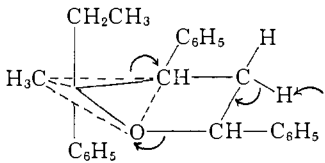
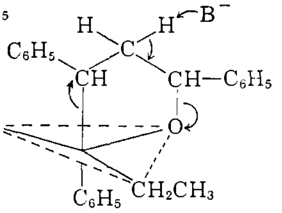
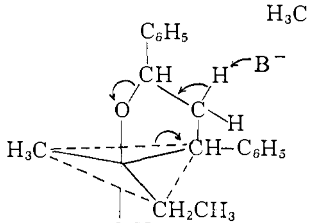


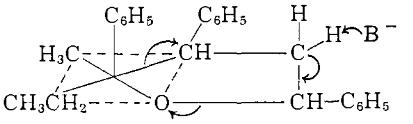
V



VI



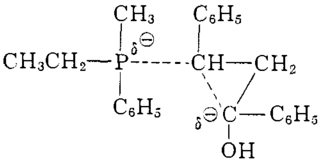
VII



VIII

small fraction of the product mixture, the amount of methylethylphenylphosphine oxide formed in conjunction with the cyclopropane derivative was also small. On the basis of Denney's mechanism,[2] it is conceivable that the phosphorus atom might be inverted, might retain the same configuration or undergo both stereochemical transformations by competitive paths. In fact, one or more of the many possible intermediates exemplified by V, VI, VII or VIII should be involved in step (2) of Denney's mechanism.

As shown in the accompanying communication,[14] methylethylphenylphosphine and benzylacetophenone arise from IV by way of the transition state IX. The fact that the phosphine is racemic is undoubtedly the result of the thermal racemization of the optically active phosphine (presumably formed with retention of configuration of the phosphorus atom) at the reaction temperature of 190–200°.[15,16]



IX

Acknowledgment.—This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is made to the donors of the fund.

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[14] W. E. McEwen and A. P. Wolf, *J. Am. Chem. Soc.*, **84**, 676 (1962).

[15] L. Horner, H. Winkler, A. Rapp, A. Mentrup, H. Hoffman and P. Beck, *Tetrahedron Letters*, 161 (1961).

[16] D. C. Velez, J. W. Johnson, C. A. VanderWerf and W. E. McEwen, unpublished observations.

ACTIVATION OF HYDROGEN BY A TRANSITION METAL COMPLEX AT NORMAL CONDITIONS LEADING TO A STABLE MOLECULAR DIHYDRIDE

Sir:

The discovery of a quadricovalent iridium(I) complex, $[\mathrm{IrCl(CO)(Ph_3P)_2}]$,[1] has afforded access to novel chemical reactions which are believed to offer new opportunities for understanding and study of certain vital processes of catalysis.

The compound responsible for this development shows a striking reactivity at normal conditions toward a large number of molecules (*e.g.*, hydrogen, oxygen, sulfur, organic halides, organic acids, hydrides of group VIIA, VIA elements, *etc.*). Yet, it displays properties which are remarkably well suited for a convenient investigation of its chemical behavior: its crystals are durable in air and stable thermally[1]; its relevant reactions represent additions to the quadricovalent species to yield octahedral complexes of Ir(III) (*cf.* equations 1, 5). These reactions are accompanied by characteristic shifts of the stretching frequency of the coördinated carbon monoxide (to higher ν) in the infrared spectrum. Indeed, the (*only one*) CO group in the molecule provides a singular means of detecting reactions, following their course, and inquiring into the nature of the products through the extent of $\Delta\nu_{\mathrm{CO}}$.

In this communication we report a reaction with molecular hydrogen, and some related observations which contribute to the understanding of metal–hydrogen interactions in this and other systems.

When hydrogen (one atm., 25°) is bubbled through a solution of $[\mathrm{IrCl(CO)(Ph_3P)_2}]$ in benzene, the color of the initially yellow solution (2×10^{-2} *M*) becomes lighter, followed by the appearance of yellow-white crystals (2 hr.). After allowing it to stand under hydrogen (same conditions) for one day a 55% yield of the crystalline product is obtained.[2] Infrared spectrum (Table I), elemental analysis, molecular weight data, non-electrolytic character (in nitrobenzene and acetone), diamagnetism, and reactions of the compound (see below) suggest that it is best formulated as a molecular dihydride of tervalent iridium, $[\mathrm{IrH_2Cl(CO)(Ph_3P)_2}]$. (*Anal.* Calcd. for $\mathrm{IrClP_2C_{37}H_{32}O}$: Ir, 24.6; Cl, 4.5; P, 7.9; C, 56.8; H, 4.12; O, 2.05; mol. wt., 782. Found: Ir, 24.8; Cl, 4.5; P, 7.9; C, 56.5; H, 4.15; O, 2.04; mol. wt. in benzene, 772.)

$$[\mathrm{Ir^{I}Cl(CO)(Ph_3P)_2}] + \mathrm{H_2} \xrightarrow[25°]{} [\mathrm{Ir^{III}H_2Cl(CO)(Ph_3P)_2}] \qquad (1)$$

Treatment of $[\mathrm{IrCl(CO)(Ph_3P)_2}]$ (in benzene) with deuterium[3] gives the corresponding dideuteride, $[\mathrm{IrD_2Cl(CO)(Ph_3P)_2}]$, showing an X-ray diffraction pattern identical with that of the dihydride (according to visual examination). Two noteworthy isotope effects are evident from the infrared spectra (Table I): ν_{CO} in the dideuteride lies markedly higher than in the dihydride; the crystals of the dideuteride apparently exhibit only one ν_{IrD} while

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[1] L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, **83**, 2784 (1961).

[2] In $\mathrm{CHCl_3}$ the rate of the reaction with $\mathrm{H_2}$ is faster, but the purity of the product has been found to suffer. A partial interaction has been observed also between the *crystals* of $[\mathrm{IrCl(CO)(Ph_3P)_2}]$ and hydrogen (1 atm., 25°).

[3] Courtesy of Dr. W. Keith Hall.

TABLE I

NATURE OF THE METAL-HYDROGEN BOND. ORIGIN OF HYDROGEN AND INFRARED SPECTRUM (CM.$^{-1}$)[a]

Formed by reacn. with	Compound (P = Ph$_3$P)	$\nu_{\mathrm{M-H,D}}$[b] Solid[c]	$\nu_{\mathrm{M-H,D}}$[b] Soln.[d]	ν_{CO}[e] Solid[c]	ν_{CO}[e] Soln.[d]
H_2	$[\mathrm{IrH_2Cl(CO)P_2}]$	2190, 2100	2220,[f] 2095	1970	1983[g]
H_2	Pt-H[h]	2110, 2060	...	...	...
D_2	$[\mathrm{IrD_2Cl(CO)P_2}]$	1571	1572[i]	1995	2030
D_2	Pt-D[h]	1515, 1480	...	...	...
HCl	$[\mathrm{IrHCl_2(CO)P_2}]$[j]	2245	...	2030	2045
C_2H_5OH	$[\mathrm{IrHCl_2P_3}]$[k]	2200	2185	...	...
$(CH_2OH)_2$	$[\mathrm{IrH_2ClP_3}]$[k]	2215, 2110	2180	...	...
$LiAlH_4$	$[\mathrm{IrH_3P_3}]$[l]	...	2110, 1745	...	...

[a] ±5 cm.$^{-1}$; NaCl optics. [b] Strong to medium-strong. [c] Halocarbon or Nujol mull. [d] In C_6H_6 or $CHCl_3$. [e] Very strong. [f] Weak. [g] Broad. [h] Chemisorbed hydrogen and deuterium on γ-alumina-supported platinum metal, data from ref. 4. [i] Medium-weak, broad. [j] Ref. 1. [k] Ref. 5. [l] Ref. 6.

the dihydride shows two ν_{IrH} values. Structures of these compounds and the course of their formation are being studied.

The dihydride is stable in air but sensitive to light (in air). In vacuum at 25° (pumping at 10^{-5} mm. for 16 hr.) the compound remains unchanged (m.p. (dec. in vac.), 315–321°).

The compound reacts with hydrogen chloride (in ether) to yield hydrogen[7] and a monohydrido complex.

$$[\mathrm{Ir^{III}H_2Cl(CO)(Ph_3P)_2}] + \mathrm{HCl} \xrightarrow[25^\circ]{} [\mathrm{Ir^{III}HCl_2(CO)(Ph_3P)_2}] + \mathrm{H_2} \tag{2}$$

This monohydride is the same compound which was first obtained by the reaction of $[\mathrm{IrCl(CO)(Ph_3P)_2}]$ with HCl.[1] We had suggested that the latter may be interpreted as involving formal oxidation of Ir(I) to Ir(III).[1] This view now becomes substantiated by this further evidence.

When a suspension of (the very insoluble) $[\mathrm{IrHCl_2(CO)(Ph_3P)_2}]$ is refluxed in a saturated solution of HCl in 1,2-dimethoxyethane for several days, conversion to a trichloro complex is observed, accompanied by evolution of hydrogen.[7]

$$[\mathrm{Ir^{III}HCl_2(CO)(Ph_3P)_2}] + \mathrm{HCl} \xrightarrow[84^\circ]{} [\mathrm{Ir^{III}Cl_3(CO)(Ph_3P)_2}] + \mathrm{H_2} \tag{3}$$

(*Anal.* Calcd. for $\mathrm{IrCl_3P_2C_{37}H_{30}O}$: Ir, 22.6; Cl, 12.5; P, 7.3; C, 52.2; H, 3.6; O, 1.9. Found: Ir, 23.1; Cl, 12.5; P, 7.3; C, 51.9; H, 3.7; O, 2.0; ν_{CO}, 2080 cm.$^{-1}$; diamagnetic; non-conducting in acetone and nitrobenzene.) This product is obtained also by these reactions

$$[\mathrm{Ir^{III}HCl_2(CO)(Ph_3P)_2}] + \mathrm{Cl_2} \xrightarrow[25^\circ]{} [\mathrm{Ir^{III}Cl_3(CO)(Ph_3P)_2}] + \mathrm{HCl} \tag{4}$$

$$[\mathrm{Ir^{I}Cl(CO)(Ph_3P)_2}] + \mathrm{Cl_2} \xrightarrow[25^\circ]{} [\mathrm{Ir^{III}Cl_3(CO)(Ph_3P)_2}] \tag{5}$$

The interrelations of the reactions described above become evident in this summary.

$$\begin{tikzcd}
 & {[\mathrm{Ir^{III}Cl_3(CO)(Ph_3P)_2}]} & \\
{[\mathrm{Ir^{I}Cl(CO)(Ph_3P)_2}]} \arrow[ur, "\mathrm{Cl_2}"] \arrow[r, "\mathrm{HCl}"] \arrow[dr, "\mathrm{H_2}"'] & {[\mathrm{Ir^{III}HCl_2(CO)(Ph_3P)_2}]} \arrow[u, "\mathrm{HCl}"'] & (6) \\
 & {[\mathrm{Ir^{III}H_2Cl(CO)(Ph_3P)_2}]} \arrow[u, "\mathrm{HCl}"'] &
\end{tikzcd}$$

Equivalence of H_2, HCl, and Cl_2 in the primary reactions indicates that they all–including hydrogen–must be considered as Lewis acids (or oxidants) in these reactions, that is to say, accepting electrons from univalent iridium for covalent bond formation. The data reproduced in Table I show that the metal-hydrogen bond character in $[\mathrm{IrH_2Cl(CO)(Ph_3P)_2}]$ is clearly of the same nature as in covalent iridium(III) hydrides prepared by reactions with protonic acids,[1] alcohols,[5] and metallic hydrides.[6]

A significant observation in relating homogeneous and heterogeneous systems emerges by comparing our results with the recent work by Pliskin and Eischens[4] describing the first tangible evidence for covalent bonding between the surface atoms of (alumina-supported) platinum and chemisorbed hydrogen (as atoms). This comparison (Table I) demonstrates a close analogy between a transition metal compound and a transition metal surface with respect to their reactions with H_2 and D_2. Another aspect of this analogy becomes evident by considering the action of halogens, hydrogen halides (*cf.* equation 6), hydrogen sulfide,[8] and oxygen[8] on $[\mathrm{IrCl(CO)(Ph_3P)_2}]$. These reagents "poison" the "active sites" of the Ir(I) complex by destroying its "surface" through oxidation.

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(4) W. A. Pliskin and R. P. Eischens, *Z. physik. Chem. N. F.*, **24**, 11 (1960).

(5) L. Vaska, *J. Am. Chem. Soc.*, **83**, 756 (1961).

(6) R. G. Hayter, *ibid.*, **83**, 1259 (1961).

(7) Determined by gas chromatography.

(8) Unpublished results.

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RECEIVED JANUARY 6, 1962

COÖRDINATION CHAIN REACTIONS

Sir:

The exchange reaction between the complex ions triethylenetetramine-nickel (II), $\mathrm{NiT^{+2}}$, and ethyl-