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Homogeneous Catalysis with *trans*-Chlorocarbonylbis(triphenylphosphine)iridium(I)

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A tetragonal d^8 complex of iridium, *trans*-[IrCl(CO)(Ph$_3$P)$_2$], catalyzes hydrogen–deuterium exchange, and hydrogenation and isomerization of olefins homogeneously in solution under mild conditions. The hydrogen–deuterium exchange appears to proceed via hydrido-deuterio complexes in which the two isotopes are simultaneously bonded to the same metal atom. The isomerization of 1-butene requires the presence of molecular hydrogen as co-catalyst.

The hydrogenation of ethylene was studied by tracer techniques in order to gain information on the mechanism of this catalytic conversion. The reaction between C_2H_4 and D_2 yields d_0, d_1, d_2, d_3, and d_4 ethanes, d_1 and d_2 ethylenes, as well as HD and H_2. The observed extensive H–D exchange suggests that both reactants are activated reversibly on the same metal atom at which the hydrogen transfer to the double bond occurs.

A four-coordinated iridium complex, *trans*-[IrCl(CO)(Ph$_3$P)$_2$] (Ph$_3$P = triphenylphosphine) (*1*), has, in recent years, emerged as a model compound in the study of homogeneous activation of several small molecules which are common reactants in many catalytic processes. The metal complex reacts reversibly at ambient conditions with molecular hydrogen (*2*, *3*), oxygen (*4*), carbon monoxide (*5*), sulfur dioxide (*6*), and a variety of olefins and related species (*3*, *7*, *8*, *9*). Although these reactions are reversible in solution, most of the metal complex–substrate adducts can be isolated as relatively stable crystalline compounds, and their structures have been determined spectroscopically and/or by X-ray diffraction methods (*10*, *11*). Because of this adduct stability, the iridium complex is not expected to exhibit a high catalytic activity; in fact, it is a rather inefficient catalyst for homogeneous hydrogenations (*3*) and oxidations (*9*). On the other hand, all these properties of the complex, including its stability in solution (*3*), render these systems suitable for studies of catalytic mechanisms and structure–reactivity correlations (*12*).

In this note we report the results of some experiments on hydrogen–deuterium exchange, hydrogenation of ethylene with deuterium, and isomerization of 1-butene,

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* Activation of Molecular Hydrogen and Related Molecules by Transition Metal Complexes. IV. For Part III, see ref. (*12*). One of us (L. V.) gratefully acknowledges the financial assistance of the Petroleum Research Fund, administered by the American Chemical Society.

all reactions catalyzed homogeneously by $[IrCl(CO)(Ph_3P)_2]$ in toluene. The primary purpose of this study was to investigate the identities of the intermediates and the products, and thereby to discern the possible mechanisms of these reactions.

EXPERIMENTAL

1. Hydrogen–deuterium exchange. Conventional vacuum line techniques were employed in this and in the following experiments.

A saturated solution of $[IrCl(CO)(Ph_3P)_2]$ in previously degassed toluene was prepared at 25°C ($\sim 10^{-2}\,M$ in Ir), and 30 ml of this yellow solution was transferred with a syringe to a 500-ml flask filled with argon; the latter was then removed by flash evaporation. [Alternatively, the degassed solution was prepared *in situ* in a special reactor to be described in a subsequent communication (*9*).] Hydrogen was added to ~380 torr, followed by deuterium up to atmospheric pressure (740 torr). The resulting reaction mixture (solution + gases) was kept at 25°C with occasional agitation for 4 days. A gas sample was then taken for mass spectrometric analysis. The results are given in Table 1.

Under the conditions cited above, some of the dihydride (dideuteride) which forms in solution is deposited as white crystals (*2, 3*). Since the hydride is less soluble than the starting material, the final concentration of iridium in solution in these experiments was $\sim 10^{-3}\,M$. At the conclusion of the experiments the precipitate was collected by filtration and a second portion of the crystalline product was obtained by treating the filtrate with hexane; the total yield was 87% based on the Ir used. The infrared spectra (Nujol and Halocarbon mulls) of the two samples were identical (see text).

2. Reaction of ethylene with deuterium. The reaction mixture was prepared in the same manner as described above. Ethylene was introduced to ~400 torr, followed by deuterium up to atmospheric pressure (740 torr) at 25°C. The closed flask was warmed to 60°C and the reaction was allowed to proceed for 7 days at this temperature. A gas sample was then taken and analyzed mass spectrometrically; the results are shown in Table 2. No precipitate was formed during this experiment and the color remained pale yellow. Under these conditions, a sizable fraction of the starting complex is present in equilibrium with its adducts (*3, 9*).

3. Isomerization of 1-butene. In this experiment, we proceeded as described in Section 2: 1-butene was introduced to 450 torr, followed by hydrogen up to 740 torr. After 7 days at 60°, a sample was taken for gas chromatographic analysis. The analytical data are given in Table 3.

The above experiment was repeated except that no hydrogen was used. Gas chromatographic analysis gave negative evidence for the presence of species other than 1-butene.

RESULTS AND DISCUSSION

Hydrogen–Deuterium Exchange

We have shown previously that the reversible reactions of the univalent d^8-complex, *trans*-$[IrCl(CO)(Ph_3P)_2]$, with molecular hydrogen and deuterium lead to six-coordinated dihydrido and dideuterio complexes (*2*), respectively,

$$[IrCl(CO)(Ph_3P)_2] + H_2 \rightleftarrows [H_2IrCl(CO)(Ph_3P)_2] \quad (1)$$

$$[IrCl(CO)(Ph_3P)_2] + D_2 \rightleftarrows [D_2IrCl(CO)(Ph_3P)_2] \quad (2)$$

It was thus of interest to examine the reaction of the Ir(I) compound with a mixture of H_2 and D_2. The result of this study indicates that the complex is a homogeneous catalyst for H_2–D_2 exchange at ambient conditions:

$$H_2 + D_2 \xrightleftharpoons{[IrCl(CO)(Ph_3P)_2]} 2\,HD \quad (3)$$

At 25°C, the reaction is quite slow, however, and equilibrium is not attained even after several days (Table 1).

Since the HD, which is produced by the catalytic exchange reaction (3) in the closed system, remains in contact with the starting complex in solution [present in the equilibrium mixtures of reactions (1) and (2)], the two are expected to react to produce $[(HD)IrCl(CO)(Ph_3P)_2]$—by analogy with the reactions (1) and (2). And, according to the data in Table 1, the hydrogen deuteride adduct should represent about one-third of the total isotopic hydrides present. The infrared spectrum of the final reaction mixture, however, gave no direct evidence for the presence of $[(HD)IrCl(CO)(Ph_3P)_2]$: All of the observed bands could be readily assigned to those found in the spectra of $[H_2IrCl(CO)(Ph_3P)_2]$ and $[D_2IrCl(CO)(Ph_3P)_2]$ (*13*). Furthermore, the band intensities appeared to suggest that the product consisted of a 1:1 mixture of the dihydride and dideuteride.

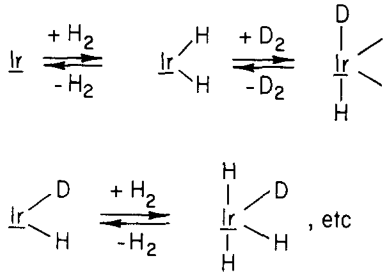
TABLE 1
RESULTS OF H_2–D_2 EXCHANGE[a]

	D_2	HD	H_2
Mole percent:	37	31	32

[a] Catalyzed by $[IrCl(CO)(Ph_3P)_2]$ in toluene (10^{-3} *M*); p_{tot}, 1 atm; 25°C; 4 days.

These results, apparently contradictory, can be readily interpreted by noting that there are two geometrical isomers for $[(HD)IrCl(CO)(Ph_3P)_2]$ (see ref. *13*), and by assuming that both are formed in a random manner to give an equimolar mixture of the two. The vibrational spectrum for each of these can be derived easily from the known spectra of the H_2 and D_2 adducts (*13*, see also *14*). The result, to be detailed elsewhere, will show that the infrared spectrum of a 1:1 mixture of the two isomeric HD adducts coincides with the spectrum of an equimolar mixture of the dihydride and dideuteride. NMR studies, currently under way, should provide further insight into this interesting problem.

Although there is presently no direct evidence available to support any of the possible mechanisms for the catalytic H_2–D_2 exchange reaction (3), we tentatively consider that it is likely to proceed via hydrido–deuterio complexes of an expanded coordination sphere of the central metal atom



(4)

$\underline{Ir} = [IrCl(CO)(Ph_3P)_2]$

The suggested scheme (4) takes into account the observations that unlike some other homogeneous catalysts, e.g., $[RhCl(Ph_3P)_3]$ (*15*), the parent compound does not measurably dissociate in solution (*1*, *3*), and that it can be recovered unchanged (i.e., with all four ligands intact) after any of the catalytic reactions reported in this paper (*3*). The formally high coordination number, eight, proposed for the expanded intermediates, is known to occur in many complexes of heavier metals (*16*). While there appear to be no confirmed precedences among the compounds of platinum metals, eight-coordination has been suggested for some isolated ethylenediamine complexes of osmium, including a d^4 complex (*17*).*

Hydrogenation of Ethylene and D_2–C_2H_4 Exchange

Of the by now numerous examples of homogeneous hydrogenations with transition metal compounds, only a few complexes have been reported to catalyze hydrogenation of ethylene (*3*, *12*, *18*, *19*) under mild conditions, and it was the ob-

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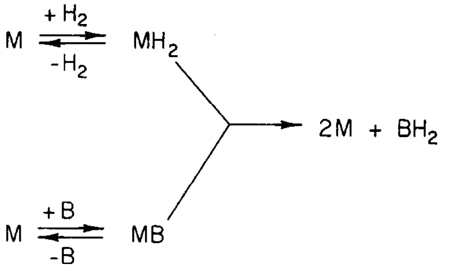
* A referee has criticized our proposed mechanisms [Eqs. (4) and (8)] in that they postulate intermediates with coordination numbers exceeding six. He points out that mechanisms involving concerted steps e.g., $\underline{Ir}H_2 + D_2 \rightleftharpoons IrHD + HD$, would eliminate the necessity for postulating such intermediates. We agree that this is a possibility, as is a mechanism which postulates that there is a partial dissociation (although not measurable) of the starting complex in solution. In this paper we are mainly concerned with that aspect of the reaction which yields the observed products [see Eq. (8)].

jective of this study to gain some further information on one of these systems (*3*).

Basically, one may distinguish between three elementary types of mechanisms for hydrogenation of ethylene by monomeric metal complexes in solution, (5), (6), and (7) (M = central metal atom of a complex; B = C_2H_4). It is considered here that the activation (dissociation) of hydrogen is a required step [if not, a further possibility arises under (5)].* In a crude sense all three types of mechanisms can be related to those considered possible in surface catalysis (*20, 21*): (5) is equivalent to gas-phase ethylene reacting with chemisorbed hydrogen; in (6), each reactant is activated on a different metal atom; in (7) both reactants are activated at the same metal atom. The latter type of mechanism is perhaps least likely to occur on a surface, and, as we shall see, the most probable one in solution.

$$M \underset{-H_2}{\overset{+H_2}{\rightleftharpoons}} MH_2 \xrightarrow{+B} M + BH_2 \quad (5)$$



(6)

$$M \underset{-H_2}{\overset{+H_2}{\rightleftharpoons}} MH_2 \underset{-B}{\overset{+B}{\rightleftharpoons}} BMH_2 \longrightarrow M + BH_2 \quad (7)$$

On hydrogenating d_0-ethylene with deuterium in *solution,* mechanisms (5) and (6) would produce d_2-ethane only, and no deuterated ethylenes should be observed. Mechanism (7), on the other hand, can, in principle, yield a wide isotopic distribution in both ethane and ethylene, and this is, approximately, what we observe with the iridium catalyst, [IrCl(CO)$(Ph_3P)_2$]. The results are summarized in Table 2.

TABLE 2

REACTION OF ETHYLENE WITH DEUTERIUM[a]

	Product, (mole %)	Isotopic distribution				
	Total	d_0	d_1	d_2	d_3	d_4
Ethane	40	18	18	57	6	1
Ethylene	50	53	33	14	—	—
Hydrogen	10	82	14	4	—	—

[a] Catalyzed by [IrCl(CO)$(Ph_3P)_2$] in toluene (10^{-2} *M*); 60°C; 7 days.

The data show that at least a substantial portion of the overall reaction must proceed via a mechanism in which both of the reactants become associated with the catalyst complex, and the transfer of hydrogen to ethylene occurs at the same metal atom. The analytical results do not, of course, exclude other concurrent mechanisms, since the presence of d_2-ethane and d_0-ethylene in high concentrations may (although not likely) be a reflection of other reaction paths [cf. reactions (5) and (6)]. (It should be noted that, unlike the situation on a metal surface, the deuterated ethanes result only from hydrogenation, i.e., there is no observable D_2–C_2H_6 exchange in this system.)

The mode of formation of some of the products is suggested in scheme (8). This model and its extensions [type (7) mechanism] readily explain the presence of each of the species given in Table 2. The key step of the exchange reactions is the addition and elimination of the hydride (deuteride) through the reversible ethylene–ethyl complexes. While the presently available data are insufficient for a detailed discussion of the isotopic distribution, a comment should be made about the relatively high percentage of H_2 produced by the reaction. This points to an isotope

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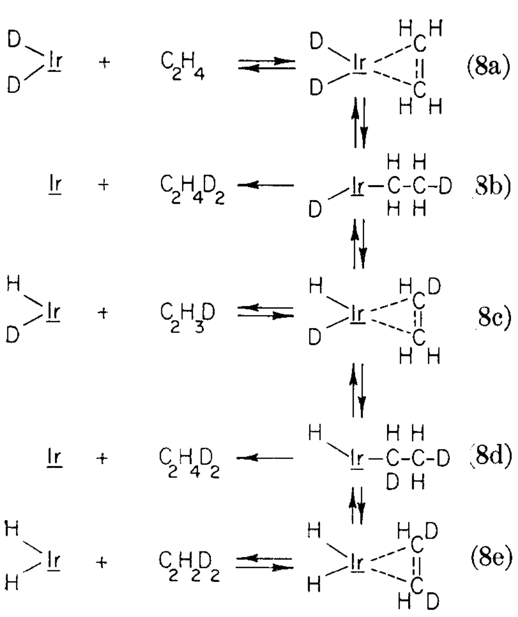
* The mode of hydrogen splitting (homolytic, heterolytic, etc.) is not specified; the dihydride formulation is given since it allows a simple expression of reaction types, and also because it is the observed one in the present system.

effect favoring retention of D over H in ethylene. A recent study on homogeneous isomerization of butenes by a rhodium catalyst gives quantitative evidence for such an effect (*22*). Thus, in the proposed scheme (8), step (d) → (e) should be favored over (d) → (c), and the HD, which results from IrHD via (8c), will yield H_2 on repeated recycling.



[*Ir* = [IrCl(CO)(Ph$_3$P)$_2$]. For simplicity, recycling of deuterated ethylenes, HD and H_2 [see Eqs. (1), (2)] are not shown.

Isomerization of 1-Butene

Homogeneous isomerization of olefins catalyzed by transition metal complexes in solution has found considerable attention in recent years. Two recent studies by Cramer (*22*, *23*) give a concise discussion of the subject and summarize the essentials of previous investigations. Our limited objective was to test the potential activity of [IrCl(CO)(Ph$_3$P)$_2$] as an isomerization catalyst. The results of an experiment in which hydrogen are present as a co-catalyst are given in Table 3.

The noteworthy observation on this system is that the catalysis proceeds only in the presence of hydrogen, i.e., no isomerization was found—in toluene solution—when hydrogen was absent. Thus, the mechanism of this reaction appears to be of the type requiring a metal hydride [which is, of course, present in our system (*2*, *3*)], and proceeding via an addition–elimination of this hydride to the olefin (*22*, *23*). As expected, this reaction (Table 3) produces also *n*-butane; the mole ratio of 2-butenes in the "final" mixture approximates to the expected equilibrium value (*24*).

TABLE 3
ISOMERIZATION OF 1-BUTENE[a]

	n-Butane	1-Butene	*cis*-2-Butene	*trans*-2-Butene
Product, mole %:	16	11	25	48

[a] Catalyzed by [IrCl(CO)(Ph$_3$P)$_2$] in the presence of H_2 in toluene solution (10^{-2} *M* in Ir); 60°; 7 days.

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