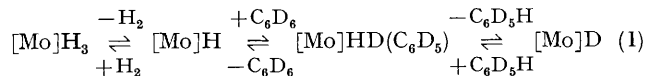


Photoinduced Hydrogen–Deuterium Exchange between Aromatic and Aliphatic Hydrocarbon Systems Catalysed by
[Mo(η -C₅H₅)(Me₂PCH₂CH₂PMe₂)H₃]

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Summary Photolysis of deuteriobenzene solutions of hydrocarbons such as *p*-xylene and ethylbenzene, dimethyl ether, or *p*-methylanisole, in the presence of [Mo(η -C₅H₅)(Me₂PCH₂CH₂PMe₂)H₃], causes the statistical exchange of all or many of the hydrogens with deuterium; the hydrogens of co-ordinated hydrocarbon ligands of ferrocene and bis- η -toluenetungsten and other organometallic compounds are similarly exchanged.

photolysis causes elimination of dihydrogen giving a highly reactive 16-electron intermediate {Mo(η -C₅H₅)(dmpe)H} which can insert reversibly into a C–D bond of C₆D₆ giving {Mo(η -C₅H₅)(dmpe)D}; see equation (1).



where [Mo] = Mo(η -C₅H₅)(dmpe)

PARSHALL and KLABUNDE¹ showed that the compounds {M(η -C₅H₅)₂H₃} (**1**), where M = Ta or Nb, could catalyse a thermal H–D exchange between deuteriobenzene and dihydrogen. The compounds {Mo(η -C₅H₅)(P–P)H₃}, where P–P = Ph₂PCH₂CH₂PPh₂ (**2**) or Me₂PCH₂CH₂PMe₂ (dmpe) (**3**), are 18-electron analogues of (**1**)^{2,3} and we were interested to determine whether they showed similar reactivity towards carbon–hydrogen bonds. The compounds (**2**) and (**3**) in deuteriobenzene solution showed no evidence for thermally induced reaction with the aromatic C–D bonds. However, photolysis of a solution of (**3**) in C₆D₆ resulted in the exchange of all hydrogens of (**3**) giving perdeuteriated (**3**).

Photolysis of (**3**) in C₆D₆ followed by determination of the mass spectrum of the less volatile products showed bands assignable to the partially deuteriated compound {Mo(η -C₅H₅)(dmpe)PhH₂}, as well as to deuteriated (**3**). Analysis of the mass spectrum showed that there was a small percentage of perdeuteriated (**3**) and monitoring of the hydrogen-1 n.m.r. spectrum of the reaction mixture showed that the hydrogens of the η -C₅H₅, MoH₃, and Me₂P groups were exchanged much more rapidly (2–3 h) compared to the CH₂ hydrogens (1–2 days).

By analogy with the photochemistry of the compounds {M(η -C₅H₅)₂H₂}, M = Mo or W,^{4,5} we presume that the

Further equilibria, both inter- and intra-molecular, can account for the exchange of the other hydrogens of compound (**3**); for example, intermolecular exchange could occur *via* the equilibria shown in equation (2), where R is any radical formed by removal of hydrogen from an exchangeable C–H bond.



The methyl hydrogens of the dmpe ligand may be presumed to exchange *via* intramolecular oxidative addition of the methyl C–H bonds to the metal centre. We do not know whether the process illustrated in equations (1) and (2) are thermally or photochemically induced.

We have explored the photochemistry of (**3**) with mixed carbon–hydrogen systems in the following manner. Solutions of a hydrocarbon or other organic compounds (20–80 mg) in deuteriobenzene were treated with a small catalytic quantity (10 mg) of (**3**) and the solution was irradiated using a 100 W medium-pressure mercury lamp. The reactions were monitored by hydrogen-1 n.m.r. spectroscopy which clearly indicated whether H–D exchange was occurring. Subsequently the mass spectra of the volatile products were determined for confirmation of the degree of H–D exchange.

TABLE. Examples of deuterium–hydrogen exchange.

Compound	Deuteriated product ^a	Approximate rates ^b
C ₆ H ₅ CH ₃	C ₆ D ₅ CD ₃	CH ₃ , 4 days ^c
1,4-C ₆ H ₄ (CH ₃) ₂	1,4-C ₆ D ₄ (CD ₃) ₂	2 days; ^d 4 days ^e
1,3,5-C ₆ H ₃ (CH ₃) ₃	1,3,5-C ₆ H ₃ (CD ₃) ₃	<i>ca.</i> 7 days
1-CH ₃ -4-CH ₃ OC ₆ H ₄	1-CD ₃ -4-CD ₃ OC ₆ D ₄	6 h; ^d OCH ₃ , 6 h; CH ₃ , 10 days
(CH ₃) ₂ O	(CD ₃) ₂ O	7 days ^e
C ₆ H ₅ CH ₂ CH ₃	C ₆ D ₅ CH ₂ CH ₃	<i>ca.</i> 6 h
CH ₃ OCH ₂ CH ₂ OCH ₃	CD ₃ OCH ₂ CH ₂ OCD ₃	14 days
CH ₃ CO ₂ CH ₂ CH ₃	CD ₃ CO ₂ CD ₂ CD ₃	CH ₃ CO, 1 day; CH ₂ , 15 days; CCH ₃ , 5 days
[Fe(η -C ₅ H ₅) ₂]	[Fe(η -C ₅ D ₅) ₂]	12 h
[W(η -C ₆ H ₅ CH ₃) ₂]	[W(η -C ₆ D ₅ CD ₃) ₂]	2 h; ^d 3 days ^e
[Mo(η -C ₆ H ₅) ₂]	[Mo(η -C ₆ D ₅) ₂]	12 h
[W(η -C ₆ H ₅ CH ₃)(η -C ₅ H ₅)(O ₂ CCH ₃)]	[W(η -C ₆ D ₅ CD ₃)(η -C ₅ H ₅)(O ₂ CCD ₃)]	6 h; ^d CCH ₃ , 4 days; O ₂ CCH ₃ , 20 days
[W(η -C ₅ H ₅) ₂ (CH ₃) ₂]	[W(η -C ₅ D ₅) ₂ (CH ₃) ₂]	3 h
[Mo(η -C ₅ H ₅) ₂ H ₂]	[Mo(η -C ₅ D ₅) ₂ D ₂]	MoH ₂ , 8 h; η -C ₅ H ₅ , 2 days

^a Solutions contained *ca.* 20–80 mg of the reactant in 1 cm³ of C₆D₆ and *ca.* 10 mg of (**3**). Where deuterium atoms are shown this indicates that H/D exchange occurred. The rate of exchange varied markedly, as indicated in the text for the hydrogens of (**3**). Hydrogens which are rapidly exchanged undergo statistical equilibration with the deuteriobenzene. ^b This gives the time taken to achieve statistical exchange of the exchangeable hydrogens; the data are derived from the hydrogen-1 n.m.r. data. ^c The exchanged aromatic hydrogens were obscured by the solvent. ^d Aromatic hydrogens. ^e Aliphatic hydrogens.

The Table shows the results of these experiments for compounds which have a variety of different C-H bonds. Aromatic C-H bonds are normally readily exchanged and failure to exchange the aromatic C-H hydrogens of mesitylene presumably reflects steric restriction by the methyl groups towards the approach of the bulky $\{\text{Mo}(\eta\text{-C}_6\text{H}_5)_2(\text{dmpe})\text{D}\}$ group.

In a similar manner we were able to catalyse the exchange of the ring-hydrogens of the sandwich compounds $\{\text{Fe}(\eta\text{-C}_6\text{H}_5)_2\}$, $\{\text{W}(\eta\text{-C}_6\text{H}_5)_2\text{Me}_2\}$, and other organometallic compounds, as indicated in the Table.

The compound (3) could be a useful reagent for the preparation of small quantities of deuteriated compounds.

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