuclear complex. This could possibly be accomplished with neat pyridine. Initial efforts were placed on the reaction with bicyclo[6.1.0]nonane (**10**) and the results are shown as eq 3.

Preparation and Characterization of Platinacyclobutanes 12 and 15. The solid-state NMR spectrum of **11** is shown in Figure 1 and it is similar to those previously observed for the platinacyclobutane ring in the norbornyl system.[4] The two resonances at 6.9 and 51 ppm are typical of resonances assigned to carbons 1 and 2 in other complexes. The C(3) resonance would be expected to be near 30 ppm but is obviously obscured by resonances of the ring carbons. Resonances in the 140–80-ppm region, which are typical of π-allyl systems,[5] are absent, thus providing further support for a platinacyclobutane complex. Subsequent treatment of **11** with *neat pyridine* gave a stable complex which appears to be the desired and heretofore unknown platinacyclobutane **12** (vide infra). The same procedure was successful in the preparation of **15** (note the difference in reaction temperatures). Although both complexes appear to be infinitely stable in neat pyridine, **15** decomposes faster (2 h) than **12** (6 h) in chloroform solution.

The structures for complexes **12** and **15** were deduced from their NMR spectral resonances which are listed in Table I. Data for

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[1] McQuillin, F. J.; Powell, K. G. *J. Chem. Soc., Dalton Trans.* **1972**, 2123.

[2] Cushman, B. M.; Earnest, S. E.; Brown, D. B. *J. Organomet. Chem.* **1978**, *159*, 431.

[3] Waddington, M. D.; Jennings, P. W. *Organometallics* **1982**, *1*, 385.

[4] Waddington, M. D.; Jennings, P. W. *Organometallics* **1982**, *1*, 1370.

[5] Phillips, R. L.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1978**, 1732.

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