

Isotopic Hydrogen Exchange in the Alkylbenzenes Using Homogeneous Platinum Catalysts

R. J. HODGES AND J. L. GARNETT

From the School of Chemistry, The University of New South Wales, Sydney, Australia

Received May 30, 1968; revised August 19, 1968

Exchange in the alkylbenzenes has been studied in acetic acid solutions using sodium and potassium chloroplatinates as catalysts. Steric hindrance to exchange has been observed in *both* aromatic and alkyl positions *ortho* to an alkyl group. Exchange proceeds at comparable rates in both aromatic and alkyl positions. The high predominance of multiple exchange reactions indicates the presence of intermediate complex species, presumably formed through π -bonding. Possible mechanisms for the reaction are discussed. Evidence indicates that exchange in alkyl positions is preceded by a reversible dealkylation of the side chain. Exchange rates in representative alkylbenzenes by acid-catalyzed, *homogeneous* platinum-catalyzed, and *heterogeneous* metal-catalyzed exchange are compared.

INTRODUCTION

The use of platinum(II) as a *homogeneous* catalyst for the isotopic hydrogen exchange of aromatic protons has been reported in a recent communication (1). The kinetics of exchange in benzene have since been thoroughly investigated (2). Exchange reactions have been studied in acetic acid solutions containing Na_2PtCl_4 , the aromatic compound, and heavy water as a source of isotope. Precipitation of the catalyst was avoided by the addition of a small quantity of hydrochloric acid (0.02 M). A mechanism involving the preliminary formation of a π -complex has been proposed to explain the relative rates of deuteration in a series of monosubstituted benzenes and polycyclic aromatics (2, 3). Both multiple and stepwise exchange have been observed in the benzene.

In the proposed mechanism, a square-planar π -complex is initially formed followed by the actual deuteration step. This involves a reversible rearrangement of the aromatic complex to a six-coordinated platinum(IV) hydride species and a conversion of the π -bonded benzene to a σ -phenyl group. Subsequent rapid hydrido exchange with the deuterated solvent leads to isotope

incorporation. A slow displacement of the π -complexed aromatic by chloride ions then produces the polydeuterated species, since several cycles of the exchange step occur.

Preliminary studies (1) with *mesitylene* and toluene have shown that the side chain alkyl groups also readily exchange under conditions identical to those for benzene. In order to further clarify the proposed mechanism, a detailed examination of a series of methyl-substituted benzenes and monoalkyl benzenes has now been performed and is reported in the present paper. Modified π -complex mechanisms are proposed to account for the observed reactivity.

In an extensive review, Bond (4) has summarized the use of complexes of the Group VIII metals in *homogeneous* catalytic isomerization, hydrogenation, oxidation, polymerization, and carbonylation; however, no previous report of exchange reactions in homogeneous metal catalysis has been made. Garnett and Sollich-Baumgartner (5) have studied the exchange using Group VIII transition metal catalysts under *heterogeneous* conditions, platinum being generally the most reactive. Associative and dissociative π -complex mecha-

TABLE I
HOMOGENEOUS METAL-CATALYZED EXCHANGE OF POLYMETHYLBENZENES^a

Compound	Wt. (g)	% D (aromatic)	% D (alkyl)	% D (theor. total hydrogens)	Deuterium distribution						
					D ₀	D ₁	D ₂	D ₃	D ₄	D ₅	D ₆
Benzene	0.352	45.9	—	74.7	16.8	11.0	15.0	18.5	19.9	14.0	4.9
Toluene	0.347	27.2	15.6	72.6	26.4	18.3	22.2	19.3	8.7	3.9	1.3
<i>o</i> -Xylene	0.352	23.4	6.6	70.6	31.2	26.8	26.6	9.8	4.0	1.2	0.3
Hexamethylbenzene	0.358	15.2	5.8 ^b	69.2	43.2	36.1	13.1	5.3	1.8	0.5	—
<i>m</i> -Xylene	0.346	13.6	16.8	71.2	32.7	24.2	16.4	15.6	6.8	2.8	1.2
Durene	0.400	7.5	4.1	65.8	66.4	15.5	10.5	4.5	1.6	1.0	0.3
<i>p</i> -Xylene	0.344	2.9	20.2	71.1	43.3	17.7	16.9	13.1	5.2	2.6	1.1
Mesitylene	0.346	1.5	13.9	69.9	46.0	16.9	14.6	10.9	5.5	3.1	1.4
Mellitene	0.200	—	0.48	78.3	95.1	2.6	1.6	0.3	0.1	0.05	0.05

^a Reaction conditions: CH₃COOD (63 mole % in D₂O) containing Na₂PtCl₄ (0.02 M) and HCl (0.005 M) heated at 100° for 50 hr; 2.5-ml aliquots used in each run.

^b Exchange in C₇ and C₉ positions, 8.0% and in C₈ position, 1.4%.

nisms have been proposed for the relevant *heterogeneous* reactions. The present paper therefore provides an important link in the causal relationship between heterogeneous and homogeneous catalysis.

π -Alkyl and hydrido complexes have been suggested as intermediates in the isomerization and polymerization of olefins (6, 7) and reviews on the preparation of alkyl metal complexes (8) and hydrido complexes (9) have been published. Rearrangement and substitution reactions involving square-planar complexes of platinum as discussed by Langford and Gray (10) and recent work by Belluco and co-workers (11) provide pertinent information for the interpretation of the reaction mechanism involved in homogeneous catalysis.

The exchange of the alkylbenzenes with a homogeneous catalyst is important for a number of reasons. The series possesses both alkyl and aromatic hydrogens and combinations of acid-catalyzed exchange with homogeneous metal-catalyzed exchange may be utilized to produce a variety of specifically deuterated aromatics. The mechanism of the exchange is of interest to fundamental catalytic theory, particularly since aromatic compounds such as benzene exchange readily, whereas saturated aliphatics such as cyclohexane do not (12). Deuteration of the side chain hydrogens in the alkylbenzenes may then be due to an initial π -complex formation through the aromatic ring.

EXPERIMENTAL

Materials

a. Catalysts. Matthey Garrett Pty. Ltd. sodium and potassium chloroplatinites were used as catalysts.

b. Solvent mixture. Heavy water (99.75% D₂O supplied by the Australian Atomic Energy Commission) was used as a source of deuterium. Acetic anhydride (May and Baker A. R.) was dried by refluxing over magnesium turnings for 1 hr and distilled. The acetic anhydride and excess D₂O were mixed to give the final required proportions of CH₃COOD and D₂O and carefully refluxed for a further 30 min. DCl (prepared from

acetyl chloride and D₂O) was then added to the solvent mixture.

In several of the experiments anhydrous stannic chloride was used in place of the DCl. Stannic chloride also adjusts the acidity of acetic acid mixtures (13) and has the following advantages: (a) no exchangeable hydrogens are added and (b) addition does not inhibit the rate to the same extent that added Cl⁻ ions do (14).

c. Alkylbenzenes. Analytical reagent grade organic compounds were used without further purification.

Exchange Procedure

Solutions containing catalyst (0.01–0.02 M) aromatic (0.200–0.400 g) dissolved in aliquots (2 ml) of the solvent mixture (50–70 mole % CH₃COOD, 0.005–0.03 M DCl or SnCl₄) were sealed under vacuum in preconstricted tubes. The samples were heated (60–120°) for the required time at constant temperature with continuous agitation.

After reaction the tubes were broken and the organics were separated by the addition of a small quantity of distilled water. The organic layer was washed once with water to remove most of the acetic acid.

Analysis

Deuterium analyses were performed using Metropolitan Vickers MS2 and MS9 mass spectrometers. Orientation of incorporation of deuterium was determined on a Varian Associates A60 nuclear magnetic resonance spectrometer.

RESULTS

In order to investigate the steric effects in the deuteration of methylbenzenes, a representative series of polymethylbenzenes were examined, as orientation of exchange in aromatic positions in these molecules is not readily obtainable using NMR. The trends obtained are presented in Table 1.

As the exchange also is observed in the alkyl groups a series of monoalkylbenzenes were deuterated. To obtain accurate orientation results for the extended side chains, e.g., *n*-propylbenzene, exchange was performed at 120°C for longer periods to intro-

TABLE 2
HOMOGENEOUS METAL-CATALYZED EXCHANGE OF MONOALKYLBENZENES^a

Compound	Wt. (g)	Reaction conditions	% D (aromatic)	% D (alkyl)		(% D (theor. total hydrogens))	Deuterium distribution								
				α	β		D ₆	D ₁	D ₂	D ₃	D ₄	D ₅	D ₇	D ₈	
Benzene	0.352	A	45.9	—	—	74.7	16.8	11.0	15.0	18.5	19.9	14.0	4.9	—	
Ethylbenzene	0.347	A	20.1	5.7	—	71.1	40.3	19.6	19.8	14.3	4.3	1.4	0.4	—	
Ethylbenzene	0.347	B	45.8	19.5	20.6	—	71.1	2.8	6.9	17.4	27.7	20.7	12.6	5.7	2.0
Isopropylbenzene ^b	0.346	A	9.5	5.2	0.15	—	69.8	70.7	12.2	10.2	5.8	0.8	0.3	—	—
n-Propylbenzene ^b	0.346	B	46.5	7.6	4.3	10.5	69.8	4.1	9.6	22.7	36.2	17.7	7.0	2.3	0.5
tert-Butylbenzene	0.348	A	22.3	—	0.0	—	68.8	42.5	19.0	22.7	15.7	—	—	—	—
tert-Butylbenzene	0.348	C	39.2	—	0.0	—	68.8	11.6	18.7	32.0	37.8	—	—	—	—

^a Reaction conditions: CH₃COOD (63 mole % in D₂O) containing Na₂PtCl₄ (0.02 M) and HCl (0.02 M); 2.5-ml aliquots used in each run. Conditions: A, 100°C for 5 hr; B, 120°C for 16 hr; C, 120°C for 6 hr.

^b Partial decomposition occurs.

TABLE 3
COMPARISON OF ALKYL EXCHANGE RATE IN *para*-SUBSTITUTED TOLUENES^a

Compound	Wt. (g)	% D (total hydrogens)	% D (aromatic)	% D (alkyl)	% D (theor. total hydrogens) —	Deuterium distribution						
						D ₀	D ₁	D ₂	D ₃	D ₄	D ₅	D ₆
<i>p</i> -Xylene	0.217	7.59	2.9	10.75	80.0	68.0	8.8	8.4	9.9	1.0	0.5	0.3
<i>p</i> -Nitrotoluene	0.196	7.54	2.0	15.0	89.0	71.3	12.7	8.5	6.9	0.6	—	—
<i>p</i> -Toluic acid ^b	0.142	7.84	5.4	11.1	89.5	67.6	17.9	7.7	5.6	1.2	—	—

^a Experimental concentrations: 2-ml aliquots of a 50 mole % aqueous acetic acid solution containing aromatic compound, Na_2PtCl_4 (0.010 M) and SnCl_4 (0.03 M) were heated for 5 hr at 100°C.

^b Labile deuterium removed from $-\text{COOH}$ group before mass analysis.

duce sufficient deuterium for NMR studies and these results are presented in Table 2.

Exchange in aromatic positions was minimized using para-substituted toluenes and effects of activating, e.g., $-\text{CH}_3$, and deactivating groups, e.g., $-\text{NO}_2$ and $-\text{COOH}$, upon the exchange rate in the alkyl group were compared (Table 3). Initial rate studies (Table 4) were performed to estimate the relative importance of multiple exchange reactions as compared to stepwise deuteration and the variation in a multiple exchange parameter (*M*) is given for *p*-xylene. The mechanistic significance of the *M* values observed will be discussed below.

Calculation of *M* Values

Percentage abundances D_0 - D_6 of the deuterated species in the initial stages of the reaction of *p*-xylene give a basis for the calculation of a multiple exchange value (*M*). For this calculation, under initial conditions, the very small amount of aromatic exchange was neglected and as the remaining

six aliphatic protons are chemically equivalent, the equations and concepts of Anderson and Kemball (15) were used. For *p*-xylene two rate equations are considered:

$$\frac{d\phi}{dt} = \frac{k_\phi}{\phi_\infty} (\phi_\infty - \phi) \quad (\text{I})$$

where ϕ is the % deuteration of the six alkyl protons; k_ϕ is the initial rate of deuterium entry per 100 molecules of D_0 -*p*-xylene; and ϕ_∞ is the equilibrium value

$$-\frac{db}{dt} = k_b \frac{(b - b_\infty)}{(100 - b)} \quad (\text{II})$$

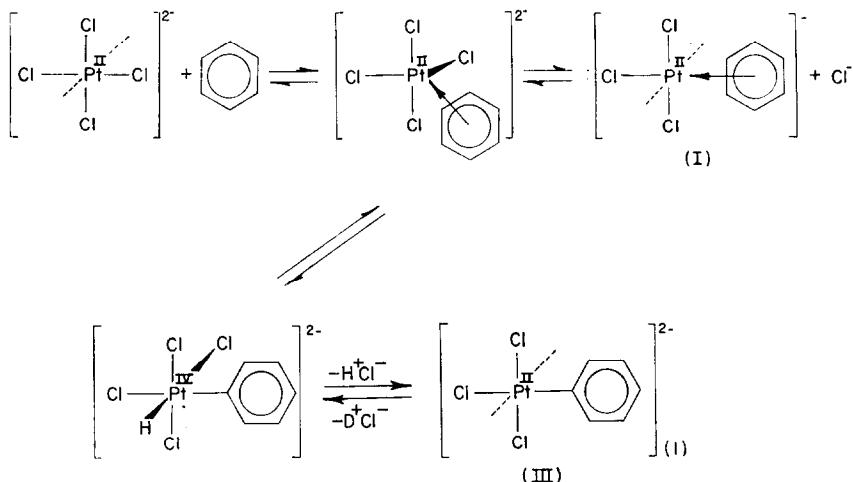
where k_b is the initial rate of disappearance of D_0 -*p*-xylene in percentage per unit time; b is the percentage of total *p*-xylene present as D_0 -benzene; and b_∞ is the equilibrium value of D_0 -*p*-xylene calculated for complete randomization. *M* is then obtained by the ratio

$$M = k_\phi/k_b \quad (\text{III})$$

TABLE 4
EXCHANGE IN *p*-XYLENE AND *p*-NITROTOLUENE AS A FUNCTION OF TEMPERATURE^a

Compound	Wt. (g)	Temp. (°C)	Reaction time (hr)	% D (total hydrogens)	% D (theor. equiv)	Deuterium distribution					<i>M</i> value (alkyl hydrogens)
						D ₀	D ₁	D ₂	D ₃	D ₄	
<i>p</i> -Xylene	0.086	64.2	50.5	1.82	91.0	92.37	2.11	1.21	3.64	0.67	2.32
<i>p</i> -Xylene	0.086	74.0	14.5	1.82	91.0	92.42	1.86	1.45	3.65	0.62	2.34
<i>p</i> -Xylene	0.086	85.5	3.9	1.82	91.0	92.10	2.24	1.65	3.42	0.62	2.24
<i>p</i> -Xylene	0.086	100.0	0.78	1.82	91.0	91.40	2.65	2.27	3.15	0.53	2.05
<i>p</i> -Nitrotoluene	0.200	70.8	19.3	1.80	90.0	93.87	2.03	1.80	2.11	0.19	—
<i>p</i> -Nitrotoluene	0.200	80.5	5.9	1.80	90.0	93.60	2.48	1.90	1.92	0.10	—
<i>p</i> -Nitrotoluene	0.200	90.3	2.17	1.80	90.0	92.98	2.95	1.60	1.74	0.13	—
<i>p</i> -Nitrotoluene	0.200	100.0	0.70	1.80	90.0	92.86	3.34	2.27	1.41	0.12	—

^a Experimental concentration: 2 ml of 50 mole % CH_3COOD in D_2O together with K_2PtCl_4 (0.015 M) and SnCl_4 (0.03 M). Results normalized to 2% approach to equilibrium.



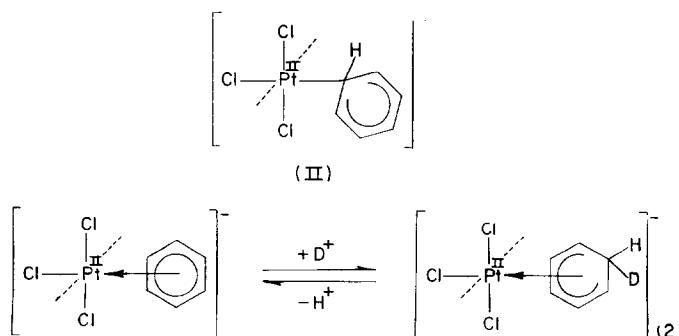
DISCUSSION

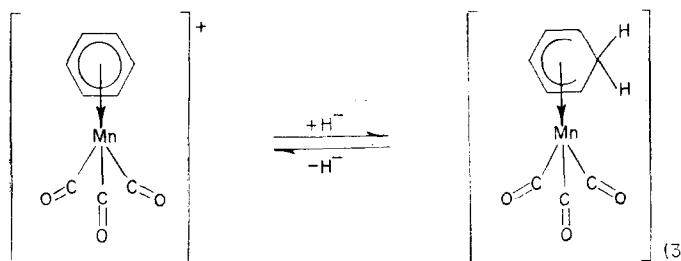
It is apparent from the foregoing results that exchange occurs in both alkyl and aromatic positions at comparable rates. Deuteration in the alkyl side chain is *not* confined to the α -hydrogen position; ethylbenzene exchanges in both α - and β -positions at almost identical rates. The rates of exchange in both the alkyl groups and the aromatic positions are not significantly affected by activating and deactivating substituents (e.g., *p*-xylene and *p*-nitrotoluene) and multiple exchange processes predominate over stepwise deuteration (Table 4). As in previous exchange work, both heterogeneously (16) and homogeneously (17), severe steric hindrance is observed in *all* ortho positions of the substituted benzenes. These results are analogous to the reactivities observed in the homogeneous platinum-catalyzed exchange of the aromatic positions with the monosubstituted benzenes (3). In order to facilitate the pres-

ent discussion the mechanism for aromatic exchange previously published (2) is summarized below.

Mechanism of Aromatic Hydrogen Exchange

From earlier studies (2) with benzene the following mechanism [Eq. (1)] was proposed to account for the observed reactivity. Under initial conditions, reactions showed a predominance of multiple deuteration processes over stepwise exchange. Several rapid exchange cycles of the π -complexed aromatic were postulated to explain this observed effect. Alternative possible mechanisms which should be considered include (i) a sterically hindered displacement of a proton of species (I) to yield species (III) by an electrophilic rearrangement giving a species such as (II) as an intermediate, and (ii) electrophilic attack of a solvated deuteron (D^+) on the π -complex (I) under the acidic conditions with the formation of an intermediate such as species (IV) [Eq. (2)].





Multiple exchange could be expected with both of these mechanisms. The important feature of such mechanisms is that the concepts analogous to heterogeneous associative and dissociative π -complex mechanisms (5, 18-20) may be applied to the present homogeneous system. In particular, species (IV) constitutes the intermediate in what may be termed the homogeneous associative π -complex exchange mechanism [Eq. (2)]. In this respect species (IV) is also similar to the intermediate proposed by Wilkinson and co-workers (21) for the reversible reduction of the manganese tricarbonyl cation [Eq. (3)].

For clarity it is therefore suggested that the mechanism depicted in Eq. (1) be termed the homogeneous dissociative π -complex exchange mechanism. This distinction in terminology has the additional advantage of relating the present homogeneous π -complex platinum work to the corresponding heterogeneous π -complex platinum exchange studies (5) and also to the earlier classical associative and dissociative adsorption experiments of Horiuti and Polanyi (22) and Farkas and Farkas (23).

In the present homogeneous studies, since monosubstituted benzenes exhibit pronounced ortho deactivation and activating and deactivating substituents (e.g., toluene, nitrobenzene) do not appreciably affect the rate of exchange, a mechanism involving species (IV) is not considered to predominate in the exchange. Instead, deuteration is thought to proceed essentially by the dis-

sociative process involving a reversible $\pi-\sigma$ conversion of the nature suggested by Eq. (1). Chatt and Davidson (24) have shown that such $\pi-\sigma$ conversions are observed with ruthenium aromatic complexes. NMR studies with *cis*-(2-C₁₀H₇) (PP)₂Ru(II)H have shown that this complex is in a tautomeric equilibrium with (π -C₁₀H₈) (PP)₂Ru(O) according to Eq. (4). Hydrido hydrogens are labile in platinum-phosphine complexes (25) under conditions similar to the present exchange conditions and an exchange sequence involving Pt(II) and Pt(IV) is therefore plausible.

Reactivity and Orientation of Isotope in Aromatic Positions

The results of Tables 1 and 2 show that severe deactivation occurs in all positions ortho to a methyl group, whereas in positions ortho to a *tert*-butyl group, deuteration is completely inhibited. As with previous studies (2, 17) the monosubstituted benzenes exchange predominantly in the meta and para positions only. This normally cannot be verified by the use of NMR alone in the case of the monoalkylbenzenes; however, a study of the polymethyl-substituted benzenes (Tables 1 and 5) indicates that this trend must be maintained. The series toluene, *o*-xylene, *m*-xylene, hemimellitene, and *p*-xylene show a progressive decrease in exchange rate of the aromatic protons corresponding to a decrease in the number of active exchange positions. With *p*-xylene, mesitylene, and durene, aromatic deutera-



TABLE 5
COMPARISON OF AROMATIC EXCHANGE USING ELECTROPHILIC HOMOGENEOUS AND HETEROGENEOUS TECHNIQUES IN ALKYLBENZENES

Compound	Electrophilic ^a exchange	Homogeneous ^b exchange	Heterogeneous ^c exchange
Benzene	1	1	1
<i>tert</i> -Butylbenzene	1.49×10^2	0.49	0.003
Toluene	1.56×10^2	0.59	0.11
Ethylbenzene	1.62×10^2	0.44	0.33
<i>p</i> -Xylene	8.50×10^2	0.06	0.03
<i>o</i> -Xylene	1.03×10^3	0.51	0.16
<i>m</i> -Xylene	3.07×10^4	0.30	0.07
Hemimellitene	1.10×10^5	0.33	0.0004
Durene	2.78×10^5	0.16	—
Mesitylene	9.50×10^6	0.03	0.0

Experimental conditions:

^a (Refs. 26, 27.) $[ArH] = 24.6$ mole %, $[D_2O] = 12.5$ mole %, $[CF_3COOH] = 62.9$ mole %. Benzene exchange at 70°C for approx. 20 hr to give 0.15% D.

^b As in Table 1; 63 mole % CH_3COOD in D_2O containing Na_2PtCl_4 (0.02 M) and HCl (0.005 M) at 100°C for 5 hr gives 45.9% D in benzene.

^c (Ref. 16.) Prereduced platinum oxide at 120°C for 2 hr gives 52.0% deuterium in benzene.

tion is very slow, confirming that homogeneous platinum-catalyzed exchange is considerably sterically hindered in the ortho positions.

Studies involving exchange by electrophilic substitution between D^+ and aromatic protons in the polymethylbenzenes (26) and monoalkylbenzenes (27) show that the acid-catalyzed exchange produces marked differences in exchange rates for this series. Relative rates of isotope incorporation in acid media are compared with the results of the present homogeneous metal-catalyzed study in Table 5.

Acid exchange is not inhibited by the presence of the *ortho*-methyl groups and is considerably faster in mesitylene than in benzene. The orientation is ortho, para in toluene for acid exchange compared with meta, para in the homogeneous platinum-catalyzed system. The contribution due to acid exchange in the latter system must be small since the exchange rate in the aromatic protons of mesitylene is low by comparison with that of benzene. There is, however, a slightly faster rate in durene but the acid exchange rate in mesitylene is faster than in durene; thus this increase is not an acid exchange contribution. It will be recalled that in the present homogeneous metal-cata-

lyzed system, small concentrations of acids are used to maintain an adequate acidity in solution, thus preventing precipitation of platinum. However, under these particular acid conditions no exchange in the alkylbenzenes was observed in the absence of the platinum catalyst.

Exchange of Alkyl Hydrogens

The results in Table 1 reveal that exchange of the alkyl hydrogens is also sterically hindered by ortho groups. The highest deuteration rate of alkyl hydrogens occurs in *p*-xylene, directly contrasting with the slow exchange rate of the aromatic proton in this molecule. Similar rates of alkyl deuteration occur in mesitylene, *m*-xylene, and toluene, where there are no ortho substituents. The molecules *o*-xylene, hemimellitene, and durene (Table 1) exchange at a slower rate in the alkyl groups due to the presence of *ortho*-methyl groups. Hemimellitene and mellitene both have methyl groups flanked by two ortho substituents and in the methyl groups the exchange rate is very slow. Deuteration in the methyl groups by acid catalysis would not be expected and this has been confirmed by experiment.

The interesting feature of the deuteration of the side chain hydrogens is that both

multiple and stepwise processes are observed analogous to the aromatic protons. To reduce complicating exchange reactions with the aromatic positions, *p*-xylene was chosen to study multiple exchange in the alkyl groups since deuteration of the aromatic positions is inhibited by the presence of *ortho*-methyl groups.

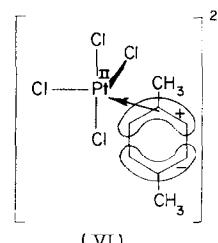
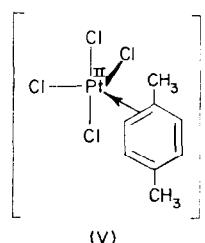
As with deuteration in the aromatic positions (2), the *M* value for *p*-xylene indicates a preference for multiple exchange processes. Results of Table 4, however, show one significant difference, namely that multiple exchange in the alkyl hydrogens is confined essentially to one methyl group per interaction with the catalyst. The low-voltage mass spectrum, when corrected for ^{13}C , clearly exhibits a cutoff at the D_3 isotope peak. Further studies with *para*-substituted toluenes (Tables 3 and 4) under initial conditions show that the exchange rate and *M* value are not greatly altered by the replacement of a *para*-CH₃ for a *para*-NO₂ substituent. Activation energies for exchange in *p*-xylene and *p*-nitrotoluene were calculated to be 29.0 and 29.1 kcal/mole, respectively.

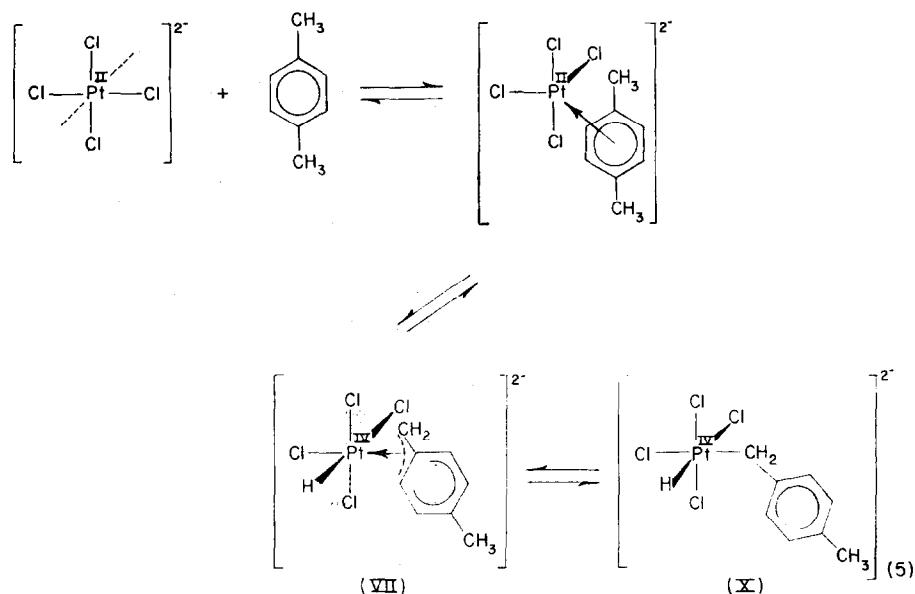
These results are analogous to the exchange observed in benzene where it was postulated that the rate-determining step is the formation of a five-coordinate intermediate (10). This effect is in accordance with other substitution reactions of platinum(II) complexes involving weakly coordinating ligands (10, 11). The mechanism then proposed for the exchange step of aromatic positions involves several π - σ conversions via an octahedral Pt(IV) species that are *not* rate-determining. When considering the deuteration of the methyl groups, again the results indicate that the exchange step is not rate-determining. However, a number of alternative possibilities for the mechanism of deuteration in the alkyl groups should also be

examined. In order to simplify this aspect of the discussion the exchange in the simple methylbenzenes will be initially treated. Extrapolation of the mechanism to explain exchange in the alkyl groups of larger side chain groups such as in ethylbenzene and propylbenzene, will be subsequently considered.

a. Exchange in alkyl hydrogens by hyperconjugation. A strong π -complex of the aromatic ring with the Pt(II) center would be expected to labilize the protons of the methyl group in *p*-xylene through an increase in hyperconjugation. Exchange would then occur by a subsequent reversible ionization of a proton. Multiple deuteration occurs if the cycle is repeated before the π -complexed aromatic is displaced. However, the fact that *p*-xylene exhibits a low-voltage mass distribution with a consistent cutoff at D_3 , is difficult to explain if deuteration by hyperconjugation and ionization were to occur, since both methyl groups should exchange during the time of one interaction with the catalyst and an appreciable quantity of D_6 should be observed under initial conditions.

b. π -Complex formation using higher energy orbitals. To explain the selective multiple exchange in only one methyl group of *p*-xylene per interaction with catalyst, an intermediate involving the localization of a double bond (V) or the use of ψ_2 π -orbitals of the *p*-xylene (VI) may be formulated. A π -complex involving either of these orbitals would allow a reversible π -aryl to π -allylic conversion to occur with the elimination of a proton. The difficulty with this proposal is to explain the existence of a ψ_2 -orbital π -bonded to platinum instead of a ψ_1 -orbital. Hyperconjugation produces a nonsymmetrical distribution of charge in the aromatic ring of *p*-xylene, thus stabilizing the ψ_2 -orbital of the molecule, possibly to the





extent that the ψ_2 -orbitals are more stable than the ψ_1 -orbital in this complex.

Once the π -allylic complex is formed the displaced proton would be initially σ -bonded to the platinum as a hydride with the simultaneous oxidation to an octahedral Pt(IV) species [Eq. (5)]. The formation of a σ -bonded species through the alkyl group of the molecule is possible; however, this is unnecessary kinetically. Rapid exchange of the hydride with the deuterated solvent completes the exchange cycle.

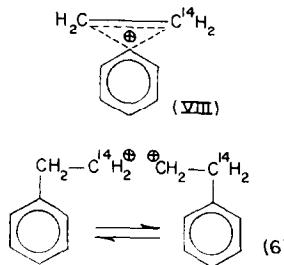
This mechanism for methyl hydrogen exchange is analogous to other reactions (28) involving homogeneous hydrogenation where metal hydrides and π -complexes are proposed as intermediates. The above mechanism is thus valid for explaining the deuteration of isolated methyl groups *only*. Extrapolation of this particular mechanism to molecules with longer side chains such as ethylbenzene will now be considered and it is complicated by the fact that exchange in the three β -hydrogen positions of the ethylbenzene occurs at an almost identical rate to that of the two α -hydrogens (Table 2). The formation of π -allylic complexes with both α - and β -carbon atoms giving almost equal reactivity is therefore difficult to explain.

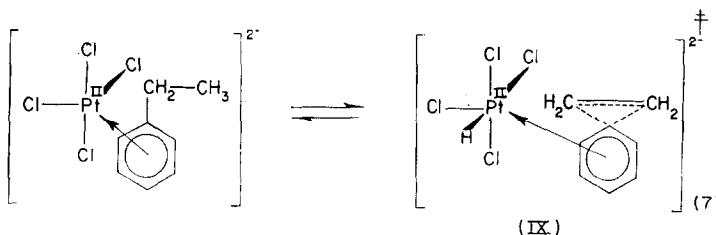
c. Exchange in alkyl hydrogens by

carbonium ion formation. As the intermediates in the present reaction appear to involve platinum hydride complexes, similar reactions proceeding via the abstraction of hydrides will now be discussed.

The similar reactivity of α - and β -carbon atoms of ethylbenzene indicates a possible rearrangement of the carbon atoms involving a symmetrical intermediate. Such rearrangements have been observed in the deoxidation of 2-phenyl-1- ^{14}C -ethanol to styrene without catalyst. Lee and Hahn (29) report a 22–26% rearrangement of the ^{14}C label from the C-1 to the C-2 position. Recovered starting material shows a 3–5% rearrangement. Some controversy (30) is associated with the existence of a short-lived nonclassical carbonium ion as in species (VIII) or the rapid equilibrium of two classical carbonium ions [Eq. (6)].

With the present system, since exchange in





the α - and β -positions is equivalent, then a symmetric intermediate involving a π -bonded ethylenephenoxy ion (IX) would be formed [Eq. (7)].

Exchange in the methyl groups would involve a classical carbonium ion but this intermediate again would require the existence of ψ_2 π -bonded orbitals to explain selective multiple exchange in only one methyl group of *p*-xylene. These intermediates would no longer retain stable ψ_2 -orbitals as carbonium ions and the rapid formation of a σ -alkyl platinum (IV) intermediate (X), as in Eq. (5), is indicated. As in previous mechanisms the deuteration cycle is completed by rapid hydrido exchange with the solvent.

The validity of these mechanisms, based essentially upon the exchange mechanism for aromatic positions, depends upon the existence of a stable ψ_2 -orbital π -bonded with platinum as an intermediate. However, multiple deuteration in the one methyl group per interaction with the platinum can also be explained by a reversible dealkylation reaction and ψ_2 -orbitals are *not* required for complexing.

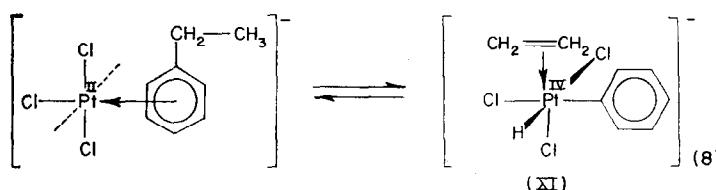
d. Exchange by reversible dealkylation. The result with ethylbenzene may be explained in terms of a dealkylation mechanism in which the two carbon atoms are equivalent in the intermediate. Isotopic carbon studies are presently being undertaken to discover whether randomization of the ethyl carbons does occur during exchange of the protons. Once a π -complex similar to

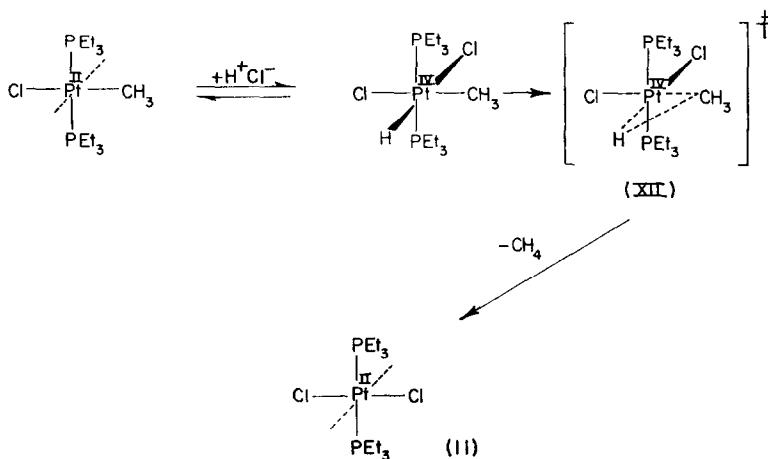
species (I) is formed, a rearrangement as in Eq. (8) would be expected. The exchange cycle is completed by a reversible hydrido exchange with the deuterated solvent.

Further evidence that dealkylation occurs is provided by other studies with *n*-propyl and isopropylbenzenes, where deuteration does not proceed to completion due to an irreversible dealkylation. Alkyl halides and olefins are by-products during prolonged heating at temperatures of 100° and above. Much precipitation of the platinum catalyst also is noted. Further, with the compound 4-phenyl-1-butene no exchange is observed, and low-voltage mass spectral analysis indicates that complete dealkylation occurs.

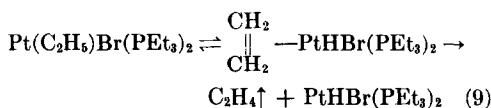
Tsuji *et al.* (31) have used rhodium pentachloride and other noble metal compounds for catalytic alkylation reactions. The Friedel-Crafts alkylation proceeds smoothly at 75° with *both* olefins and alkyl halides. Since platinum forms very stable π -complexes with the olefins, ethylbenzene, upon dealkylation, would form a species such as (XI). The strong π -complex would *not* liberate the ethylene in this process and as platinum halides also act as Friedel-Craft catalysts, then dealkylation would be reversible. In this reversible process a symmetrical ethylene π -complex would randomize the carbon atoms in the ethyl group and would explain the observation that exchange proceeds at similar rates in both the α - and β -positions.

Recent studies involving reversible reactions between olefins and platinum hydrides

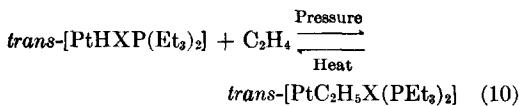




by Chatt *et al.* (32) support the reversible dealkylation process. The elimination of ethylene from *trans*-[Pt(C₂H₅)Br(PEt₃)₂] by heat gives *trans*-[PtHBr(PEt₃)₂]. The hydridic hydrogen originates from both the α - and β -carbon atoms of the ethyl group. The hydrogen-deuterium scrambling that takes place is consistent with the carbon atoms of the ethyl group being symmetrically placed with respect to the platinum atom in the transition state. The reaction proceeds according to Eq. (9).



Earlier work by Chatt and Shaw (33) involving insertion reactions of olefins into metal hydride bonds according to Eq. (10) have particular relevance to many other homogeneous metal-catalyzed reactions such as hydroformylation (34, 35), hydrosilation (36), and hydrogenation (37, 38). As the present homogeneous exchange experiment indicates equal reactivities in the α - and



β -carbon atoms, then an exchange sequence similar to the mechanism of Eq. (9) is indicated.

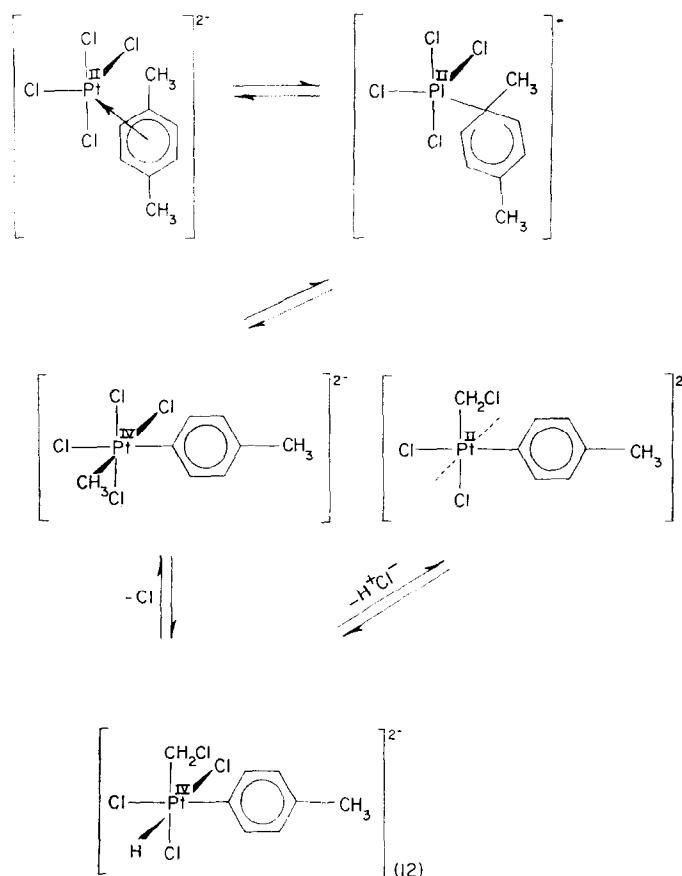
Osborn *et al.* (37) in the hydrogenation of olefins with homogeneous rhodium catalysts indicate the existence of a triangular transi-

tion state in the transfer of a hydride to the olefin. More recently, Bellico *et al.* (39) proposed a similar transition state (XII) in the displacement of CH₄ from [PtCl(CH₃)(PEt₃)₂] by HCl. The reaction sequence for the solvent-independent path is given in Eq. (11). An energy profile for this reaction shows that the six-coordinated platinum(IV) hydrido complex is regarded as an intermediate.

Using the concepts involved in hydride transfer, insertion and elimination reactions as outlined above, a mechanism for multiple exchange in *p*-xylene involving only one methyl group per interaction with the catalyst may be formulated. This mechanism, involving the reversible dealkylation to methylene chloride, does not involve π -complexing with ψ_2 orbitals and is given in Eq. (12).

The alkyl chloride mechanism would also be applicable to the ethylbenzene exchange and an analogous intermediate would be formed. Equal reactivities, however, of the α - and β -positions indicate that the symmetrical intermediate involving a stable π -bonded ethylene is preferentially formed. Such intermediates have been proposed by Eberhardt and Vaska (40) in the hydrogen-deuterium exchange, hydrogenation, and isomerization of olefins homogeneously using *trans*-[IrCl(CO)Ph₃P)₂]. Exchange and hydrogenation of ethylene involved hydride intermediates and reversible π - σ conversions of ethylene to ethyl groups.

e. Extension of dealkylation mechanism



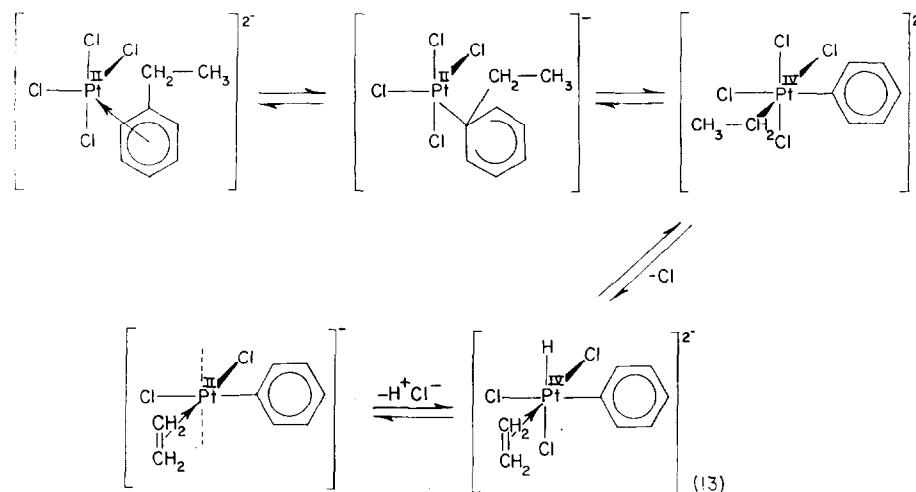
to propylbenzene. Further studies by Chatt and co-workers (32) involving higher olefins indicate that in the insertion reactions of olefins with *trans*-[PtHCl(PEt₃)₂] [Eq. (10)] and the action of alkyl Grignards with *cis*- and *trans*-[PtCl₂(PEt₃)₂], *n*-alkylplatinum derivatives are formed more readily than isoalkyl derivatives. In the present study, with isopropyl and *n*-propylbenzene, the isopropylbenzene decomposed more readily to metallic platinum and exchange reactions were quickly inhibited due to the formation of an apparently unstable intermediate (Table 2). *n*-Propylbenzene (Table 2) exchanges with significantly less decomposition and deuteration is higher in the α - and γ -positions than in the β -positions. This indicates that during the dealkylation exchange step, *n*-propyl derivatives σ -bonded to the platinum are more readily formed than isopropyl derivatives. This evidence suggests that exchange in the alkyl hydrogens pre-

cedes the reformation of a π -bonded alkylbenzene.

Summary of Exchange Mechanisms for Alkyl Hydrogens

Because of the number of plausible mechanisms which have been considered for the exchange of the alkyl hydrogens in the preceding section, a critical summary of these mechanisms will now be made.

Exchange of the alkyl hydrogens in the alkylbenzenes is envisaged as a preliminary reversible dealkylation and while the alkyl group is detached from the σ -Pt-bonded phenyl group, exchange in the alkyl hydrogens proceeds through either alkyl chloride, hydride interactions or olefin, hydride interactions. This process for ethylbenzenes is depicted in Eq. (13) and the exchange in *n*-propylbenzene is explained by double-bond migration and reversible *n*-propyl σ -bonded intermediates, thereby giving



higher rates of exchange in the terminal carbon atoms. This mechanism for exchange is thus distinctly different from the exchange reactions involving aromatic protons in that π - σ conversion reactions for exchange are preceded by a reversible dealkylation.

Comparison of Acid, Homogeneous and Heterogeneous Metal-Catalyzed Exchange in Alkylbenzenes

The results of Table 5 indicate that acid-catalyzed exchange is not subject to ortho steric effects as exchange is very fast in mesitylene. By contrast, heterogeneous exchange exhibits severe ortho steric hindrance and severe hindrance to the formation of a π -bond on extended crystal surfaces when bulky groups, e.g., *tert*-butyl, are present. The π -bond is inhibited almost completely in hemimellitene and no exchange occurs with mesitylene (16). Further complications with heterogeneous exchange occur in polycyclic compounds where delocalized π -orbitals form strong π -bonds with extended crystal planes and exchange is inhibited (41). In this respect, although the homogeneous technique does have pronounced ortho steric effects, exchange in the active positions is not greatly affected by the nature of the substituents. Thus many compounds previously difficult to label by other techniques, e.g., *tert*-butylbenzene, nitrobenzene, and polycyclic compounds, may be deuterated

using the simple one-step procedure outlined in this paper.

The exchange mechanism of the aromatic protons in active positions possesses similar concepts in both homogeneous and heterogeneous processes and associative and dissociative mechanisms have been proposed [Eqs. (1), (2), also refs. (5, 18)]. It is apparent, however, from the foregoing discussion on homogeneous alkyl exchange, that the process is independent to a large extent of the aromatic exchange. Garnett and Sollich-Baumgartner (16) have indicated that alkyl exchange by the heterogeneous technique may also occur by an independent dissociative mechanism involving different but more numerous catalyst sites. Orientation studies of both homogeneous and heterogeneous exchange are compared in Table 6. The fact that different sites are involved in heterogeneous exchange is accentuated by the fact that both nickel (18) and palladium (42) give high rates of exchange in alkyl hydrogens but are relatively inert for aromatic exchange.

As the heterogeneous exchange in the α - and β -positions using PdO and PtO_2 (Table 6) is consistently different from the ratio observed in homogeneous exchange, a different mechanism is indicated. The heterogeneous result may be interpreted without introducing dealkylation as the amount of deuteration in the α -position in ethylbenzene is the same as in the β -position in terms of H atoms replaced per molecule, even

TABLE 6
COMPARISON OF ALKYL HYDROGEN EXCHANGE BY HOMOGENEOUS AND HETEROGENEOUS TECHNIQUES

Aromatic	Reaction time (hr)	Temp. (°C)	% D aromatic	% D in α -posn.	% D in β -posn.	% D in γ -posn.
<i>Homogeneous^a</i>						
Toluene	5	100°	27.2	15.6	—	—
Ethylbenzene	16	120°	45.8	19.5	20.6	—
<i>n</i> -Propylbenzene	16	120°	46.5	7.6	4.3	10.5
<i>tert</i> -Butylbenzene	6	120°	39.0	—	0.0	—
<i>Heterogeneous^b</i>						
Toluene	100	130°	44.7	50.3	—	—
Ethylbenzene	100	130°	55.0	45.0	31.3	—
Ethylbenzene ^c	100	130°	1.60	14.7	10.7	—
<i>n</i> -Propylbenzene	48	140°	36.8	9.5	3.0	3.0
<i>tert</i> -Butylbenzene	48	140°	17.4	—	0.67	—

^a Using conditions indicated in Table 2.

^b Self-activation reaction with PtO₂ (ref. 42).

^c Exchange using PdO (ref. 42).

though the percentage D differs. This would indicate that the heterogeneous exchange process involves the simultaneous replacement of one proton on both the α - and β -positions per interaction with the catalyst. This distinction from homogeneous exchange, which is postulated to involve dealkylation and randomization of alkyl carbons could be verified using carbon isotope studies.

ACKNOWLEDGMENTS

The authors thank the Australian Research Grants Committee and the Australian Institute of Nuclear Science and Engineering for financial assistance. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. The authors are also grateful to Johnson Matthey and Co. Ltd. for the gift of samples of the transition metal salts used in this study.

REFERENCES

1. GARNETT, J. L., AND HODGES, R. J., *J. Am. Chem. Soc.* **87**, 4546 (1967).
2. HODGES, R. J., AND GARNETT, J. L., *J. Phys. Chem.* **72**, 1673 (1968).
3. HODGES, R. J., AND GARNETT, J. L., *J. Phys. Chem.*, in press.
4. BOND, G. C., *Ann. Rept. Progr. Chem. (Chem. Soc. London)* **63**, 27 (1966).
5. GARNETT, J. L., AND SOLLICH-BAUMGARTNER, W. A., *Advan. Catalysis* **16**, 95 (1966).
6. SPARKE, M. B., TURNER, L., AND WENHAM, A. J. M., *J. Catalysis* **4**, 332 (1965).
7. BAWN, C. E. H., COOPER, D. G. T., AND NORTH, A. M., *Polymer* **7**, 113 (1966).
8. GREEN, M. L. H., AND NAGY, P. L. I., *Advan. Organometallic Chem.* **2**, 325 (1965).
9. GINSBERG, A. P., *Transition Metal Chem.* **1**, 112 (1965).
10. LANGFORD, C. H., AND GRAY, H. B., "Ligand Substitution Processes," Chap. 2. W. A. Benjamin, New York, 1965.
11. BELLUCO, U., CROATTO, U., UGUAGLIATI, P., AND PIETROPAOLI, R., *Inorg. Chem.* **6**, 718 (1967).
12. GARNETT, J. L., AND SOLLICH, W. A., *Australian J. Chem.* **18**, 993 (1965).
13. SATCHELL, D. P. N., *J. Chem. Soc.*, p. 3910 (1958).
14. WEST, J. C., AND GARNETT, J. L., unpublished data.
15. ANDERSON, J. R., AND KEMBALL, C., *Advan. Catalysis* **9**, 51 (1957).
16. GARNETT, J. L., AND SOLLICH-BAUMGARTNER, W. A., *J. Phys. Chem.* **69**, 1850 (1965).
17. GARNETT, J. L., AND HODGES, R. J., *Chem. Commun.*, p. 1001 (1967).
18. CRAWFORD, E., AND KEMBALL, C., *Trans. Faraday Soc.* **58**, 2452 (1962).
19. ROONEY, J. J., *J. Catalysis* **2**, 53 (1963).
20. HARTOG, F., TEBBENS, J. H., AND WETERINGS, C. A. M., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam* **2**, 1210 (1964).
21. WINKHAUS, G., PRATT, L., AND WILKINSON, G., *J. Chem. Soc.* p. 3807 (1961).
22. HORIUTI, J., AND POLANYI, M., *Nature* **132**, 819, 931 (1933).
23. FARKAS, A., AND FARKAS, L., *Proc. Roy. Soc. (London)* **A144**, 467, 481 (1934).

24. CHATT, J., AND DAVIDSON, J. M., *J. Chem. Soc.* p. 843 (1965).
25. FALK, C. D., AND HALPERN, J., *J. Am. Chem. Soc.* **87**, 3523 (1965).
26. LAUER, W. M., AND STEDMAN, G., *J. Am. Chem. Soc.* **80**, 6439 (1958).
27. LAUER, W. M., MATSON, G. W., AND STEDMAN, G., *J. Chem. Soc.* **80**, 6433, 6437 (1958).
28. HALPERN, J., HARROD, J. F., AND JAMES, B. R., *J. Am. Chem. Soc.* **88**, 5150 (1966).
29. LEE, C. C., AND HAHN, B., *Canadian J. Chem.* **45**, 2129 (1967).
30. SKELL, P. S., AND STAREK, I., *J. Am. Chem. Soc.* **84**, 3962 (1962); SKELL, P. S., AND MAXWELL, R. J., *ibid.*, p. 3963 (1962).
31. TSUJI, J., NOGIT, AND MARIKAWA, M., *Bull. Chem. Soc. Japan* **39**, 714 (1966).
32. CHATT, J., COFFEY, R. S., GOUGH, A., AND THOMPSON, D. T., *J. Chem. Soc. (A)*, p. 190 (1968).
33. CHATT, J., AND SHAW, B. L., *J. Chem. Soc.* p. 5075 (1962).
34. HECK, R. F., AND BRESLOW, D. S., *J. Am. Chem. Soc.* **83**, 4023 (1961).
35. HARROD, J. F., AND CHALK, A. J., *J. Am. Chem. Soc.* **87**, 1133 (1965).
36. EVANS, D., OSBORN, J. A., JARDINE, F. H., AND WILKINSON, G., *Nature* **208**, 1203 (1965).
37. OSBORN, J. A., JARDINE, F. H., YOUNG, J. F., AND WILKINSON, G., *J. Chem. Soc. (A)*, p. 1711 (1966).
38. VASKA, L., *Inorg. Nuclear Chem. Letters* **1**, 89 (1965).
39. BELLUCCO, U., GIUSTINIANI, M., AND GRAZIANI, M., *J. Am. Chem. Soc.* **87**, 6494 (1967).
40. EBERHARDT, G. C., AND VASKA, L., *J. Catalysis* **8**, 183 (1967).
41. GARNETT, J. L., AND SOLLICH, W. A., *Australian J. Chem.* **15**, 56 (1962).
42. FISHER, B. D., AND GARNETT, J. L., *Australian J. Chem.* **19**, 2299 (1966).