helpful and stimulating discussions. Sincere gratitude is extended to Drs. Interrante and Stucky for preprints of their work.

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Hydrogen–Deuterium Exchange between η^5-$C_5H_5Rh(C_2H_4)_2$ and Aromatic Hydrocarbons

Sir:

We wish to report a novel isotopic hydrogen exchange between benzene-d_6 and η^5-$C_5H_5Rh(C_2H_4)_2$. The exchange, which occurs at 130°, introduces deuterium into both the cyclopentadienyl and ethylene ligands. With one exception, previous examples of homogeneous exchange with aromatic hydrocarbons require the presence of hydride,[1] proton,[2] or elemental hydrogen.[3] In the one exception, organoaluminum dihalides catalyze hydrogen exchange between two aromatic hydrocarbons.[4]

The exchange is observed after heating at 130° a sealed, evacuated tube typically containing 0.20 mmol of η^5-$C_5H_5Rh(C_2H_4)_2$ and 0.4 ml of benzene-d_6. Prior to heating, the proton nmr spectrum consists of a small resonance for isotopically impure benzene, a sharp doublet at 4.90 ppm (from external TMS) for η^5-C_5H_5, and complex doublets centered at 2.74 and 1.22 ppm for coordinated C_2H_4. No change is noted in the spectrum after the tube is heated for 1 hr at 100°, but, after 1 hr at 130°, the area of the aromatic signal is substantially larger. The area of the ligand signals are correspondingly smaller. Typical peak areas are as shown in Table I.

Table I

	Benzene	Cyclo-pentadienyl	Ethylene
No heat	9	71	103
130°, 1 hr	119[a]	26	39

[a] The areas after heating are normalized using hexamethyldisiloxane, which does not exchange, as internal standard.

The changes in the nmr spectrum are attributed to isotopic hydrogen exchange between benzene-d_6 and η^5-$C_5H_5Rh(C_2H_4)_2$. The rhodium complex can be recovered by sublimation. Analysis by mass spectroscopy shows no nondeuterated complex. Most of the complex from a 1-hr run contains from 8 to 11 deuterium atoms per molecule, see Table II. Mass spectroscopic analysis of the recovered benzene shows that the major exchanged species is C_6D_5H. As seen in Table II, the percentages found for the deuterated benzene species agree very well with the percentages calculated from the terms of the expanded polynomial

(1) E. K. Barefield, G. W. Parshall, and F. N. Tebbe, *J. Amer. Chem. Soc.*, **92**, 5234 (1970).
(2) J. L. Garnett, *Catal. Rev.*, **5**, 229 (1971).
(3) U. Klabunde and G. W. Parshall, *J. Amer. Chem. Soc.*, **94**, 9081 (1972).
(4) J. L. Garnett, M. A. Long, and R. F. W. Vining, *J. Amer. Chem. Soc.*, **94**, 5913 (1972).

Table II. Deuterium Distribution from Exchange between C_6D_6 and η^5-$C_5H_5Rh(C_2H_4)_2$

	Benzene				η^5-$C_5H_5Rh(C_2H_4)_2$	
	A[a]		B		A	B
	Calcd[b]	Found	Calcd	Found	Found	
d_0	0	0	0	0	0.6	0
d_1	0	0.3	0	0	3.4	0
d_2	0	0	0.03	0	9.4	0
d_3	0.08	1.2	0.54	2.7	16.7	0.2
d_4	1.6	0.3	5.5	3.0	19.9	0.6
d_5	17.8	15.2	29.2	26.6	17.5	1.9
d_6	80.7	82.9	64.7	67.2	11.2	4.9
d_7					5.6	10.1
d_8					2.1	17.0
d_9					3.4	22.2
d_{10}					3.8	19.7
d_{11}					3.3	13.8
d_{12}					1.8	5.6
d_{13}					0.9	1.7

[a] A, 0.200 mmol of η^5-$C_5H_5Rh(C_2H_4)_2$, 0.4 ml of C_6D_6, 130° for 0.5 hr; B, 0.200 mmol of η^5-$C_5H_5Rh(C_2H_4)_2$, 0.4 ml of C_6D_6, 130° for 1.0 hr. [b] Calculated from the expanded polynomial $(a + b)^6$.

$(a + b)^n$, where $a = f_H = 1 - f_D$, $b = f_D$ = fraction of deuterium, and n = number of exchangeable deuterium atoms in the aromatic compound. $f_D = C_iM_i/100n$ where C_i = percentage of the i deuterated species with M deuterium atoms.[3] This calculation assumes that (1) only one hydrogen is incorporated per act of exchange and (2) all aromatic deuteriums exchange at the same rate.

The exchange is apparently homogeneous. Although the color of the solutions changes from yellow to purple-black and in some cases small amounts of solids are present, metallic rhodium is never visually detected. The extent of exchange is not affected by addition of solid from a previous experiment or elemental rhodium as sponge or supported on carbon.

Free ethylene, or ethylene-d_4, inhibits the exchange. Addition of 0.40 mmol of C_2D_4 (or C_2H_4) to a solution of 0.21 mmol of η^5-$C_5H_5Rh(C_2H_4)_2$ in 0.4 ml of C_6D_6 completely suppresses exchange even after heating for 2 hr at 130°. Free C_2D_4 exchanges with coordinated C_2H_4, however. Lesser amounts of ethylene (0.02–0.04 mmol) partially suppress exchange.

The inhibition of exchange by ethylene and the fact that exchange is observed only at temperatures at which ethylene dissociates at a reasonable rate from η^5-C_5H_5-$Rh(C_2H_4)_2$,[5] suggest that the initial step in the exchange mechanism is ethylene dissociation, Figure 1.

Ethylene dissociation may also be the first step in exchange of hydrogen between coordinated ethylene and cyclopentadienyl ligands. After 0.5 hr at 130°, hydrogen in η^5-$C_5H_5Rh(C_2D_4)_2$ had equilibrated between cyclopentadienyl and ethylene ligands. (The solvent was cyclohexane-d_{12}, which does not exchange with η^5-$C_5H_5Rh(C_2H_4)_2$.) Exchange can be stopped short of equilibrium by heating for shorter times, *e.g.*, 8–10 min. No exchange is observed at 100°. This exchange is also inhibited by free ethylene.

Arenes other than benzene exchange with η^5-C_5H_5Rh-$(C_2H_4)_2$. In order of decreasing reactivity they are $C_6D_6 \geq C_5D_5N > C_6D_5NO_2 \geq C_6D_5CD_3$. Pyridine exchanges primarily with coordinated ethylene. Only the aromatic deuterium atoms of toluene exchange.

(5) R. D. Cramer, *J. Amer. Chem. Soc.*, **94**, 5681 (1972).
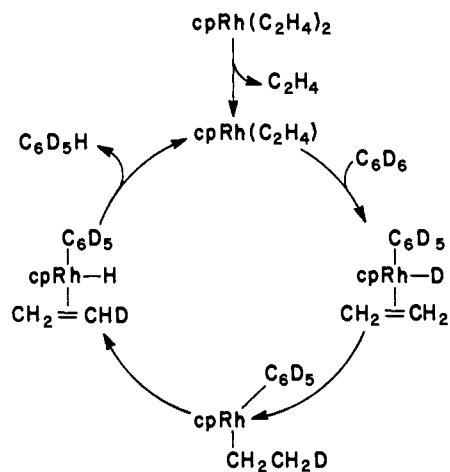
Figure 1. Proposed mechanism for exchange between benzene-d_6 and coordinated ethylene in η^5-$C_5H_5Rh(C_2H_4)_2$.

Other rhodium–olefin complexes which were observed to exchange hydrogen with benzene after 1 hr at 130° include acacRh(C_2H_4)₂, η^5-$C_5(CH_3)_5Rh(C_2H_4)_2$, and η^5-$C_5H_5Rh(C_2H_3CN)_2$. The amount of exchange with η^5-$C_5(CH_3)_5Rh(C_2H_4)_2$ is comparable to the amount with η^5-$C_5H_5Rh(C_2H_4)_2$, based on exchangeable hydrogen. The methyl hydrogens do not exchange. Much less exchange is observed with acacRh(C_2H_4)₂ and η^5-$C_5H_5Rh(C_2H_3CN)_2$. Only a trace of exchange was observed with η^5-$C_5H_4CNRh(C_2H_4)_2$ and η^5-C_5H_5Rh-(1,5-COD) under the same conditions.

A mechanism by which exchange between arenes and coordinated ethylene on η^5-$C_5H_5Rh(C_2H_4)_2$ could occur is suggested in Figure 1. While this mechanism has not been substantiated, there is precedence for the individual steps. Ethylene dissociation from η^5-C_5H_5Rh-(C_2H_4)₂ provides entry into the exchange cycle.[5] Oxidative addition of benzene then generates a phenylrhodium deuteride.[6] Insertion of ethylene into the Rh–D bond gives an ethylrhodium species. Collapse of the ethylrhodium species followed by reductive elimination of benzene results in one exchange.[7]

An analogous scheme for transferring D from coordinated ethylene to cyclopentadiene can be envisioned. In this scheme a coordinated cyclopentadienyl reacts as does benzene in Figure 1 via oxidative addition to rhodium to give

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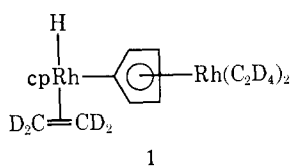
Evidence for 1 was obtained by heating for 10–20 min at 130° η^5-$C_5H_5Rh(C_2D_4)_2$ and η^5-$C_5H_5RhC_8H_{12}$ in cyclohexane-d_{12}. Deuterium appeared on the cyclopentadienyl ligands of both complexes. It is not likely that the 1,5-cyclooctadiene ligand is involved in this exchange because η^5-$C_5H_5RhC_8H_{12}$ showed very little exchange with benzene-d_6, even after 2 hr at 130°. In a similar experiment using η^5-$C_5H_5Rh(C_2D_4)_2$ and ferrocene, deuterium again appeared on the cyclopentadienyl

(6) M. L. H. Green and P. J. Knowles, J. Chem. Soc. A, 1508 (1971).
(7) R. D. Cramer, Accounts Chem. Res., 1, 186 (1968).

ligands of both complexes. Ferrocene does not, however, exchange hydrogen with benzene under similar conditions.

According to the mechanism of Figure 1, the extent of exchange might be affected by the ease of both ethylene dissociation and benzene addition. The amounts of exchange observed with different rhodium complexes suggest this is true. For example, ethylene dissociates from acacRh(C_2H_4)₂ and η^5-$C_5H_5Rh(C_2H_4)_2$ at comparable rates,[5] yet acacRh(C_2H_4)₂ gives much less exchange with benzene. A study of the kinetics of exchange is in progress.

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Intervention of the 1,4-Diradical 1-Oxatetramethylene in the Thermodecarboxylation of γ-Peroxylactones[1]

Sir:

While tetramethylene diradicals 1, a controversial class of reaction intermediates of current theoretical

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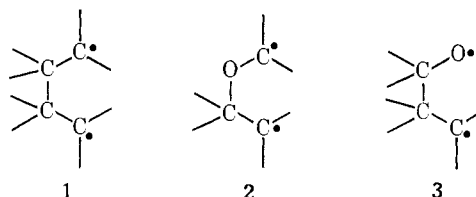
and mechanistic dispute,[2] are implicated in such diverse reactions as cyclobutane pyrolysis,[3] Norrish type II photolysis of alkanones,[4] or thermocycloaddition of olefins,[5] the only well-documented oxygen hetero-analogs are the 2-oxatetramethylenes 2, generated in the Paterno–Büchi[6] photocycloaddition of ketones and olefins. Oxetanes are potential precursors to 1-oxaheteroanalogs 3 of tetramethylenes; yet competitive C–C fission leading to 2 can render mechanistic conclusions ambiguous.[7] Similarly, the oxadi-π-methane rearrangement may involve such 1,4-diradical inter-

(1) Paper XXXIV in the cyclic peroxide series. For Paper XXXIII cf. W. Adam, G. A. Simpson, and F. Yany, J. Phys. Chem., in press.

(2) (a) G. Jones, II, J. Chem. Educ., 51, 175 (1974); (b) R. G. Bergman in "Free Radicals," Vol. 1, J. K. Kochi, Ed., Wiley-Interscience, New York, N. Y., 1973, Chapter 5; (c) L. M. Stephenson, T. A. Gibson, and J. I. Brauman, J. Amer. Chem. Soc., 95, 2489 (1973); (d) L. Salem, Pure Appl. Chem., 33, 317 (1973); L. Salem and C. Rowland, Angew. Chem., 84, 86 (1972).

(3) (a) G. Jones II, and M. F. Fatina, J. Chem. Soc., Chem. Commun., 375 (1973); (b) P. C. Beadle, D. M. Golden, K. D. King, and S. W. Benson, J. Amer. Chem. Soc., 94, 2943 (1972).

(4) (a) H. E. O'Neal, R. G. Miller, and E. Gunderson, J. Amer. Chem. Soc., 96, 3351 (1974); (b) P. J. Wagner, A. E. Kemppainen, and E. Gunderson, ibid., 95, 5604 (1973); P. J. Wagner, Accounts Chem. Res., 4, 168 (1971).

(5) P. D. Bartlett and G. M. Cohen, J. Amer. Chem. Soc., 95, 7923 (1973).

(6) (a) N. C. Yang, M. Kimura, and W. Eisenhardt, J. Amer. Chem. Soc., 95, 5068 (1973); (b) T. R. Darling, N. J. Turro, R. H. Hirsch, and F. D. Lewis, ibid., 96, 434 (1974); N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemczyk, and N. Schore, Accounts Chem. Res., 5, 92 (1972).

(7) G. Jones II, S. B. Schwartz, and M. T. Marton, J. Chem. Soc., Chem. Commun., 374 (1973).