TABLE I

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

| Formed by reacn. with | Compound (P = $Ph_3P$) | $\nu_{M\text{-}H,D}$[b] Solid[c] | $\nu_{M\text{-}H,D}$[b] Soln.[d] | $\nu_{CO}$[e] Solid[c] | $\nu_{CO}$[e] Soln.[d] |
|---|---|---|---|---|---|
| $H_2$ | $[IrH_2Cl(CO)P_2]$ | 2190, 2100 | 2220,[f] 2095 | 1970 | 1983[g] |
| $H_2$ | Pt-H[h] | 2110, 2060 | ... | ... | ... |
| $D_2$ | $[IrD_2Cl(CO)P_2]$ | 1571 | 1572[i] | 1995 | 2030 |
| $D_2$ | Pt-D[h] | 1515, 1480 | ... | ... | ... |
| HCl | $[IrHCl_2(CO)P_2]$[j] | 2245 | ... | 2030 | 2045 |
| $C_2H_5OH$ | $[IrHCl_2P_3]$[k] | 2200 | 2185 | ... | ... |
| $(CH_2OH)_2$ | $[IrH_2ClP_3]$[k] | 2215, 2110 | 2180 | ... | ... |
| $LiAlH_4$ | $[IrH_3P_3]$[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 $\gamma$-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 $\nu_{IrH}$ 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.

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

This monohydride is the same compound which was first obtained by the reaction of $[IrCl(CO)(Ph_3P)_2]$ 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) $[IrHCl_2(CO)(Ph_3P)_2]$ 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]

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

(*Anal.* Calcd. for $IrCl_3P_2C_{37}H_{30}O$: 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; $\nu_{CO}$, 2080 cm.$^{-1}$; diamagnetic; non-conducting in acetone and nitrobenzene.) This product is obtained also by these reactions

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

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

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

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

*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 $[IrH_2Cl(CO)(Ph_3P)_2]$ 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 $[IrCl(CO)(Ph_3P)_2]$. 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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## COÖRDINATION CHAIN REACTIONS

*Sir:*

The exchange reaction between the complex ions triethylenetetramine-nickel (II), $NiT^{+2}$, and ethylenediaminetetraacetato-cuprate(II), $CuY^{-2}$

$$NiT^{+2} + CuY^{-2} \longrightarrow CuT^{+2} + NiY^{-2}$$

is found to proceed by a chain reaction mechanism. This, we believe, is the first example of a chain reaction in aqueous solution caused by coördination substitution reactions.

The $NiT^{+2}$ and $CuY^{-2}$ complexes are both extremely slow in their dissociation reactions (substitution by water) in neutral solution.[1,2] Yet, the exchange reaction between these complexes occurs readily. The reaction is initiated by the trace concentration (approx. $10^{-6}$ $M$) of free triethylenetetramine ($T_T = H_3T^{+3} + H_2T^{+2} + HT^{+} + T$) which is in equilibrium with the complex.

$$NiT^{+2} \rightleftharpoons Ni^{+2} + T_T$$

This trace of $T_T$ attacks the $CuY^{-2}$ complex, greatly accelerating the rate of EDTA displacement. The trace of EDTA liberated in turn attacks the $NiT^{+2}$ greatly accelerating the rate of triethylenetetramine displacement. Thus, the chain propagating steps are

$$T_T + CuY^{-2} \rightleftharpoons CuT^{+2} + Y_T$$
$$Y_T + NiT^{+2} \longrightarrow NiY^{-2} + T_T$$

Traces of metal ions which can complex triethylenetetramine or EDTA act as chain inhibitors. The $Ni^{+2}$ may act as a chain terminator by the reactions

$$Ni^{+2} + T_T \longrightarrow NiT^{+2}$$
$$Ni^{+2} + Y_T \longrightarrow NiY^{-2}$$

Slight excesses of either ligand greatly increase the exchange rate as expected by this mechanism. The observed kinetic orders with excess $CuY^{-2}$ or $NiT^{+2}$ support the mechanism.

Thus when an excess of $NiT^{+2}$ is present the reaction rate is proportional to $[CuY^{-2}][NiT^{+2}]^{1/2}$ while with an excess of $CuY^{-2}$ present the reaction rate is proportional only to $[NiT^{+2}]^{3/2}$ at high pH and has a more complex dependence at lower pH. These reaction orders are consistent with the proposed mechanism and the detailed kinetic arguments as well as the evaluation of the individual rate constants will be published. Furthermore, the chain initiating step and the chain terminating step both may be eliminated from the exchange rate by the addition of an excess of either trien or EDTA. Under these conditions with excess $NiT^{+2}$ the rate is proportional to $[T_T]_{added}$ $[CuY^{-2}]$ and with excess $CuY^{-2}$ the rate is proportional to $[Y_T]_{added}$ $[NiT^{+2}]$.

Chain reaction mechanisms for metal complex-metal complex exchange reactions should be expected for many other systems when sufficient free ligand is available to increase the dissociation rates of the complexes. Multidentate ligand complexes should be particularly susceptible to this type of reaction because their dissociation rates are slower and lower concentrations of the ligands are needed to accelerate their displacement of one another than is the case for lower dentate ligands.

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(1) J. F. G. Clarke, Ph.D. Thesis, Purdue University, 1960.

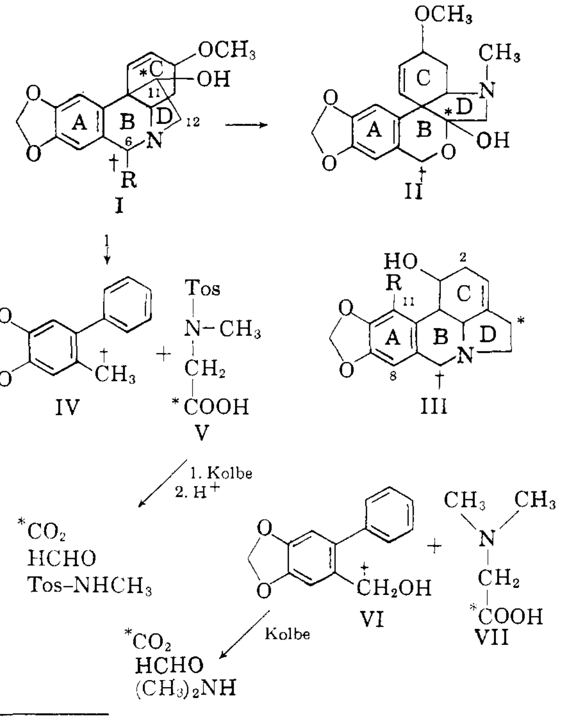
(2) H. Ackerman and G. Schwarzenbach, *Helv. Chim. Acta*, **35**, 485 (1952).

## BIOSYNTHESIS IN THE AMARYLLIDACEAE. THE INCORPORATION OF 3-C¹⁴-TYROSINE IN SPREKELIA FORMOSISSIMA

*Sir:*

Previous biogenetic experiments with plants of the family *Amaryllidaceae* have been concerned largely with the origin of the $C_6$-$C_2$ fragment which elaborates the hydroaromatic ring C and the 5-membered ring D in many alkaloids. Experimental evidence has been obtained for the incorporation of both 2-$C^{14}$-tyrosine[1-3] and 1-$C^{14}$-norbelladine[3-5] by various plants within the family to afford alkaloids shown in several cases to be labelled solely at the expected position.

We have been concerned with possible precursors of the $C_6$-$C_1$ unit in the *Amaryllidaceae* alkaloids which is represented by the aromatic ring A and the benzylic carbon adjacent to the basic nitrogen. Feeding 3-$C^{14}$-tyrosine to the stems of flowering *Sprekelia formosissima* gave rise to radioactive haemanthamine (I, R = H) (isolated by dilution with inactive alkaloid), haemanthidine (I, R = OH) (0.20% incorporation), and tazettine (II) (0.16% incorporation). Based on previous biosynthetic experiments,[3] it was anticipated that radioactivity would be found at the carbon atoms of I (R = H or OH) and II at the positions marked by the asterisk. If 3-$C^{14}$-tyrosine were to serve also as a precursor of ring A and the benzylic carbon ($C_6$ in I and $C_8$ in II), radioactivity at the position marked by the dagger would be expected in addition.



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