to be stable only in the form of dianion. It seems therefore more likely that the dioxalato complex has the structure of an open chain complex in which chromium(VI) retains its usual coordination number of four.

The nature of the rate law indicates that although the dianion is the predominant form in which the 1:2 complex is present, the kinetically active reaction intermediate is the monoanion. We believe that this monoanion in the rate-limiting step decomposes to yield a hexaaquochromium(III) ion, three molecules of carbon dioxide, and a $\cdot CO_2H$ radical. We are thus assuming that the rate-limiting step of the reaction consists of the one-step three-electron oxidation. The three-electron oxidation provides an attractive explanation for the obvious preference of oxalic acid to react *via* the 1:2 complex. This mechanism provides a route by which the formation of the highly unstable chromium(IV) intermediate can be avoided. The three-electron oxidation leads to the direct formation of three molecules of carbon dioxide and one relatively stable free radical.[24] It correctly predicts that at least 50% of chromium is formed originally in the form of $[Cr(H_2O)_6]^{3+}$.

In the absence of a free-radical scavenger, the $\cdot CO_2H$ radical will react with a chromium(VI) species to yield carbon dioxide and a chromium(V) compound which then can react further with one or more molecules of oxalic acid. The observation that a larger amount of oxalato chromium(III) than would be expected from a simple equilibration is formed seems to indicate that chromium(V) forms a complex with more than one oxalic acid molecule prior to the oxidation step. Be-

sides undergoing oxidation, some $\cdot CO_2H$ radicals probably react in a bimolecular reaction to recombine to oxalic acid, or to disproportionate to carbon dioxide and formic acid. This reaction is necessary to explain the observed initial rate of chromium(III) formation[25] and is in agreement with the earlier observation[26] that free radicals undergo bimolecular dimerization and/or disproportionation reactions even in the presence of chromic acid.

In the presence of a free-radical scavenger, the reaction will be modified as

$$\cdot CO_2H + CH_2{=}CHR \longrightarrow HO_2CCH_2\dot{C}HR$$

$$HO_2CCH_2\dot{C}HR + nCH_2{=}CHR \longrightarrow HO_2CCH_2(CHCH_2)_n\dot{C}HR$$
$$\underset{R}{|}$$

$$HO_2CCH_2(CHCH_2)_n\dot{C}HR + Cr(VI) \longrightarrow$$
$$\underset{R}{|}$$

$$HO_2CCH_2(CHCH_2)_n\dot{C}HOH + Cr(V)$$
$$\underset{R}{|} \quad \underset{R}{|}$$

$$Cr(V) + OxH_2 \longrightarrow Cr(III) + 2CO_2$$

The stoichiometry of the reaction then will be

$$3OxH_2 + 2Cr(VI) + nCH_2{=}CHR \longrightarrow$$
$$5CO_2 + 2Cr(III) + HO_2CCO_2(CHCH_2)_n CHOH$$
$$\underset{R}{|} \quad \underset{R}{|}$$

Thus, in the presence of a sufficient excess of a free-radical scavenger to trap all $\cdot CO_2H$ radicals, the yield of carbon dioxide should be reduced from six molecules to five molecules per two molecules of chromic acid, which is in exact agreement with our results.

(24) *Cf.*, Part I of this series for a more detailed discussion and references.

(25) *Cf.* ref 17 for a more detailed discussion.
(26) M. Rahman and J. Roček, *J. Amer. Chem. Soc.*, 93, 5455 (1971).

Activation of Aromatic Carbon–Hydrogen Bonds by Transition Metal Complexes. II.[1] Substituted Benzenes

U. Klabunde and G. W. Parshall*

Contribution No. 1908 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898. *Received April 28, 1972*

Abstract: Competitive exchange between D_2 and aromatics is catalyzed by polyhydride transition metal complexes. The relative rates of exchange of mono- and disubstituted benzenes increase in the order $p\text{-}(CH_3)_2 < CH_3 \sim OCH_3 < H < CF_3 \sim F < p\text{-}F_2$ for the $NbH_3(C_5H_5)_2$, $[NbH(C_5H_5)(\mu\text{-}C_5H_4)]_2$, and $IrH_5[(CH_3)_3P]_2$ catalyzed reactions. Except for p-xylene, only slight differences in rates were observed with $TaH_3(C_5H_5)_2$ and $TaH_3(C_5H_4CH_3)_2$. Differences in rates of the various positions were observed with the largest effect due to steric hindrance by the substituents. A mechanism involving a series of alternating reductive–elimination and oxidative–addition steps is proposed.

In recent years it has been recognized that transition metal complexes can catalytically activate aromatic C–H bonds.[2] Synthetic applications of this effect have included the selective ortho chlorination of azobenzene[3]

and the ortho deuteration of triphenylphosphine.[4] These reactions seem to involve intramolecular attack on an aryl C–H bond of a coordinated ligand.

Relatively few intermolecular reactions of this sort have been observed. The reported examples include

(1) Part I in this series is considered to be: E. K. Barefield, G. W. Parshall, and F. N. Tebbe, *J. Amer. Chem. Soc.*, 92, 5234 (1970).
(2) G. W. Parshall, *Accounts Chem. Res.*, 3, 139 (1970).
(3) D. R. Fahey, *J. Organometal. Chem.*, 27, 283 (1971).

(4) G. W. Parshall, W. H. Knoth, and R. A. Schunn, *J. Amer. Chem. Soc.*, 91, 4990 (1969).

Table I. Comparison of Observed and Calculated[a] Deuterium Distributions of $NbH_3(h^5\text{-}C_5H_5)_2$-Catalyzed Exchange Reaction at 92% Completion

Substituted benzene		d_0	d_1	d_2	d_3	d_4	d_5	f_D
$p\text{-}C_6H_4F_2$	Found	19	38	30	12	1.5		0.350
	Calcd	18	38	31	11	1.5		
C_6H_5F	Found	28	41	23	7	1		0.224
	Calcd	28	41	23	7	1		
C_6H_6	Found	43	39	15	3			0.125
	Calcd	45	39	14	3			
$C_6H_5OCH_3$	Found	62	32	6				0.09
	Calcd	63	31	6				
$C_6H_5CH_3$	Found	70	25	5				0.064
	Calcd	72	25	3				
$p\text{-}C_6H_4(CH_3)_2$	Found	97	3					0.007
	Calcd	97	3					
$C_6H_5F^b$	Found	0.4	2.0	7.3	22	40	28	0.78
	Calcd	0.1	1.0	6.7	23	41	28	
	Calcd[c]	0	1.2	6.0	23	42	28	
$C_6H_5OCH_3^b$	Found	1	13	36	38	10	2	0.42
	Calcd	4	18	31	30	14	2	
	Calcd[c]	1.6	14	39	36	9	0.5	

[a] Calculated using the expanded polynominal $(a + b)^n$. [b] Samples from Table III. [c] Calculated using the expanded polynominal: $(o_h + o_d)^2(m_h + m_d)^2 - (p_h + p_d)$.

oxidative addition of aromatic C–H bonds to reactive Ru(0)[5] and W(II)[6] species and the catalytic deuteration of benzene by D_2O[7] and by D_2.[1]

We now report a systematic study of the HD exchange between D_2 and substituted benzenes catalyzed by polyhydride complexes.

Experimental Section

All operations were carried out in a dry nitrogen atmosphere. Prior to use all solvents were dried over 4A Davison molecular sieves and saturated with dry nitrogen.

The complexes pentahydridobis(trimethylphosphine)iridium(V),[1] trihydridobis(*pentahapto*cyclopentadienido)niobium(V)[8] and -tantalum(V),[9] bis-μ-[(*pentahaptomonohapto*cyclopentadienyl)]-bis[hydrido(*pentahapto*cyclopentadienido)niobium],[8] titanocene dimer,[10] bis[1,2-bis(dimethylphosphino)ethane]ruthenium(0),[5] and dihydridobis(*pentahapto*cyclopentadienido)tungsten(IV)[11] were prepared by published methods.

Trihydridobis(*pentahapto*methylcyclopentadienido)tantalum(V). To an 800-ml 1:1 tetrahydrofuran–benzene solution containing 0.6 mol of lithium methylcyclopentadienide, 71 g (0.2 mol) of tantalum pentachloride was added at such a rate that the temperature never exceeded 45°. After addition, the dark brown suspension was stirred for 30 min and then 30 g (0.8 mol) of lithium aluminum hydride was added at such a rate that the temperature did not exceed 50°. The orange suspension was heated to 80° and stirred at this temperature for 1 hr.

With mechanical stirring the reaction mixture was hydrolyzed with 35 ml of water at 0°. The light olive-green suspension was filtered through Celite. After the solid was washed with 500 ml of benzene at *ca.* 40°, the solvent was removed under reduced pressure. The brown solid was dissolved in 300 ml of benzene at 25°, treated with 20 g of Darco charcoal, and filtered through Celite. After 200 ml of heptane was added to the pale violet filtrate and the volume of the solution reduced, 31 g (46%) of pale violet crystals was obtained. An additional treatment with Darco yielded white crystals that melted at 89.5–91°. *Anal.* Calcd for $C_{12}H_{17}Ta$: C, 42.11; H, 5.01. Found: C, 42.10; H, 5.02.

The ^1H nmr spectrum (220 MHz, C_6D_6) consists of two triplets (J_{HH} = 5 Hz) at τ 5.17 and 5.30, assigned to ring protons, a methyl

signal at τ 8.02, and the hydride resonances as a triplet at τ 10.69 and a doublet at τ 12.20 (J = 10.5 Hz), in the area ratio of 1:2, respectively.

The ir spectrum (Nujol mull) exhibited the Ta–H stretching vibration at 1740 (s) cm^{-1} and other vibrations characteristic of the methylcyclopentadienide ring.

Benzene–D_2 Exchange-Scouting Technique. Initial screening for catalytic activity in the exchange between benzene and D_2 was carried out in 4-ml sealed glass tubes. A typical experiment is that with $NbH_3(C_5H_5)_2$.[12] The tube was charged with 25 mg of the complex and 2.0 ml of benzene and was cooled to −78° and filled to 600 mm pressure with deuterium (98.99% D_2). The tube was sealed at the 4.0 ml mark, thus enclosing *ca.* 6 × 10^{-5} mol of gas and was heated at 100° for 19 hr. The solution, originally yellow, became dark brown but remained clear. The tube was chilled in liquid nitrogen and was opened directly into the antechamber of the mass spectrometer. Analysis of the gas showed 99.8% H_2 and 0.2% HD.

A similar experiment in which the tube was tumbled at 25° for 19 hr gave 36.1% H_2, 2.7% HD, and 61.2% D_2. If it is assumed that the H_2 evolved from the complex, it corresponds to 30% dissociation. When 0.06 mmol of $NbH_3(C_5H_5)_2$ in 2.0 ml of benzene was agitated under N_2 for 24 hr, 0.04 mmol of hydrogen was evolved.

Deuterium Exchange in Mixtures of Substituted Benzenes. A 15-ml ampoule containing a magnetic micro-stirring bar was charged with 7 ml of a cyclohexane solution containing 0.46 mmol of each of the benzenes, 0.07 mmol of complex, and 1.2 mmol of deuterium gas. With more than 90% of the ampoule immersed in liquid nitrogen the flask was sealed and then placed in a 107° temperature bath for 64.5 hr.

Initially, all complexes dissolved completely at 107°. Later, excepting the $TaH_3(CH_3C_5H_4)_2$, $IrH_5[P(CH_3)_3]_2$, and $Ru[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2$ solutions which remained clear, the solutions turned brown and solids precipitated. In no case was a metal observed.

The ampoule and a gas sample tube were connected with polyisobutylene tubing ($^1/_4$ in. i.d., $^1/_8$ in. wall) to a glass tee. After the ampoule was placed in liquid nitrogen and evacuated, the tip of the ampoule was broken by squeezing the rubber tubing with a pair of pliers. The gas tube was replaced with a small flask. The liquid was distilled at 1 μ pressure (50°) into the flask which was immersed in liquid nitrogen. The remaining solid, which was further dried at 0.01 μ (25°), showed new infrared absorptions some of which can be ascribed to C–D and M–D stretching vibrations. In no case was metal observed.

Results of this experiment are shown in Table I. Similar procedures were followed for the other exchange reactions for which the conditions are given in the tables.

Isotope Effect. Deuterium–Benzene-h_6 and Hydrogen–Benzene-d_6 Exchange. A 115-ml ampoule containing a magnetic stirring bar

(5) J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 843 (1965).

(6) M. L. H. Green and P. J. Knowles, *J. Chem. Soc. D*, 1677 (1970), *J. Chem. Soc. A*, 1508 (1971).

(7) R. J. Hodges and J. L. Garnett, *J. Phys. Chem.*, 73, 1525 (1969).

(8) F. N. Tebbe and G. W. Parshall, *J. Amer. Chem. Soc.*, 93, 3793 (1971).

(9) M. L. H. Green, J. A. McCleverty, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4854 (1961).

(10) G. W. Watt, L. J. Baye, and F. O. Drummond, Jr., *J. Amer. Chem. Soc.*, 88, 1138 (1966).

(11) Gift from Dr. R. A. Schunn; prepared according to ref 9.

(12) For convenience the prefix h^5 is omitted before C_5H_5.

Table II. Isotope Effect in the Niobium Hydride Catalyzed Exchange

Experiment[a]	Time, hr	Gas f_D[b]	Percentages of the benzenes-d_n							f_D[c]	k_H/k_D
			$n = 0$	1	2	3	4	5	6		
$C_6H_6 + D_2$	0	0.995	99.9	0.1						0.0	
	60	0.234	90.6	9.4						0.016	
	∞[d]	0.022	87.6	11.8	0.7					0.022	
$C_6D_6 + H_2$	0	0.0						2.9	97.1	0.995	
	60	0.309						8.2	91.8	0.986	
	∞[d]	0.970					1.2	15.5	83.3	0.970	2.9
1,3,5-$D_6H_3D_3 + H_2/D_2$	0	0.516				1.0	98.9	0.1		0.498	
	19	0.489				1.9	96.4	1.7		0.500	1.9
	62	0.467			0.1	4.4	88.3	7.1	0.2	0.505	2.1
	129	0.451			0.1	5.2	85.4	9.1	0.3	0.507	2.2

[a] See Experimental Section under Isotope Effect. [b] Fraction of D in the gas. [c] Fraction of D in the benzene. [d] Calculated; all exchangeable H and D atoms of the gas, catalysts, and benzene were included.

was charged with 21.5 mg (0.095 mmol) of $NbH_3(C_5H_5)_2$, 4.30 g (55 mmol) of benzene-h_6, and 605 mm at 0° (3.7 mmol) of deuterium. The flask was sealed and kept at 100° for 60 hr.

The hydrogen–benzene-d_6 experiment was run under identical conditions.

Deuterium/Hydrogen–Benzene-d_3 Exchange. Three 37-ml ampoules containing a magnetic stirring bar were charged with 22.8 mg (0.051 mmol) of $[NbH(C_5H_4)(C_5H_5)]_2$, 2.0 ml of a cyclohexane solution containing 0.101 g (1.25 mmol) of 1,3,5-trideuteriobenzene, and ca. 4 mmol (700 mm at −195°) of a 1:1 hydrogen–deuterium gas mixture. The sealed ampoules were placed in a 105° temperature bath and removed at various time intervals for mass spectral analyses of the gas and the benzene which was separated from the cyclohexane by gas chromatography. The results are summarized in Table II.

Instrumental Analyses and Calculation Methods. The gases and pure benzenes were analyzed on a Consolidated Electrodynamic Corporation mass spectrometer, CEC-21-103C.

The benzene mixtures were analyzed at 70 eV on the Du Pont mass spectrometer, Model No. 2-1490, coupled with a gas chromatograph and a built-in helium separator. The conditions for the gas chromatography were the following: column, 2 m × $^1/_8$ in. 10% Triton X-305 on chromosorb W; flow rate, 25 ml/min; column temperature, 30–150° programmed at 12°/min., no H–D exchange occurred on the column or in the mass spectrometer. However, the various deuterated species were partially separated; the front of the peak was rich in the deuterated species. The mass spectrum close to the gas chromatograph peak maximum corresponded very well to the true extent of deuterium incorporation as determined independently.

Since the mass spectral patterns of the deuterated substituted benzenes were not available, the percentage of deuterated benzene was calculated using the reference patterns of the nondeuterated benzenes obtained at 70 eV where M + 1 and M − 1 intensity was 7 and 3–30, respectively, except for toluene where M − 1 was the most intense peak.

The extents of deuterium determined in this manner agreed to within ±3%, except for toluene where the error could be as large as ±8%. They also agree well with those determined of the separated benzenes without the use of the gas chromatograph.

The 220-MHz ¹H nmr spectra were recorded on a Varian instrument. The benzenes were separated by preparative gas chromatography and then dissolved in solvents where maximum separation of the various proton absorptions occurred. The resonances were assigned according to published data.[13] The average of the integral of three or four runs was used to calculate the amount of deuterium incorporated in each of the three positions.

In all experiments, hydrogen and deuterium in the gas phase were completely scrambled as the observed ratio $H_2:HD:D_2$ agreed with that calculated from the equilibrium constant of 3.43 at 107°.[14]

Kinetics

Isotope Effect. For the H_2–benzene-d_6 and D_2–benzene-h_6 experiment, the isotope effect can be cal-

(13) J. W. Emsley, I. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1966, p 750.
(14) G. C. Bond, "Catalysis by Metals," Academic Press, New York, N. Y., 1962, p 151.

culated from

$$\frac{k_H}{k_D} = \frac{\log (f^\infty - f^0) - \log (f^\infty - f^t)}{\log (f^0 - f^\infty) - \log (f^t - f^\infty)}$$

where f^0, f^t, and f^∞ represent the fractions of deuterium in the benzene at time 0, t, and equilibrium. The only assumption for this experiment is that the concentration of the catalytic species is the same in both experiments.

For the H_2/D_2–benzene-d_3 experiment, the isotope effect can be calculated from

$$\frac{k_H}{k_D} = \frac{[\text{benzene-}d_4]_t - [\text{benzene-}d_4]_0}{[\text{benzene-}d_2]_t - [\text{benzene-}d_2]_0}$$

The equation holds if the H/D concentration of the gas remains constant.

Parallel Competitive Isotopic Exchange Reactions. The following treatment correlates the fractions of deuterium incorporated into each substrate (BH_n or TH_m) with the rates or rate constants for exchange. (AD is a deuterium source such as D_2, HD, or metal deuteride.)

$$BH_n + rAD \rightleftharpoons BH_{n-r}D_r + rAH \quad (1)$$

$$TH_m + rAD \rightleftharpoons TH_{m-r}D_r + rAH \quad (2)$$
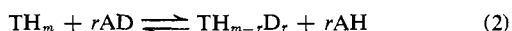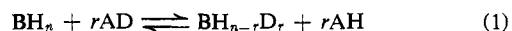
If we let [BH] and [BD] represent the concentrations of sites of BH_n which contain hydrogen and deuterium, respectively, and $[BH_n] = a$, then the concentrations for (1) can be designated as

$$[\text{BH}] + [\text{BD}] = na, [\text{BD}] = x$$

and

$$[\text{AH}] + [\text{AD}] = b, [\text{AD}] = z$$

Regardless of the exchange mechanism, the rate of formation of [BD] is

$$\frac{dx}{dt} = R_B\left(\frac{z}{b}\right)\left(\frac{na - x}{na}\right) - R_B\left(\frac{x}{na}\right)\left(\frac{b - z}{b}\right) \quad (3)$$

where R_B is a basic rate of exchange that may be a function of a, b, and catalyst concentration but remains constant during a run.[15]

The second term in (3) is due to the reverse reaction which can be neglected because the isotope effect, CH/CD ≈ 3, favors the forward reaction and because x/na is small compared to $(na - x)/na$ when $na > b$.

(15) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, p 192.

Thus (3) reduces to

$$\frac{dx}{dt} = R_B\left(\frac{z}{b}\right)\left(\frac{na - x}{na}\right) \tag{4}$$

Since $1 - f_{BD} = (na - x)/na$ and $dx = na\,df_{AD}$, (4) becomes

$$\frac{na\,df_{BD}}{1 - f_{BD}} = R_B\left(\frac{z}{b}\right)dt \tag{5}$$

A similar expression may be derived for eq 2 in which $a = [BH_n] = [TH_m]$ (under conditions of equal substrate concentration).

$$\frac{ma\,df_{TD}}{1 - f_{TD}} = R_T\left(\frac{z}{b}\right)dt \tag{6}$$

Division of (5) by (6) leads to

$$\frac{df_{BD}}{1 - f_{BD}} = \frac{mR_B}{nR_T}\left(\frac{df_{TD}}{1 - f_{TD}}\right) \tag{7}$$

Integration of (7) leads to

$$\ln(1 - f_{BD})/\ln(1 - f_{TD}) = mR_B/nR_T \tag{8}$$

Assuming first-order dependence on substrate and the same mechanism to apply for each substrate, then R_B or R_T may be written as

$$R_B = k_B[na][b][\text{catalyst}], \quad R_T = k_T[na][b][\text{catalyst}] \tag{9}$$

Substituting (9) into (8) gives

$$\frac{\ln(1 - f_{BD})}{\ln(1 - f_{TD})} = \frac{k_B}{k_T} \tag{10}$$

For a series of substrates (10) may be expanded to $\ln(1 - f_B)/\ln(1 - f_T)/\ln(1 - f_F)/\ldots = k_B/k_T/k_F/\ldots$

Results

Benzene–D_2 Exchange. As an initial probe for catalytic activation of aromatic C–H bonds, a series of metal complexes were incubated with a mixture of benzene and deuterium (1–2 atm pressure) at 80–110°. Appearance of H_2 and HD in the gas phase was taken to be an indication of catalytic activity. As reported earlier,[1] $TaH_3(C_5H_5)_2$ and $IrH_5[P(CH_3)_3]_2$ showed modest activity. The newly synthesized complexes TaH_3-$(C_5H_4CH_3)_2$, $NbH_3(C_5H_5)_2$,[8] and $[(C_5H_5)NbH(C_5H_4)]_2$[8] also were active. It may be significant that no H_2 or HD formation was noted with $WH_2(C_5H_5)_2$ or with $Ru[(CH_3)_2PC_2H_4P(CH_3)_2]_2$, both of which interact with benzene under other conditions to form isolable phenylmetal hydrides.[5,6] The dimer of titanocene[10,16] showed no interaction with benzene even though titanocene itself undergoes exchange of cyclopentadienyl C–H with deuterium.[17]

The inverse reaction, exchange of H_2 with benzene-d_6, was used as a confirmatory experiment whenever catalysis was detected by the benzene–D_2 experiment. This set of experiments showed whether there was exchange with the hydrogens of only the ligand or of both the ligand and benzene.

The relative activities of the polyhydride complexes in the C_6H_6–D_2 exchange reaction were determined at 107° for 64.5 hr to be the following: $NbH_3(C_5H_5)_2$,

(16) H. H. Brintzinger and J. E. Bercaw, *J. Amer. Chem. Soc.*, 92, 6182 (1970).
(17) R. H. Marvich and H. H. Brintzinger, *ibid.*, 93, 2046 (1971).

5.5; $[NbH(C_5H_5)(\mu\text{-}C_5H_4)]_2$, 4.8; $TaH_3(C_5H_5)_2$, 1.7; $TaH_3(C_5H_4CH_3)_2$, 1.0. The similarity between the results for the niobium trihydride and for the dimeric monohydride is expected because these two species are interconvertible by loss or gain of hydrogen.[8]

$$2NbH_3(C_5H_5)_2 \rightleftharpoons [NbH(C_5H_5)(C_5H_4)]_2 + 3H_2$$
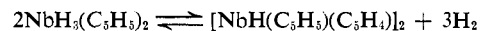
In experiments under these conditions, the MH_3-$(C_5H_5)_2$ solutions ($M = Nb$, Ta) deposited brown solids, probably the μ-C_5H_4 dimers, but solutions of TaH_3-$(C_5H_4CH_3)_2$ remained clear. Reaction of the cyclopentadienyl ring hydrogens is implicated by the appearance of ν_{C-D} adsorption in the infrared spectra of the recovered C_5H_5 complexes. Similarly, solutions of $IrH_5[P(CH_3)_3]_2$ turned orange although they remained clear and deuteration of the ligand methyl groups was observed.[18]

Attempts were made to determine the benzene–D_2 isotope effect. The exact magnitude of the isotope effect is difficult to assess because some of the complex undergoes a side reaction and precipitates, and thus the actual concentration of the catalytic species may vary. Two approaches were taken in an attempt to avoid this concentration problem. The first involved separate exchanges of D_2–benzene and H_2–benzene-d_6 where we assume that the concentrations of the catalytic species, $[NbD(C_5H_5)_2]$ and $[NbH(C_5H_5)_2]$, respectively, were the same. The second approach involved a competition experiment of equimolar amounts of H and D and 1,3,5-trideuteriobenzene, in which variations in the concentrations of the catalytic species do not affect the result. (The Nb–H/Nb–D isotope effect is superimposed on this result; we have assumed here that it is one.) The results from these experiments are shown in Table II. Although the magnitude of the isotope effect is different for the two experiments, 2.9 and 2.1, respectively, we can however say that there is one and that it is probably larger than 2.

The benzene-d_3/H_2–D_2 experiment allows us to assign relative rates to the three kinds of isotopic exchange reactions. After 62 hr the deuterium in the gas phase is almost completely scrambled, *ca.* 0.3 mequiv of deuterium is incorporated into the catalyst, and 0.14 mmol of the benzene has undergone exchange. Thus the order for the niobium hydride catalyzed exchanges is as follows: gas > ligand > benzene.

Substituted Benzenes. In order to probe steric and electronic effects on the catalysts for benzene–D_2 exchange, the exchange was carried out with a mixture of benzenes under conditions of internal competition. In a typical experiment a solution of equimolar quantities of benzene, anisole, fluorobenzene, p-difluorobenzene, toluene, and p-xylene in cyclohexane was treated with D_2 in the presence of $NbH_3(C_5H_5)_2$ until 92% of the statistical amount of H appeared in the gas phase. The individual benzenes were then separated by gas chromatography and were analyzed for deuterium content by mass spectrometry. The first six entries in Table I illustrate a low D-incorporation experiment in which even the most reactive aromatic, p-difluorobenzene, remains 19% undeuterated.

With low deuterium incorporation, there is excellent agreement between the observed fractions of mono-, di-, tri-, and tetradeuterated species for a given ben-

(18) E. K. Barefield, unpublished observations.

Table III. Positional Deuterium Substitution of Some Monosubstituted Benzenes

C_6H_5X X	No. of D atoms incorporated[a]			f_D as determined by	
	$m/2$	p	$o/2$	Nmr	Mass spec
CF_3[b]	0.45	0.46	0[d]	0.46[g]	0.45
CF_3[c]	0.72	0.76	0[d]	0.74[g]	0.73
F[c]	0.95	0.60	0.80		0.78
OCH_3[c]	0.78	0.58[e]	0.12[e]	0.43[h]	0.48
		$^1/_3(o + p)$[f]			
CH_3[b]	0.23	0.08		0.17[h]	0.12
OCH_3[b]	0.28	0.07		0.14[h]	0.16

[a] Conditions: 8 mmol of deuterium and 1.8 mmol of NbH_3-$(C_5H_5)_2$ in a 115-ml ampoule at 108° for 62 hr. [b] Run as a mixture of 5 mmol of each substituted benzene, 10 mmol of benzene-d_6, and 0.03 mol of cyclohexane. [c] Run separately, 0.4 g of the substituted benzene in 4.0 g of benzene-d_6. [d] Highest deuterated species found in the mass spectrum was $C_6D_3H_2CF_3$. [e] Addition of 0.03 g of the shift reagent, $Eu(dpm)_3$, to a 1 ml cyclohexane solution containing 0.1 ml of anisole completely separated the ortho, meta, and para resonances. [f] Ortho and para resonances not sufficiently separated. [g] Ortho resonance intensity used as internal standard. [h] Methyl resonance intensity used as internal standard.

served and calculated values seems to validate assumption 1.

The same competitive deuteration experiments of substituted benzenes were carried out with each metal complex catalyst that was found to catalyze C_6H_6–D_2 exchange. The results shown in Table IV are presented in terms of relative rate constants as defined in the kinetics analysis in the Experimental Section. As shown for the niobium trihydride catalyst, the relative rates differ slightly with degree of conversion (of D_2) attained. However, the qualitative pattern of reactivity for a given catalyst does not change with conversion. (It should be noted that these are not absolute rate constants. The rate of C_6H_6–D_2 exchange is much faster for $NbH_3(C_5H_5)_2$ than for its tantalum analog.)

Discussion

Perhaps the most noteworthy result of the competitive exchange experiments (Table IV) is the striking difference in reactivity patterns between the niobium and

Table IV. Relative Rate Constants for H–D Exchange

Catalyst	p-$C_6H_4F_2$	C_6H_5F	C_6H_6	$C_6H_5OCH_3$	$C_6H_5CH_3$	p-$C_6H_4(CH_3)_2$	% completion[a]
$NbH_3(C_5H_5)_2$		1.7	1.0	0.7	0.6		98
	3.2	1.9	1.0	0.7	0.5	0.02	92
	4.0	2.1	1.0	0.7	0.7	0.01	50
	4.2	2.1	1.0	0.8	0.8	0.04	35
$[NbH(C_5H_5)(C_5H_4)]_2$	3.9	1.9	1.0	0.7	0.5	0.05	88
$IrH_5[P(CH_3)_3]_2$		4.0	1.0	0.9	0.6		~60
$TaH_3(C_5H_5)_2$		0.9	1.0	0.8	1.3		82
	1.1	1.0	1.0	0.8	0.9	0.3	51
$TaH_3(C_5H_4CH_3)_2$	0.8	0.9	1.0	0.8	0.7	0.3	29

[a] Calculated from the total amount of exchangeable deuterium atoms including those of the catalyst.

zene and the values calculated from the various terms of the expanded polynomial $(a + b)^n$. In this calculation, $a = f_H = 1 - f_D$; $b = f_D$ and $n =$ the number of exchangeable hydrogen atoms for the aromatic. For C_6H_5X, $10a^3b^2$ corresponds to the amount of $C_6H_3D_2X$. The fraction of deuterium, f_D, is equal to the sum $\Sigma a_i m_i/100n$ where a_i is the percentage of the i deuterated species with m deuterium atoms. However, this calculation of distribution assumes two conditions: (1) only one deuterium is incorporated per exchange (in contrast to the polydeuteration[19] characteristic of heterogeneous metal catalysts), (2) all hydrogens in a given benzene molecule exchange at or about the same rate.

As shown for fluorobenzene and anisole in the last two entries of Table I, the simple polynomial expansion does not necessarily predict distributions in high-conversion experiments (high ratio of D_2 to benzenes). The defect seems to lie in assumption 2 since nmr analysis of deuterium distribution in the products (Table III) shows differing reactivities of, for example, the ortho, meta, and para protons in fluorobenzene. Using the empirically determined reactivities of the various ring positions, a satisfactory prediction of degrees of deuteration is obtained from a modified polynomial $(o_h + o_d)^2(m_h + m_d)^2(p_h + p_d)$ in which o_d, m_d, and p_d are the fractions of deuterium in the ortho, meta, and para positions and o_h, m_n, and p_h the corresponding fractions of hydrogen. The agreement between observed

(19) Reference 14, p 316.

iridium catalysts on one hand and the tantalum trihydrides on the other. The tantalum catalysts do not seem to discriminate among the various substrates except for p-xylene which is slowest in every experiment. In contrast, the Nb and Ir complexes show faster exchange with the fluorobenzenes and $C_6H_5CF_3$ (Table III) and slower exchange with anisole and toluene. The differences are not large, less than a factor of 10 between toluene and p-difluorobenzene, but are real. Any proposed mechanism must account for the observed acceleration by electron-withdrawing substituents on the aromatic ring.

The results can at least be rationalized on the basis of a mechanism previously proposed[2] for intramolecular catalytic activation of an aryl C–H bond. An expanded version of this scheme involving alternating reductive–elimination and oxidative–addition steps is shown in Figure 1.[20] For convenience, the complex used as a catalyst in the exchange is designated as MH_3. In step 1 reductive elimination of H_2 generates 1 which might be considered the active catalyst in this reaction.[21] Equilibria 2 and 3 are images of (1) and serve to generate the deuterium analog of 1. These steps must be

(20) The cyclic representation of the reaction follows the convention suggested by C. A. Tolman, *Chem. Soc. Rev.*, 1, 332 (1972).

(21) Although hydrogen is lost readily from $MH_3(C_5H_5)_2$ [M = Nb or Ta], the species corresponding to 1, *i.e.*, $MH(C_5H_5)_2$, have not been isolated, but phosphine, carbonyl, and ethylene adducts of 1 as well as $[MH(C_5H_4)(C_5H_5)]_2$ are isolable.[8] The rates of formation of these adducts appear to be the same,[22] suggesting that hydrogen is unimolecularly lost to give 1.

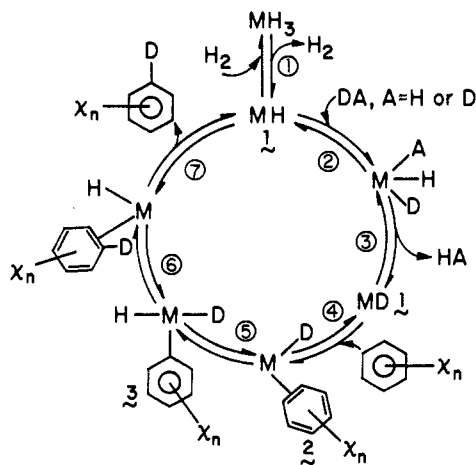(22) F. N. Tebbe, private communication.

Figure 1. Proposed mechanism for catalytic exchange of aromatic C–H with D_2 or HD.

fast relative to the subsequent oxidative addition of C–H because the gas-phase distribution of H and D is always statistical, i.e., H_2–D_2 scrambling is faster than CH–D_2 exchange.

The formal oxidative addition of an aryl C–H bond to the d^2 niobium or tantalum species **1** via a coordinated arene has sound precedent. A $WH(C_6H_5)$-$(C_5H_5)_2$ complex analgous to **3** is formed by oxidative addition of benzene to $W(C_5H_5)_2$, a compound closely related to **1**.[5] A tautomerism between $Ru(dmpe)_2$-$C_{10}H_8$ and $RuH(C_{10}H_7)(dmpe)_2$, dmpe = $(CH_3)_2PCH_2$-$CH_2P(CH_3)_2$, similar to the equilibrium 5 was observed.[4] It is interesting that $WH_2(C_5H_5)_2$ and $Ru(dmpe)_2$ showed no catalytic activity in C_6H_6–D_2 exchange. As noted above, the latter two complexes do interact with benzene, but a requirement for exchange is that the active complex must have deuteride ligands that can be transferred to the σ-phenyl group formed by oxidative addition of benzene.

The simplest explanation for the differing reactivity patterns of the niobium and tantalum complexes is that different steps are rate controlling. For niobium and iridium the observed rate is proportional to the product K_4k_5. For tantalum, on the other hand, the constancy of the reaction rates can be explained in two ways. Either step 1 is rate limiting and the intermediate **1** is indiscriminately reactive with the substituted benzenes or the product K_4k_5 is, by coincidence, constant for the competing benzenes. The latter assumption requires that the effect of the substituents on K_4 be opposite to that on k_5. Indeed, consistent with opposing effects on K_4k_5, the substituent effects for the niobium- and iridium-catalyzed exchanges are small by comparison with the large substituent effect for classical aromatic substitution reactions.

We suggest that the substituent effect on K_4 is similar to that observed for arene complexes of silver ion in which the relative stability of the complex is increased by electron-donating substituents. Thus the order of increasing stability observed is $F < H < OCH_3 < CH_3 < p\text{-}(CH_3)_2$.[23]

In order to account for the near constancy of K_4k_5, the substituent effect on k_5 must have an order similar

(23) C. D. M. Beverwijk, et al., Organometal. Chem. Rev., Sect. A, 5, 215 (1970), and references cited there.

to the order of substituent effects in nucleophilic substitution reactions or in the potassium amide-catalyzed H–D exchange reaction.[24] Step 5 may be regarded as a carbon to metal hydrogen migration, i.e., oxidative addition, in which the acidity of the various aryl hydrogens is important, similar to the oxidative addition of carboxylic acids to an iridium(I) complex.[25] In the latter reaction the rate is increased by an increase in the acidity of the acid.

The possibility that K_4 and k_5 may be counterbalancing but with opposite substituent effect to those we suggest is discounted by the data of Table III. The meta hydrogens exchange faster than ortho and at about the same rate as, or faster than, para, unlike the sequence expected if step 5 were electrophilic in character. The data are consistent, if steric effects are considered, with the order of kinetic acidities of the various positional hydrogens. For electron withdrawing substituents the order observed is ortho ≫ meta ≥ para; the reverse order holds for electron-donating substituents.[24]

A strong sensitivity to steric effects is indicated by the meager deuteration of p-xylene by all catalysts[26] and by the absence of ortho deuteration in benzotrifluoride. The steric effects are consistent with step 4 being complexation through interaction of metal orbitals with an isolated C=C double bond, rather like that observed for copper(I)[28] and silver(I)[29] complexes. Coordination of the metal to a double bond bearing a substituent in **2** should be unfavorable relative to coordination of a unsubstituted bond since the space between the two canted cyclopentadienyl rings in niobocene derivatives is quite small.[30]

Failure to observe deuteration of the much more acidic hydrogens of the methyl group in toluene and anisole is in accord with proposal that hydrogen is transferred only from the coordinated double bond in step 5.

One interesting facet of the exchange results with $IrH_5[P(CH_3)_3]_2$ is that the substituent effect is the opposite of that found by Bennett and Milner[31] in intramolecular aromatic substitution. In the oxidative addition of an aryl C–H bond of a triphenylphosphine ligand to the central metal atom of the complex

$$IrCl[P(C_6H_4X)_3]_3 \longrightarrow (XC_6H_4)_2P{-\!\!-}IrCl[P(C_6H_4X)_3]_2$$
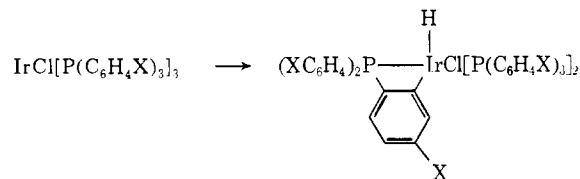
they found the rate sequence $F < H < OCH_3 < CH_3$. In the intramolecular system, it seems likely that the cumulative effect of the substituents transmitted to

(24) A. I. Shatenshtein, Tetrahedron, 18, 95 (1962).

(25) A. J. Deeming and B. L. Shaw, J. Chem. Soc. A, 1802 (1969).

(26) The uniqueness of p-xylene is apparent when rates of deuteration with the niobium catalyst are plotted vs. the averaged field and resonance parameters[27] of the benzene substituents. All the rates fall close to a straight line defined by σ = 0.53 + 0.5ℜ except that for p-xylene which is substantially slower than that predicted.

(27) C. G. Swain and E. C. Lupton, J. Amer. Chem. Soc., 90, 4328 (1968).

(28) R. W. Turner and E. L. Amma, ibid., 88, 1877 (1966).

(29) R. W. Turner and E. L. Amma, ibid., 88, 3243 (1966).

(30) F. W. Siegert and J. H. de Liefde Meijer, J. Organometal. Chem., 23, 177 (1970).

(31) M. A. Bennett and D. L. Milner, J. Amer. Chem. Soc., 91, 6983 (1969).

the iridium *via* the phosphorus atoms outweighs the small substituent effect observed in intermolecular substitution. Hence, electron-withdrawing substituents which reduce electron density on the metal atom make it less susceptible to oxidative addition.

The observed deuteration of the cyclopentadienyl groups in the catalysts suggests that the reactive intermediate 1 can oxidatively add a metallocene C–H bond, perhaps *via* a "double decker" sandwich intermediate. This type of oxidative addition is presumably involved

in the formation of niobocene and tantalocene dimers[8] with bridging cyclopentadienyl groups.

Acidities and Spectral Properties of α-Silyl and α-Germyl Carboxylic Acids and Their Carboxylates

P. M. Kuznesof,* F. B. T. Pessini, and R. E. Bruns

Contribution from the Instituto de Química, Universidade Estadual de Campinas, São Paulo, Brazil. Received May 8, 1972

Abstract: The order of acidity observed for R_3MCO_2H (R = CH_3 and/or C_6H_5, M = C, Si, Ge; R = H, M = C, Ge) is Si ≥ Ge > C. We find this order is best explained in terms of the larger sizes and polarizabilities of Si and Ge relative to C which would facilitate stabilization of the negative charge in the conjugate base. CNDO/2 results on the model systems H_3CCO_2H, H_3SiCO_2H, and their anions are presented (with and without inclusion of d orbitals for Si) which predict the correct order of acidity and indicate $p\pi \rightarrow d\pi$ interaction is of little importance, contrary to previous suggestions. The importance of Si–O (1,3) $d\pi$–$p\pi$ interactions is also considered. For a consistent thermodynamic explanation the relative electron affinities of $CH_3\cdot$ and $SiH_3\cdot$ (Si > C) appear to be the key factors. The electronic spectra of the title compounds indicate a symmetry (C_{2v}) forbidden n $\rightarrow$ π^* transition as the lowest energy transition. CNDO/2 predicts an allowed $\sigma \rightarrow \pi^*$ which cannot be ruled out at present as incorrect. $d\pi$–π^* interactions (M = Si) do appear important in determining electronic properties for which there are significant excited-state contributions. Differences in CO stretching frequencies are explained qualitatively in terms of relative Si and C inductive effects. However, comparison of the ir (ν(CO)) characteristics of the acids with those of the α-group-IV metal ketones and dihalocarbonyls (for which force constant and normal coordinate data are available) suggest kinetic effects (mass and geometric differences) and potential energy terms not involving the CO bond are more important than electronic effects for determining ν(CO).

The ionization constants of a series of α-silyl and α-germyl carboxylic acids, $(C_6H_5)_n(CH_3)_{3-n}MCO_2H$ (M = C, Si, Ge)[1a] and H_3GeCO_2H,[1b] have been measured. An intriguing observation is the order of acidity found to be $R_3SiCO_2H \geq R_3GeCO_2H > R_3CCO_2H$. This is contrary to that expected on the basis of inductive effects, Si and Ge being more electropositive than C, but rather has been ascribed[1] to the (p–d)π bonding capabilities[2] of Si and Ge which should favor delocalization of negative charge and therefore stabilization of $R_3MCO_2^-$. Ramsey[3] has noted, however, that the highest filled π molecular orbital of the carboxylate group is *nodal* at the carbon atom and suggests that 1,3 (p–d)π bonding between M and oxygen in the anion may be important.

In addition to the acidity problem, the unusual electronic spectra and infrared carbonyl stretching frequencies exhibited by the α-group-IV metal car-

boxylic acids and carboxylates are of interest. In the few determinations of the electronic spectra of these compounds, the low-energy n $\rightarrow$ π^* transition is observed[1b,4] to be red shifted with respect to the analogous carbon compound. The bathochromic shift of this transition is similar to the dramatic shift observed in the spectra of α-silyl and α-germyl ketones[5-7] with respect to their carbon analogs. Recent work[5,7a] suggests that this shift is due to the strong positive inductive effect of silicon or germanium raising the energy of the nonbonding MO while considerable Si(dπ)–CO(π*)

(1) (a) O. M. Steward, H. W. Irwin, R. A. Gartska, and J. O. Frohliger, *J. Chem. Soc. A*, 3119 (1968); (b) P. M. Kuznesof and W. L. Jolly, *Inorg. Chem.*, 7, 2574 (1968). The preparation and properties of the potassium salt are given but the acid itelf was never isolated.

(2) For a recent review of π bonding in group IVB, see C. J. Attridge, *Organometal. Chem. Rev., Sect. A*, 5, 323 (1970).

(3) B. G. Ramsey, "Spectroscopy in Inorganic Chemistry," Vol. II, C. N. R. Rao and J. R. Ferraro, Ed., Academic Press, New York, N. Y., 1971, p 249.

(4) (a) $(CH_3)_3GeCO_2H$ and $(CH_3)_3GeCO_2^-$: O. W. Steward and J. E. Dziedzic, *J. Organometal. Chem.*, 16, P5 (1969); $(CH_3)_3SiCO_2H$: O. W. Steward and J. E. Dziedzic, *Int. Symp. Organometal. Chem.*, *4th* (1969). (b) It is appropriate also to include the ester $(CH_3)_3$-$SiCO_2CH_3$: G. J. D. Peddle and R. W. Walsingham, *J. Amer. Chem. Soc.*, 91, 2154 (1969). (c) The n $\rightarrow$ π^* transition for phenyl-substituted α-silyl and α-germyl carboxylic acids is not observed due to masking by the phenyl $\pi \rightarrow \pi^*$ transition in the region 247–271 nm (ref 4a).

(5) F. Agolini, S. Klemenko, I. G. Csizmadia, and K. Yates, *Spectrochim. Acta, Part A*, 24, 169 (1968).

(6) A. G. Brook, *J. Amer. Chem. Soc.*, 79, 4373 (1957). The current interest in α-silyl and α-germyl ketones (ref 5, 7) has derived from Brook's striking observation that triphenylsilyl phenyl ketone is yellow.

(7) (a) H. Bock, H. Alt, and H. Seidl, *ibid.*, 91, 355 (1969); (b) B. G. Ramsey, "Electronic Transitions in Organometalloids," Academic Press, New York, N. Y., 1969, p 94 ff; (c) reference 3, p 238. (d) These references serve as excellent sources into the literature regarding electronic properties of organometalloids in general.