Reversal of (3) is not effected by removal of oxygen from solutions of the adduct (*e.g.*, 3 days in CH_3OH at 25°) or by pumping (10^{-4} mm) on the crystals at 110° (24 hr).[11]

Table I. Some Properties of Four-, Five-, and Six-Coordinated Iridium Complexes

	Complex[a]	Color	Dec pt, °C (air)	Infrared data[b] cm^{-1}	ν
1	$[Ir(P–P)_2]Cl$	Orange	225		
2	$[Ir(P–P)_2]BF_4$	Orange	270	1065 vs, 1036 vs	B–F
3	$[(CO)Ir(P–P)_2]Cl$	White	260	1933 vs	C–O
4	$[(PF_3)Ir(P–P)_2]Cl$	White	270	778 s	P–F
5	$[(O_2)Ir(P–P)_2]Cl$	Cream	185	845 m	$Ir–O_2$
6	$[(O_2)Ir(P–P)_2]BPh_4$	Cream	175	844 m	$Ir–O_2$
7	$[(H_2)Ir(P–P)_2]BPh_4$	White	220	2091 s, 2080 s	Ir–H[c]
8	$[(D_2)Ir(P–P)_2]BPh_4$	White	226	1515 m, 1499 ms	Ir–D[c]
9	$[(HCl)Ir(P–P)_2]Cl$	White	270	2216 w	Ir–H
10	$[(HBr)Ir(P–P)_2]Cl$	White	272	2209 w	Ir–H
11	$[(SO_2)_2Ir(P–P)_2]Cl$	White	238	1276 s, 1163 vs	S–O
12	$[(NO_2)_2Ir(P–P)_2]Cl$	Cream	163	1410 m, 1340 vs	N–O

[a] See ref 5. The molecule preceding Ir in the formulas (O_2, etc.) refers to the additament (*cf.* eq 3 and 4). [b] The spectra were measured as Nujol or halocarbon mulls on a Beckman IR-12 spectrophotometer. Only some selected characteristic stretching frequencies are given; analysis of complete spectra will be reported later. [c] ν_{IrH}/ν_{IrD} = 1.38, 1.39.

With molecular hydrogen, an equally facile reaction (eq 4) in solution occurs under normal conditions. The Ir–H stretching frequencies (**7**, Table I)[12] of the

$$[Ir(P–P)_2]Cl + H_2 \longrightarrow [H_2Ir(P–P)_2]Cl \qquad (4)$$

resulting dihydrido cation suggest that the two hydrogens occupy *cis* positions.[12] The stability of this complex parallels that of the oxygen complex. Thus, both the H_2 and O_2 adducts of $[Ir(P–P)_2]Cl$ demonstrate a considerably higher dissociative stability than the corresponding reversible complexes of $[IrCl(CO)(Ph_3P)_2]$,[2,13] and the bisphosphine chelate shows a higher reactivity toward these and a variety of other molecules cited below.

With carbon monoxide, a *reversible* five-coordinated adduct is formed (eq 2) which is stable in the solid state (*cf.* ref 4). Other quinquecovalent species are produced by reactions with PF_3 (**4**), and probably with NO and SO_2 which, when used in excess, add a second molecule to the cation (**11**; complex **12** results by reaction with excess NO *in air*). Gaseous hydrogen halides, H_2S, and halogens react almost instantly with the crystals of the starting complex giving six-coordinated adducts.[14] In the hydride derivatives (**9**, **10**), the H is probably *trans* to the coordinated halogen.[12] Rapid reactions are also observed with organic and metallic halides and pseudo-halides (*e.g.*, CH_3I, HgOAc), BF_3, and $(CN)_4C_2$ (among other types of covalent molecules). The compositions and structures of these complexes are currently under study.

Representative compounds and some of their properties are given in Table I. Satisfactory analyses have been obtained for the derivatives shown, except for **9** and **10**.[14] The solutions (*ca.* 5×10^{-4} *M*) of the complexes behave as uni-univalent electrolytes (Λ_M, ohm^{-1}: 60–70 in methanol, 100–150 in acetone).[14] Replacement of the chloride with heavier anions (**2**, **6**, **7**, **8**) confirms the ionic structures as indicated.

The four-coordinated Ir(I) complex, $[Ir(P–P)_2]X$, appears to represent the second reported type of transition metal compound capable of activating H_2, O_2, CO, etc., homogeneously in solution and of producing isolable and well-defined 1:1 adducts with all these molecules.[15] The present study originates from our concept that low-valent and coordinatively unsaturated metal complexes behave as bases toward even such a "weak acid" as hydrogen molecule.[1,16] The Ir in the bisphosphine chelate appears to be in a somewhat lower valence state (*i.e.*, the chelate is a stronger reductant or base) than in its precursor, $[IrX(CO)(Ph_3P)_2]$, as suggested by a comparison of dissociative stabilities of corresponding pairs of adducts of the two complexes (see above and ref 2, 4, 6, 13, and 16).[17]

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(11) Deoxygenation of the solid adduct appears to set in above 150°. On heating in 2-methoxyethanol (123°), complex **5** is converted to a hydride (ν_{IrH}, 2080 cm^{-1}) which is being investigated.

(12) For review, see A. P. Ginsberg in "Transition Metal Chemistry," Vol. 1, R. L. Carlin, Ed., Marcel Dekker, Inc., New York, N. Y., 1965, Chapter 3.

(13) L. Vaska and R. E. Rhodes, *J. Am. Chem. Soc.*, **87**, 4970 (1965).

(14) With Cl^- as anion, the adducts with halogens and hydrogen halides include varying amounts of the reactant which appears to be associated with the anion, and no satisfactory analyses on these complexes are presently available. Some of the hydrides show abnormally high conductances, reflecting the presence of the reactant acid.

(15) Reference is made to $[IrX(CO)(Ph_3P)_2]$.[2,4,6,13,16]

(16) L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, **84**, 679 (1962).

(17) NOTE ADDED IN PROOF. Three recent and independent reports on the subjects of this note have come to our attention since this manuscript was submitted; see A. Sacco, M. Rossi, and C. F. Nobile, *Chem. Commun.*, 589 (1966); W. Hieber and V. Frey, *Chem. Ber.*, **99**, 2607 (1966); K. A. Taylor, Abstracts of Papers, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

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Stereospecific Addition of Hydrogen Halides to Tetragonal d^8 Complexes

Sir:

We have investigated the reactions of the *crystals* of *trans*-$[IrY(CO)(Ph_3P)_2]$ (Y = halogen)[1] with *gaseous* hydrogen halides and derived the molecular structures of the resulting six-coordinated adducts (eq 1–4) from their vibrational spectra (Table I). The heterogeneous conversions proceed smoothly at 25° and under 1 atm of the gas.[2] The white or yellowish crystalline products have been characterized by their infrared spectra, X-ray diffraction patterns, and elemental analyses of selected derivatives.[3]

$$[IrY(CO)(Ph_3P)_2] + RX \longrightarrow [(RX)IrY(CO)(Ph_3P)_2] \qquad (1)$$

$$(Y = Cl, Br, I, SCN; RX = HF, HCl, DCl, HBr, HI, H_2S)^2$$

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

(2) With HF, only a partial conversion is observed under these conditions and in some experiments HF was used in ether solution. With HI, more than one product is obtained. Full results, including the reactions with H_2S, will be reported elsewhere.

(3) Complete analyses are available for compounds **2**, **4**, **8**, and **10** (Table I). The complexes are too insoluble for molecular weight, dipole moment, and nmr measurements.

This study was undertaken with the view to gaining information on the mechanism of these (eq 1) and related oxidative reactions of tetragonal d^8 complexes. No definite data have been previously reported on the mode of addition of *heteronuclear* molecules ($R \neq X$, eq 1) to these compounds.[4] Of the reactions with homonuclear addenda ($R = X$),[4] the iridium(I) complex (eq 1) is known to yield a *cis* adduct with hydrogen,[5] and the oxidation of isoelectronic (d^8) platinum(II) complexes by halogens has been reported to effect either *trans*[6] or *cis*[7] additions. Since a primary question regarding the mechanism of these synthetic reactions concerns the configuration of the initial product, and since all previous structural data cited appear to have been obtained on complexes resulting from experiments carried out in solution where the initial product may undergo subsequent isomerization, a specific aim of the present study was to render such a possibility less probable.

The results and significance of this inquiry are summarized in the following observations.

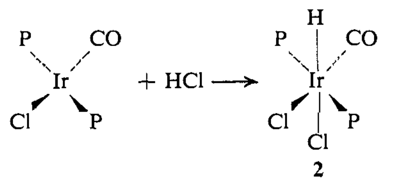
1. The X-ray powder patterns of the HX adducts of $[IrY(CO)(Ph_3P)_2]$ show, according to visual examination, that the complexes given in Table I are isomorphous. This implies that all these compounds have the same *basic* molecular structure.

Table I. Ir–H(D), C–O, and Ir–Cl Vibrational Frequencies (cm^{-1})[a] of HX Adducts of $[IrY(CO)(Ph_3P)_2]$

	Complex[b]	$\nu_{Ir-H(D)}$[c]	$\delta_{Ir-H(D)}$[c]	ν_{C-O}[d]	ν_{Ir-Cl}[c]	
1	$[(HF)IrCl(CO)P_2]$	2240	876,836	2024	. . .	266
2	$[(HCl)IrCl(CO)P_2]$	2240	876,836	2024	313	265
3	$[(DCl)IrCl(CO)P_2]$	1608	667,607	2024	312	266
4	$[(HBr)IrCl(CO)P_2]$	2240	870,835	2022	. . .	269
5	$[(HF)IrBr(CO)P_2]$[e]	2230		2024	. . .	. . .
6	$[(HCl)IrBr(CO)P_2]$	2227	865,824	2024	312	. . .
7	$[(DCl)IrBr(CO)P_2]$	1599	660,600	2025	314	. . .
8	$[(HBr)IrBr(CO)P_2]$	2231	862,822	2024	. . .	. . .
9	$[(HF)IrI(CO)P_2]$	2200	837,805	2023	. . .	. . .
10	$[(HCl)IrI(CO)P_2]$	2200	835,805	2022	310	. . .
11	$[(DCl)IrI(CO)P_2]$	1580	648,592	2022	312	. . .
12	$[(HBr)IrI(CO)P_2]$	2203	831,803	2023	. . .	. . .

[a] From the infrared spectra of the complexes measured as Nujol or halocarbon mulls on Beckman IR-9 and IR-12 spectrophotometers. [b] The molecule preceding Ir in the formulas (HF, etc.) refers to the additament, eq 1–4. $P = Ph_3P$. [c] Medium to medium strong. [d] Very strong. [e] Partial reaction, weak bands.

2. This basic configuration, *e.g.*, **2** in eq 2 ($P = Ph_3P$), emerges from the combined evidence cited below. Of the six possible geometrical isomers for $[(HCl)IrCl(CO)(Ph_3P)_2]$, two with *trans* H–CO structures are

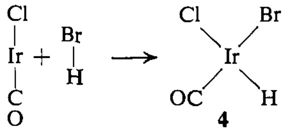


2

(2)

eliminated because of the absence of H–CO vibrational interaction,[8] and two further ones with *trans* H–P arrangements are not compatible with the observed high ν_{IrH} values[9–11] and the pattern of their variation. Of the remaining two, **2** is favored over a *cis*-P–P, *cis*-Cl–Cl isomer[12] on the basis of the observed Ir–Cl stretching frequencies (see below and Table I).[14]

3. Obviously, configuration **2** gives no clue as to whether the HX addition is *cis* or *trans*.[15] Information regarding this question derives from the total infrared data shown in Table I. Iridium–hydrogen vibrational frequencies (ν_{IrH} and δ_{IrH}) are seen to be insensitive to or only slightly affected by the addenda X (of HX), but they do vary significantly with the halogen (Y) of the starting complex.[19] Compare also the Ir–D frequencies in **3**, **7**, and **11**. Taken together with the well-known infrared *trans* effect,[6,10,14] these observations suggest that the mode of HX addition is *cis*,[20] *i.e.*, the hydrogen enters a stereospecific position *trans* to the original halogen (Y). For example, reactions 3 and 4 yield two geometrical isomers of $[IrHClBr(CO)(Ph_3P)_2]$,[20] **4** and **6**,



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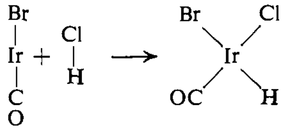
(3)



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(4)

respectively. (The two *trans*-Ph_3P, not shown in the diagrams, are normal to the plane of the paper.)

This mechanism is corroborated by the evidence from iridium–chlorine stretching frequencies.[21] By analogy with a related complex,[22] and in accordance with the known high *trans* effect of the hydride ligand,[6,10,14] the band at *ca.* 267 cm^{-1} is assigned to the ν_{IrCl} *trans*

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[4] We refer here only to the cases in which RX (eq 1) dissociates and six-coordinated complexes are formed.

[5] L. Vaska and R. E. Rhodes, *J. Am. Chem. Soc.*, 87, 4970 (1965).

[6] For a review, see F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, 4, 381 (1962), and pertinent references cited therein.

[7] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 705, 4020 (1959).

[8] L. Vaska, *J. Am. Chem. Soc.*, **88**, 4100 (1966).

[9] $\nu_{MH\text{-}trans\text{-}P}$ are found at considerably lower frequencies than the ν_{IrH} given in Table I.[10,11]

[10] For recent reviews on transition metal hydride complexes, see (a) A. P. Ginsberg in "Transition Metal Chemistry," Vol. 1, R. L. Carlin, Ed., Marcel Dekker, Inc., New York, N. Y., 1965, Chapter 3; (b) M. L. H. Green and D. J. Jones, *Advan. Inorg. Chem. Radiochem.*, 7, 115 (1965).

[11] (a) L. Vaska, *J. Am. Chem. Soc.*, **86**, 1943 (1964); (b) P. L. Orioli and L. Vaska, *Proc. Chem. Soc.*, 333 (1962).

[12] This structure requires a substantial rearrangement which is not very likely to occur under our experimental conditions. It should also be noted that the two Ph_3P's have been found *trans* to one another in all established structures of the adducts of $[IrY(CO)(Ph_3P)_2]$.[5,13]

[13] (a) S. J. La Placa and J. A. Ibers, *J. Am. Chem. Soc.*, **87**, 2581 (1965); *Inorg. Chem.*, **5**, 405 (1966); (b) see also L. Vaska, *Science*, **152**, 769 (1966).

[14] J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.*, 6789 (1965).

[15] After our discovery of reaction 2,[1] other workers have repeated this experiment and structure **2** has been suggested as a likely possibility.[16,17] The same isomer, **2** (with $P = Et_2PhP$), has also been synthesized by a different method.[18]

[16] R. S. Nyholm and K. Vrieze, *J. Chem. Soc.*, 5337 (1965).

[17] R. C. Taylor, J. F. Young, and G. Wilkinson, *Inorg. Chem.*, **5**, 20 (1966).

[18] J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.* 1625 (1964).

[19] ν_{IrH} varies linearly with the electronegativity of the halogen Y. The same is approximately true for the higher frequency band of δ_{IrH}.

[20] Contrary to a previous suggestion; see R. S. Nyholm in "Proceedings of the Third International Congress on Catalysis," Vol. 1, W. M. H. Sachtler, G. C. A. Schuit, and P. Zwietering, Ed., North-Holland Publishing Co., Amsterdam, and John Wiley and Sons, New York, N. Y., 1965, p 73.

[21] ν_{IrF} and ν_{IrBr} have not been found definitely, and ν_{IrI} must occur below 200 cm^{-1} (lower limit of the available spectrophotometer).

[22] In $[H_2IrCl(CO)(Ph_3P)_2]$, the Cl is *trans* to H,[5] and the ν_{IrCl} appears near 270 cm^{-1}.

to H (eq 2, 3). This band appears only in the spectra of the adducts of $[IrCl(CO)(Ph_3P)_2]$. On the other hand, all the adducts of HCl (**2**, **3**, **6**, **7**, **10**, **11**) show a common property in the other ν_{IrCl} near 312 cm^{-1}, and this is compatible with the suggestion that the reacting halide (of HX) is found *trans* to CO in the adduct (eq 3, 4).[23]

The studies reported here are being extended to include observations on potential isomerization of the initial products (Table I) and formation of the HX adducts homogeneously in solution. We are also examining the structures of other types of adducts of $[IrY(CO)(Ph_3P)_2]$, *e.g.*, with organic and metallic halides, and these will be described in subsequent communications.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Institutes of Health (Grant No. HE-09678) of the U. S. Public Health Service, for partial support of this research. The author thanks Mr. S. L. Lindenberger for experimental assistance.

[23] In *trans*-$[IrCl(CO)(Ph_3P)_2]$ and *trans*-$[RhCl(CO)(Ph_3P)_2]$, the ν_{MCl}'s are found at 321 and 315 cm^{-1}, respectively.

[24] Address inquiries to this location.

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Stable Carbonium Ions. XXVIII.[1] Protonated Aliphatic Alcohols

Sir:

We reported in previous work[2,3] that tertiary and certain secondary alcohols such as *t*-butyl alcohol, *t*-amyl alcohol, 1-adamantanol, 2-*exo*-norborneol, and miscellaneous phenylethyl alcohols ionize to stable carbonium ions in the extremely strong acid FSO_3H-SbF_5, generally diluted with SO_2. It was also found that less reactive secondary phenylethyl and phenylpropyl alcohols such as 3-phenyl-2-butanol and 1-phenyl-1-*p*-tolyl-2-propanol are only protonated in the same acid system, and at −60° (using SO_2 as diluent) the protonated alcohol shows extremely slow exchange rates allowing the observation of well-resolved nmr spectra.[3]

To our knowledge, with the exception of the observation of MacLean and Mackor[4] who found that the exchange of ethyl alcohol in $HF-BF_3$ can be slowed down at −70°,[5] no observation relating to other protonated aliphatic primary and secondary alcohols was known.[6]

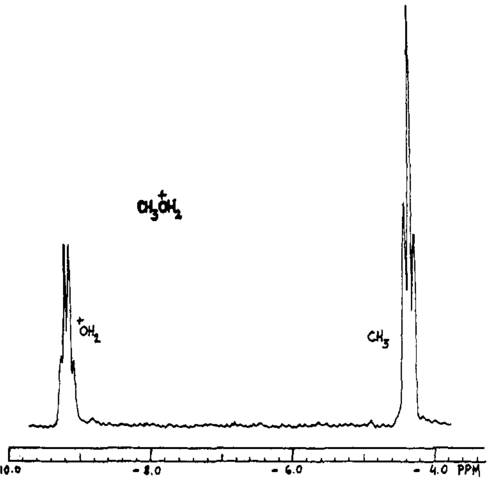

Figure 1.

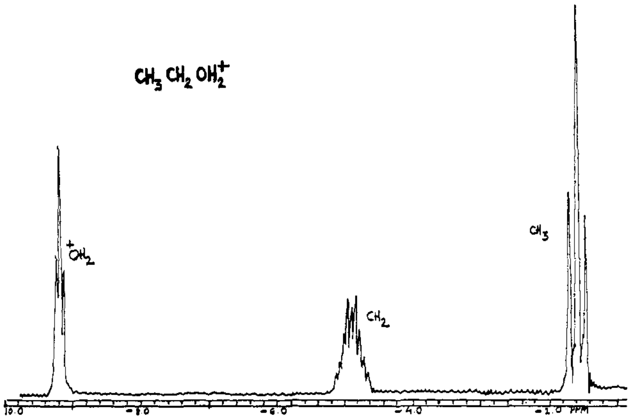

Figure 2.

We wish now to report the observations that in $FSO_3H-SbF_5-SO_2$ solvent system not only primary alcohols such as methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol, but also secondary alcohols such as 2-propanol can be observed at −60° as the protonated alcohols, with very slow exchange rates.

$$ROH \xrightarrow[-60^\circ]{FSO_3H-SbF_5-SO_2} ROH_2^+SbF_5FSO_3^-$$

Protonated methanol, $CH_3OH_2^+$, shows the methyl triplet at −4.35 ppm and the $^+OH_2$ quadruplet at −9.2 ppm, J_{H-H} = 3.7 cps (Figure 1). Protonated ethanol, $CH_3CH_2OH_2^+$, shows the methyl triplet at −1.6 ppm (J_{H-H} = 7.3 cps) and the $^+OH_2$ triplet at −9.2 ppm (J_{H-H} = 3.6 cps). The methylene signal is the expected nine-line pattern at −4.86 ppm (Figure 2) as the coupling with the CH_3 group is about twice that with $^+OH_2$.

Protonated 1-propanol shows the methyl triplet at −0.92 ppm (J_{H-H} = 7.2 cps), the C_2 methylene multiplet at −1.73 ppm, the C_1 methylene multiplet (seven lines) at −4.63 ppm, and the $^+OH_2$ triplet (J_{H-H} = 3.6 cps) at −8.98 ppm (Figure 3). Protonated 2-propanol shows the methyl doublet at −1.5 ppm (J_{H-H} = 6.3 cps), the $^+OH_2$ doublet at −8.92 ppm (J_{H-H} = 2.9 cps), and the methine proton multiplet at −5.2 ppm (Figure 4).

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[1] Part XXVII: G. A. Olah and M. B. Comisarow, *J. Am. Chem. Soc.*, **88**, 4442 (1966).

[2] G. A. Olah, M. B. Comisarow, C. A. Cupas, and C. U. Pittman, Jr., *ibid.*, **87**, 2997 (1965).

[3] G. A. Olah, C. U. Pittman, Jr., E. Namanworth, and M. B. Comisarow, *ibid.*, in press.

[4] C. MacLean and E. L. Mackor, *Discussions Faraday Soc.*, **34**, 165 (1962).

[5] T. Birchall and R. F. Gillespie (*Can. J. Chem.*, **43**, 1045 (1965)) in FSO_3H solution at low temperature also observed protonated ethyl alcohol but were unable to observe any fine structure of the $^+OH_2$ peak or coupling with the methylene protons.

[6] M. Brookhart, A. Diaz, and S. Winstein (*J. Am. Chem. Soc.*, **88**, 3136 (1966)), after completion of the work reported in this communication, mentioned the observation of protonated methyl alcohol, without, however, giving details.