

Activation of C–H Bonds in Saturated Hydrocarbons. H–D Exchange between Methane and Benzene catalysed by a Soluble Iridium Polyhydride System

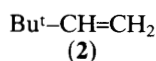
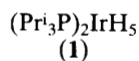
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The soluble iridium pentahydride (Pr_3P)₂IrH₅ (activated by $\text{Bu}^t\text{--CH=CH}_2$) catalyses H–D exchange between C_6D_6 and CH_4 under mild conditions.

Pioneering work by Shilov, by Garnett, and by Webster in the late 1960's and early 1970's led to the discovery that a number of soluble transition metal chlorides (notably Pt^{II} and Ir^{III}) in acidic media are efficient catalysts for H–D exchange between D_2O and saturated hydrocarbons (including methane).¹ More recently, a variety of other soluble transition metal systems have been found to activate C–H bonds in alkanes *via* non-radical pathways.^{2,3} Insofar as they have been applied to methane, however, all but one of these systems have led to stoichiometric, rather than catalytic, reactions. The exception is the photochemical system recently discovered by Jones, in which catalytic H–D exchange between deuteriobenzene and methane occurs upon irradiation in the presence of $\text{cp}(\text{PPh}_3)_2\text{ReH}_2$ ($\text{cp} = \eta^5\text{-C}_5\text{H}_5$).⁴

Here we report that methane is catalytically deuterated thermally under mild conditions (using C_6D_6 as the deuterium source) in the presence of the soluble iridium pentahydride (1), activated by neohexene (2).



The pentahydride (1) catalyses (stereoselective) H–D exchange between C_6D_6 and the vinylic hydrogen *trans* to the *t*-butyl group in neohexene (2);⁵ it also catalyses the conversion of alkanes into alkenes, using an olefin, *e.g.* (2), as a (thermodynamically necessary) hydrogen acceptor.⁶ In the latter reaction, the relative kinetic reactivities of various types of alkane C–H bonds were found to be approximately: *sec*-alkyl-H (CH_2 in cyclohexane), 1; *iso*-alkyl-H (CH_3 in methylcyclohexane), 8; and *n*-alkyl-H (CH_3 in *n*-hexane), >60.⁷ This suggested that methane would be an extremely reactive substrate. Methane cannot, of course, undergo the same reaction as its higher homologues (dehydrogenation to olefin), but deuteration (as with neohexene) remained a possibility.

In the event, we have found that when an initially colourless

solution of 0.00239 mmol of (1) and 0.0048 mmol of (2) in 0.4 ml of C_6D_6 was sealed in an n.m.r. tube with 0.20 mmol of methane and then heated (80 °C), CH_3D was indeed formed. After seven days, the methane in the tube was *ca.* 15% monodeuterated, corresponding to about 13 catalytic turnovers; traces (too small to measure) of CH_2D_2 were also formed.[†] After a further 46 days at 80 °C, the methane contained *ca.* 30% CH_3D , *ca.* 10% CH_2D_2 , and traces of CHD_3 , corresponding to at least 40 catalytic turnovers. The final colour of the solution was orange.

Owing to overlap of peaks,[†] the ratios of the various deuterated methanes could not be determined very accurately, but it is nevertheless clear that multiple exchange *via* carbene intermediates, as observed with transition metal halides in acidic media,⁸ is not occurring to any significant extent in our system.

The relatively slow deuteration of methane was preceded by conversion of all the neohexene (2) into neohexane, and by H–D exchange between the solvent and both the hydride ligands and all the hydrogens on the phosphine ligands. This exchange also occurs (more slowly) in the absence of neohexene,⁹ but under these conditions no deuteration of methane could be detected.

Similar reactions carried out using non-deuterated benzene and an excess of neohexene (5–20 equiv.) afforded some ethane (identified by g.c.) and, in some cases, small and variable amounts of toluene (identified by g.c.–m.s.) and biphenyl (identified by g.c.). Propane was also formed.¹⁰

The conditions required for catalytic H–D exchange between methane and C_6D_6 are more vigorous than those which lead to the catalytic deuteration of the *trans* vinylic

[†] The H–D exchange was followed by 400 MHz ^1H n.m.r. spectroscopy. Chemical shifts were determined using the residual protons of the deuteriobenzene solvent ($\text{C}_6\text{D}_5\text{H}$, δ 7.2400 at 20 °C) as the internal reference: 0.2379 (s, CH_4), 0.2233 (t, J_{HD} 1.95 Hz, CH_3D), 0.2098 (quintet, J_{HD} 1.95 Hz, CH_2D_2).

position in neohexene; thus, exchange with methane was extremely slow at 36 °C (only traces of CH₃D were formed after 12 days), whereas exchange between benzene and neohexene is quite fast even at room temperature (ca. 200 catalytic turnovers/h).⁵ Moreover, when the solution contained an excess of neohexene (10 equiv., instead of 2 as above), it rapidly turned deep red when heated to 80 °C, but no deuteriomethane could be detected after 5 days; under these conditions, the higher alkanes are catalytically converted into alkenes.^{6,7}

These results suggest that the catalytic intermediates involved in the deuteration of methane are different from the ones involved in the activation of the aromatic or vinylic C–H bonds of benzene and neohexene, and in the activation of alkanes leading to alkenes. It seems fairly certain that all these reactions involve, as their key step, the insertion of a co-ordinatively unsaturated organometallic intermediate into a C–H bond of the substrate.^{3,6} We imagine that the neohexene serves to strip hydride ligands off the catalyst precursor (1),³ and that the first-formed 16e intermediate L₂IrH₃ (L = Pr₃P) is sufficiently reactive to insert into the C–H bonds of benzene^{9a} and neohexene, which can pre-coordinate to the metal through their π -electrons.¹¹ Alkanes, however, cannot pre-coordinate in this way and may require more reactive (14e) intermediates such as L₂IrH or LL'Ir (L' = the cyclometallated ligand Pr₂P–CHMe–CH₂). Only the deuteriated analogue of the first of these, the formation of which would require just two equivalents of neohexene per pentahydride (1), can lead to H–D exchange in methane, whereas both may be capable of catalysing the conversion of alkanes into alkenes.^{6,7} The ethane, toluene, and biphenyl which we observe may be formed by reductive elimination of R–R' from an intermediate such as LL'IrRR' (R and R' = Me or Ph); they may also arise from a route involving radicals.

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