by conventional treatment with 0.4 *M* sodium hydroxide. Work-up of the products afforded 21 mg of trityldeoxycytidine and the fractions listed in Table VI.

Table VI. Products from Preparation of TrdCpTpT on LowCross-Linked Support

Peak	Tube no.	Total vol., ml	OD_{270}	OD_{270} × vol.
i	6–38	430	1.62[a]	700
ii	42–105	850	1.375	1170
iii	121–200	1040	1.175	1220
iv	212–240	375	0.67	251
v	242–345	1500	1.15	1720

[a] OD after evaporation to remove pyridine and then redilution.

Paper chromatography in solvent A indicated that i was mainly thymidine with a trace of trityldeoxycytidine; ii contained two components, R_f 0.49 (probably TrdCp) and 0.71; iii was largely TrdCpT (R_f 0.73) with a trace of material with R_f 0.15; iv had one compound with R_f 0.29; and v showed one component with R_f 0.62, which was the desired TrdCpTpT. Fraction v contained 34% of the ultraviolet-absorbing material removed from the the support polymer. The OD units of TrdCpTpT correspond to 21% of the amount calculated assuming quantitative conversion of the TrdC on the polymer to TrdCpTpT.

Spectral Determinations and Enzyme Assays. For spectral determinations and enzyme assay, the oligonucleotide derivatives were dissolved in water and rechromatographed on DEAE-cellulose. Better than 90% of the solids were recovered in all cases (Table I). This purification procedure had little effect on the ϵ value for TrdCpT, but increased the ϵ values for TrdCpTpT and TrdCpTpTpT by about 10%.

Table VII. Products of Enzymatic Degradation

Compound	TrdC OD_{278} units	pT OD_{267} units	TrdC/pT Found, %	TrdC/pT Calcd, %
TrdCpt	2.45	1.9	1.1	1
TrdCpTpT	0.75	1.15	2.1	2
TrdCpTpTpT	0.60	1.35	3.1	2

Hydrolyses were carried out by incubating 0.4–1.0-mg samples of the nucleotide derivatives with 0.1 ml of an aqueous solution of snake venom phosphodiesterase for 7 hr at 37°. The enzyme solution was made up by dissolving 500 units of phosphodiesterase (Russel's viper venom, lyophilized)[15] in 2.5 ml of 0.33 *M* Tris buffer at pH 9.1. Turbidity which developed due to formation of trityldeoxycytidine was cleared by addition of two drops of pyridine and the clear solution was chromatographed on 3MM paper in solvent A. Product spots were cut out and eluted by soaking for 24 hr in 30% ethanol–water 0.01 *M* in HCl (for the phosphates) or 90% ethanol–water 0.01 *M* in HCl (for trityldeoxycytidine). Appropriate blanks were cut from other areas of the chromatograms and soaked in the same solvents. Concentrations of the nucleotides and trityldeoxycytidine were determined from differences between the absorbances of solutions resulting from elution of the spots and the blanks. Values used for extinction coefficients in these calculations were 13,200 for trityldeoxycytidine and 9600 for thymidine 5′-phosphate. A similar hydrolysis of TrdCpTpA proceeded well and afforded approximately equal amounts of trityldeoxycytidine, thymidine 5′-phosphate, and adenosine 5′-phosphate, as judged visually from the spots produced on paper chromatography.

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[15] Calbiochem.

Communications to the Editor

A New Series of Four-, Five-, and Six-Coordinated Iridium Complexes

Sir:

In the course of our continuing inquiries into the determinants of activation of molecular hydrogen,[1] oxygen,[2] nitrogen,[3] and related molecules[4] by transition metal complexes, we have discovered a *cationic* Ir(I) complex, $[Ir(P\text{–}P)_2]X$ (P–P = bis(1,2-diphenylphosphino)ethane,[5] X = univalent anion), which displays a reactivity and versatility reminiscent of the notable compound, *trans*-$[IrX(CO)(Ph_3P)_2]$,[1–4,6] from which it has been synthesized (eq 1 and 2).

$$[IrCl(CO)(Ph_3P)_2] + 2P\text{–}P \longrightarrow [Ir(CO)(P\text{–}P)_2]Cl + 2Ph_3P \quad (1)$$

$$[Ir(CO)(P\text{–}P)_2]Cl \overset{\Delta}{\rightleftarrows} [Ir(P\text{–}P)_2]Cl + CO \quad (2)$$

The four-coordinated bisphosphine chelate is best prepared by a two-step synthesis involving a five-coordinated carbon monoxide adduct as intermediate (eq 1 and 2). White crystals of the latter are formed[7,8] upon mixing benzene solutions of the reactants at 25° (eq 1). Reaction 2 is carried out by heating the CO complex in a 10:1 mixture of toluene-1-propanol[9] to 100° which results in a bright orange precipitate of $[Ir(P\text{–}P)_2]Cl$.[7,8]

The crystals of the novel d^8 complex (**1**, Table I)[10] are moderately air stable, but they do react with atmospheric oxygen slowly on standing. In solution (*e.g.*, $CHCl_3$, alcohols), a conversion to a cream-colored oxygen adduct takes place within minutes (eq 3). The reaction is

$$[Ir(P\text{–}P)_2]Cl + O_2 \longrightarrow [O_2Ir(P\text{–}P)_2]Cl \quad (3)$$

accompanied by appearance of an infrared band at 845 cm^{-1} which, by analogy with $[O_2IrCl(CO)(Ph_3P)_2]$,[2] is tentatively assigned to the Ir–O_2 stretching vibration.

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[1] L. Vaska, *Inorg. Nucl. Chem. Letters*, **1**, 89 (1965), and references quoted.

[2] L. Vaska, *Science*, **140**, 809 (1963).

[3] Unpublished results.

[4] L. Vaska, *Science*, **152**, 769 (1966), and references cited therein.

[5] P–P = $Ph_2PCH_2CH_2PPh_2$ throughout this paper.

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

[7] Yields, based on $[IrCl(CO)(Ph_3P)_2]$, range from 85 to 95%.

[8] The chlorides tend to be hygroscopic and acquire one to four molecules of water (on standing in air); these can be removed on heating the crystals near 90°.

[9] When CH_3OH or C_2H_5OH is used in step 2, the chelate precipitates with alcohol of crystallization.

[10] The numerals cited in text refer to the complexes given in Table I.

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] $\nu_{IrH}/\nu_{IrD} = 1.38, 1.39$.

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 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.

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

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.