bond angles were used and Hoffmann's parameters (ref 10) were used for H, C, and F (H exponent = 1.3). Phosphorus parameters were H_{ii}: 3s −18.6 eV, 3p −14.0 eV, and an exponent of 1.6. Similar calculations were performed using 3d orbitals at −6.0 eV with an exponent of 1.4.

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Photochemical Reductive Elimination of Oxygen, Hydrogen, and Hydrogen Chloride from Iridium Complexes

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Abstract: Ultraviolet irradiation of the H_2 and O_2 adducts of $[IrCl(CO)(Ph_3P)_2]$, $[IrI(CO)(Ph_3P)_2]$, $[Ir(2\text{-phos})_2]^+$, and $[Ir(2{=}phos)_2]^+$ (2-phos is 1,2-bis(diphenylphosphino)ethane and 2=phos is *cis*-1,2-bis(diphenylphosphino)ethylene) induces reductive elimination of molecular hydrogen and oxygen and regeneration of the square-planar complexes. The reactions occur in argon-purged solutions and in glasses at 77°K. Deoxygenation of $[O_2IrCl(CO)(Ph_3P)_2]$ can be made to go essentially to completion even in air-saturated solutions. Production of $O_2(^1\Delta_g)$ is not observed. Reductive elimination of HCl from $[H(Cl)IrCl(CO)(Ph_3P)_2]$ also occurs upon irradiation of argon-purged solutions. Electronic spectral data suggest that the lowest electronic excited state in each complex possesses iridium-to-phosphine charge-transfer character. It is believed that the photoelimination process is initiated in this CT excited state, but the detailed mechanism of formation of the diatomic product molecule (O_2, H_2, or HCl) is not known.

Oxidative-addition reactions of square-planar complexes of iridium(I) have been extensively investigated.[2-14] Vaska's complex, $[IrCl(CO)(Ph_3P)_2]$, and the related complexes $[IrI(CO)(Ph_3P)_2]$, $[Ir(2\text{-phos})_2]^+$,[15] and $[Ir(2{=}phos)_2]^+$,[15] among others, oxidatively add molecular oxygen and hydrogen, hydrogen chloride, and a large variety of other small molecules.[2,9] Of the O_2, H_2, and HCl adducts of these four complexes, however, only $[O_2IrCl(CO)(Ph_3P)_2]$ and $[H_2Ir(Cl)(CO)(Ph_3P)_2]$ undergo reductive-elimination reactions under mild conditions.[2,9,11] For example, $[O_2IrCl(CO)(Ph_3P)_2]$ loses oxygen when a solution of the complex is purged with an inert gas or when the solid is heated. By comparison, loss of oxygen does not occur from purged solutions of $[O_2Ir(2\text{-phos})_2]^+$ or when a solid sample of $[O_2Ir(2\text{-phos})_2]Cl$ is heated in vacuo at 110° for 24 hr.[9]

Very little is known about the photochemical behavior of the aforementioned adduct complexes. Vaska has briefly reported that orange crystals of $[O_2IrCl(CO)(Ph_3P)_2]$ are sensitive to light and change to green and then to blue-black on prolonged exposure and that the photoproduct probably contains triphenylphosphine oxide and an Ir(IV) complex.[5] In another communication, mention was made of an observation that the deoxygenation reaction of $[O_2IrCl(CO)(Ph_3P)_2]$ is photocatalyzed, but no details were given.[12] These observations prompted us to make an extensive study of the photochemistry of several adduct complexes of iridium. We find that thermally nonlabile adducts are labilized by ultraviolet irradiation of fluid solutions, under an inert gas purge, and of glasses at low temperature.

Experimental Section

Samples of $[IrCl(CO)(Ph_3P)_2]$ were obtained from Alfa Chemical Corporation and were used without further purification. $[Ir(2\text{-phos})_2]Cl$ and $[Ir(2{=}phos)_2]Cl$ were prepared by published methods.[9] $[IrI(CO)(PPh_3)_2]$ was provided by Professor J. G. Gordon, and $[O_2Co(2{=}phos)_2]ClO_4$ by Dr. V. Miskowski. Infrared and electronic absorption spectra of all five complexes were measured and found to be in excellent agreement with published data.[2,9,10] Tetramethylethylene (TME) was obtained from the Aldrich Chemical Co. All other chemicals used were reagent grade.

Preparation of Adducts. Adduct complexes were prepared by passing gaseous oxygen, hydrogen, or hydrogen chloride through solutions containing the four-coordinate iridium(I) complexes. Benzene solutions were employed for $[IrCl(CO)(Ph_3P)_2]$ and $[IrI(CO)(Ph_3P)_2]$, whereas adducts of $[Ir(2\text{-phos})_2]Cl$ and $[Ir(2{=}phos)_2]Cl$ were prepared in ethanol or acetonitrile. The reactions were considered to be complete when the characteristic visible absorption bands of the square-planar complexes disappeared. $[O_2IrCl(CO)(Ph_3P)_2]$ was isolated by concentrating the benzene solution, cooling in an ice bath under an atmosphere of oxygen, and filtering the resultant precipitate. $[O_2Ir(2\text{-phos})_2]Cl$ and $[O_2Ir(2{=}phos)_2]Cl$ were isolated by evaporation of the solvent followed by recrystallization from methylene chloride–diethyl ether. $[O_2IrI(CO)(Ph_3P)_2]$ was not isolated from benzene solution. The reactions with H_2 and HCl are much faster than the corresponding reactions with oxygen, and solid complexes were isolated in all cases.

Solution Irradiation. All irradiations were performed with a 150-W medium-pressure Hg lamp equipped with Corning glass 0-52 and 7-37 filters which pass only 366-nm light. The intensity of the lamp is ca. 10^{-7} einstein/min. The compound to be studied was dissolved in a suitable solvent (benzene for neutral complexes; ethanol or acetonitrile for ionic complexes) and placed in a 1-cm quartz spectrophotometer cell fitted with 3-in. neck and a serum cap. Solutions were purged by passing the appropriate gas (Ar, O_2, H_2) through the serum cap using standard syringe needle techniques.[16] The quartz cell was placed in a jacketed cell holder in front of the lamp and cooled with tap water. The cell was periodically removed and the absorption spectrum of the solution measured.

The relative rate of reductive-elimination of H_2 from $[H_2IrCl(CO)(PPh_3)_2]$ was determined by following the electronic absorption spectral changes of two 3-ml aliquots from a benzene so-

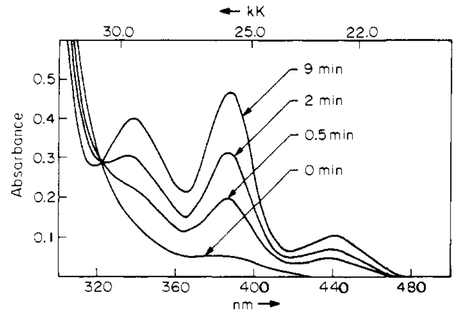


Figure 1. Electronic spectral changes accompanying 366-nm (27.3 kK) photolysis of $[O_2IrCl(CO)(Ph_3P)_2]$ in benzene solution.

lution of the complex. The 3-ml samples were placed in spectrophotometer cells, and one cell was irradiated while the other cell was shielded from light. A slow Ar purge was maintained in each cell and great care was taken to ensure that the same purge rate was used in both solutions.

Experiments to test for the production of O_2 ($^1\Delta_g$) were conducted by irradiating 10^{-3} M ethanol solutions of $[O_2Ir(2\text{-}phos)_2]Cl$ and 10^{-3} M benzene solutions of $[O_2IrCl(CO)(PPh_3)_2]$, each approximately 0.1 M in TME. The solutions were irradiated for various time periods (1-48 hr), both with and without a continuous O_2 purge. Aliquots were periodically taken and, after addition of BH_4^-, were analyzed by VPC techniques.

Low Temperature Glass Irradiation. The appropriate complex was dissolved in a 12:1 EPA:chloroform mixture and placed in a 20 cm long 15 mm o.d. glass tube with a round bottom. The solution was then cooled with liquid nitrogen in an unsilvered Pyrex dewar to yield a clear glass. Irradiation was conducted by placing the dewar in front of a Hanovia 1000-W Hg-Xe lamp equipped with water and Pyrex filters. A portion of the dewar was covered with black tape to limit the area of irradiation to about 1-in. of the sample tube.

Spectral Measurements. Infrared spectra were recorded on a Perkin-Elmer 225 infrared spectrophotometer using KBr pellets prepared from ir spectrograde powder (MC and B), or in 0.1 mm path length NaCl liquid ir cells. Electronic absorption spectra were measured using a Cary 17 spectrophotometer. Spectra at liquid nitrogen temperature were obtained using a low temperature dewar fitted with Suprasil quartz windows, and modified to hold a standard 1.00-cm cell. Emission and excitation spectra were recorded on a Perkin-Elmer MPF-3A fluorescence spectrophotometer fitted with a low temperature, unsilvered Pyrex dewar.

Results and Discussion

Although $[O_2IrCl(CO)(PPh_3)_2]$ loses O_2 when solutions of the complex are purged with inert gas, the reaction is not detectable in the absence of a purge. Apparently, the equilibrium

$$[O_2IrCl(CO)(PPh_3)_2] \rightleftharpoons [IrCl(CO)(PPh_3)_2] + O_2 \quad (1)$$

lies far to the left, and yellow solutions of $[IrCl(CO)(PPh_3)_2]$ slowly add oxygen from room air to give colorless solutions of the adduct. Irradiation of air-saturated benzene solutions of $[O_2IrCl(CO)(PPh_3)_2]$, however, does induce loss of oxygen and regeneration of the square-planar species (Figure 1). As the photolysis proceeds, the 22.7, 25.8, and 29.5 kK bands of $[IrCl(CO)(PPh_3)_2]$ grow in, with the isosbestic point indicating a smooth conversion to a single product. *Even in air-saturated solutions the deoxygenation reaction can be made to go essentially to completion.* Electronic absorption spectral measurements show that the thermal oxygenation-photochemical deoxygenation reactions can be cycled several times without decomposition of the complex. Although some decomposition does occur upon very prolonged irradiation in the absence of oxygen, the process has a low quantum yield. Solutions of $[IrCl(CO)(PPh_3)_2]$ in toluene and benzene were irradiated with and without added PPh_3, and the carbonyl stretching frequency at 1965 cm^{-1} was monitored.[17] In no case did either the intensity or band shape change at an appreciable rate.

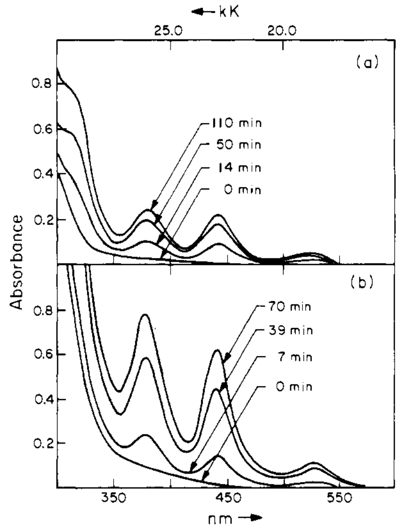
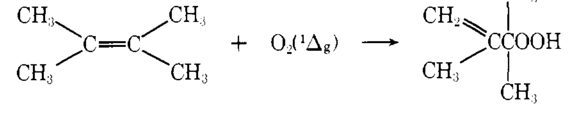


Figure 2. Electronic spectral changes accompanying 366-nm (27.3 kK) photolysis of ethanol solutions of (a) $[O_2Ir(2\text{-}phos)_2]Cl$ and (b) $[O_2Ir(2{=}phos)_2]Cl$.

The complex $[O_2IrI(CO)(PPh_3)_2]$, which binds oxygen much more strongly than the chloride analog and cannot be readily deoxygenated thermally,[2,11] undergoes photochemical reactions very similar to those described above. Spectral changes indicate that irradiation of the adduct does induce deoxygenation and regeneration of $[IrI(CO)(PPh_3)_2]$. However, the square-planar complex itself is quite photosensitive and rapidly decomposes when irradiated in solution. Consequently, the deoxygenation cannot be made to go to completion, and the oxygenation-deoxygenation reactions cannot be cycled.

Perhaps of greatest interest is the observation that both $[O_2Ir(2\text{-}phos)_2]^+$ and $[O_2Ir(2{=}phos)_2]^+$ can be photochemically deoxygenated (Figure 2). The O-O distance in $[O_2Ir(2\text{-}phos)_2]^+$ is the longest yet found in Ir(I)-oxygen adducts and neither complex has an observable rate of thermal deoxygenation.[18] The photoelimination reaction only proceeds to a significant extent if solutions are purged with an inert gas during irradiation. In air-saturated solutions, thermal addition is rapid enough to maintain the system nearly completely in the oxygenated form at the photostationary states achieved with the light intensities used in this work. With purging, photoinduced deoxygenation can be carried to high conversion, and when oxygen is readmitted to the solutions, readdition occurs and the systems can be cycled repeatedly. The square-planar complexes appear to be completely insensitive to uv irradiation, even in the presence of oxygen. These results have some practical utility, as very severe conditions were required previously to regenerate the square planar-species once oxygenation had occurred.[19,20]

Experiments have been performed to determine if photolysis produces the $^1\Delta_g$ excited state of oxygen. Foote has shown[21] that O_2 ($^1\Delta_g$) reacts with tetramethylethylene (TME) according to eq 2. The peroxide can be reduced to


(2)

$$(CH_3)_2C{=}C(CH_3)_2 + O_2(^1\Delta_g) \longrightarrow CH_2{=}C(CH_3)C(CH_3)_2OOH \quad (2)$$

2,3-dimethyl-3-hydroxy-1-butene by BH_4^-, and the alcohol can be detected by VPC techniques. Solutions of $[Ir(2\text{-}phos)_2O_2]^+$ and $[IrCl(CO)(PPh_3)_2O_2]$ were irradiated in the presence of TME, with and without an oxygen purge, and BH_4^- was added. In no case were quantities of 2,3-dimethyl-3-hydroxy-4-butene detected greater than the very small amount found in control experiments. Apparently singlet oxygen is not formed in the photoinduced deoxygenation reactions.

Dehydrogenation and Dehydrochlorination Reactions. Molecular hydrogen adds to $[IrCl(CO)(PPh_3)_2]$ to form *cis*-$[H_2IrCl(CO)(PPh_3)_2]$,[2] a rather stable compound which does, however, eliminate hydrogen when solutions are purged with an inert gas at room temperature. Irradiation of purged solutions of the adduct markedly enhances the rate of dehydrogenation (by a factor of 2.6 at the same purge rate), although no photochemical reductive-elimination is observed without the purge. Addition of H_2 to $[IrI(CO)(PPh_3)_2]$ is thermally "irreversible", but when solutions of the adduct are irradiated and purged, loss of H_2 occurs and the square-planar complex is regenerated. Photosensitivity of the latter species precludes efficient recycling.

Dehydrogenation of the "irreversible" adducts, *cis*-$[H_2Ir(2\text{-}phos)_2]^+$[9] and *cis*-$[H_2Ir(2{=}phos)_2]^+$,[13] can also be induced by irradiation of purged solutions. The dehydrogenation can be made to go to completion and the systems can be cycled many times. Although 366-nm irradiation is effective in causing dehydrogenation of *cis*-$[H_2Ir(2\text{-}phos)_2]^+$, it will not induce loss of H_2 from *cis*-$[H_2Ir(2{=}phos)_2]^+$. However, dehydrogenation of the latter complex does occur with 313- or 254-nm irradiation. This observation is consistent with the electronic absorption spectra of the compounds to be discussed later.

Hydrogen chloride reacts with $[IrCl(CO)(PPh_3)_2]$,[2,14] $[Ir(2\text{-}phos)_2]^+$,[9] and $[Ir(2{=}phos)_2]^+$,[13] to give thermally stable HCl adducts, which are probably best considered as H^- and Cl^- complexes of Ir(III). *Irradiation of purged solutions of* $[(H)(Cl)IrCl(CO)(PPh_3)_2]$ *induces loss of HCl and regeneration of* $[IrCl(CO)(PPh_3)_2]$. The photoelimination reaction can be made to go to completion, and the rate of dehydrochlorination is about one-fifth the rate of dehydrogenation of $[H_2IrCl(CO)(PPh_3)_2]$ under similar experimental conditions. Irradiation of purged solutions of $[H(Cl)Ir(2\text{-}phos)_2]^+$ and $[H(Cl)Ir(2{=}phos)_2]^+$ does not lead to regeneration of $[Ir(2\text{-}phos)_2]^+$ and $[Ir(2{=}phos)_2]^+$. Although electronic absorption spectral changes are consistent with some type of photochemical reaction, the lack of good isosbestic points suggests that secondary photoprocesses occur. No product has been isolated from these solutions.

Low Temperature Photolysis. Interesting results were obtained when the adduct complexes were irradiated at 77°K in an EPA glass. The irradiations were conducted through a clear Pyrex dewar filled with liquid nitrogen. All but a small area was masked so that light reached only a well-defined region of the sample tube. When the H_2 and O_2 adducts of $[IrCl(CO)(PPh_3)_2]$ were irradiated, the portion of the sample that was exposed changed from colorless to yellow. The yellow color is that of $[IrCl(CO)(PPh_3)_2]$, and thus the reductive-elimination reactions can also be induced in a solid matrix at 77°K. When the samples were allowed to warm to room temperature, the color persisted in solution, but then slowly disappeared as oxygenation or hydrogenation occurred.

When O_2 and H_2 adducts of $[Ir(2\text{-}phos)_2]^+$ and $[Ir(2{=}phos)_2]^+$ were immersed in liquid nitrogen during irradiation, no color changes were observed in the exposed areas. However, in each case if a sample was removed from the nitrogen bath after the irradiation and allowed to warm slightly but not enough to melt the glass, the irradiated area turned the bright orange color associated specifically with low energy d → a_{2u} absorptions of the complexes in planar geometry.[22] If the sample was then cooled again to 77°K, the orange coloration persisted and upon excitation also showed characteristic a_{2u} → d emission.[22] It is reasonable to suggest, therefore, that the photoinduced reductive-elimination reaction occurs in a glass at 77°K, but that the rigid medium prohibits the IrP_4 system from relaxing to square-planar geometry.

Table I. Lowest Electronic Absorption Bands in Iridium Adduct Complexes

Complex	$\bar{\nu}_{max}$, kK	ϵ_{max}, M^{-1} cm^{-1}
$[H_2IrBr(CO)(P(C_6H_{11})_3)_2]$[a]	27.4	38.6
$[H_2IrI(CO)(P(C_6H_{11})_3)_2]$[a]	27.0	34.2
$[H_2IrCl(CO)(P(i\text{-}C_3H_7)_3)_2]$[a]	27.6	35.2
$[H_2IrBr(CO)(P(i\text{-}C_3H_7)_3)_2]$[a]	27.4	6.6
$[H_2IrI(CO)(P(i\text{-}C_3H_7)_3)_2]$[a]	27.0	26.1
$[H_2Ir(2\text{-}phos)_2]Cl$[b]	27.0	26
$[H_2Ir(2{=}phos)_2]Cl$[b]	28.6	40
$[H_2IrCl(CO)(PPh_3)_2]$[b]	26.3	25
$[O_2Ir(2\text{-}phos)_2]Cl$[b]	27.4	200
$[O_2Ir(2{=}phos)_2]Cl$[b]	26.0	130
$[H(Cl)Ir(2\text{-}phos)_2]Cl$[b]	27.8	60
$[H(Cl)Ir(2{=}phos)_2]Cl$[b]	27.8	135
$[H(Cl)IrCl(CO)(PPh_3)_2]$[b]	26.7	140

[a] Reference 23. [b] This work.

Spectroscopic Results and Mechanistic Considerations. Electronic absorption spectra of the adducts were measured with the aim of making definitive band assignments, especially for the least energetic transitions, and of elucidating the nature of the photochemically active excited states. Spectral data for some of the adducts of $[IrCl(CO)(PPh_3)_2]$, $[Ir(2\text{-}phos)_2]^+$, and $[Ir(2{=}phos)_2]^+$, along with data reported by Strohmeier[23] for a series of $[H_2IrX(CO)L_2]$ complexes, are summarized in Table I.

Each of the adducts examined in this work shows a low intensity shoulder (ϵ <200) in the 26.3–27.8-kK region. This shoulder is part of an intense absorption system, which includes several additional shoulders (ϵ >5000) between 33.3 and 43.4 kK. The intense absorption must be due in part to phosphine intraligand transitions, as the spectrum of the free ligand exhibits similar bands. However, the 26.3–27.8-kK shoulder has no counterpart in the spectrum of any of the uncomplexed phosphines, suggesting that one or more metal orbitals are involved in the transition. The low-energy shoulder falls in the region of 313 or 366 nm irradiation, so it must represent a transition to a photochemically active excited state.

The relatively low intensity of the shoulder suggests that the transition is at least partially forbidden. Further, the presence of this feature in the 2-phos and 2=phos complexes establishes that the transition does not involve an orbital localized on either CO or coordinated halide. The very small shift in band position upon variation of the halide in the complexes examined by Strohmeier[23] rules out both d-d and ligand-to-metal charge transfer (LMCT) interpretations, as the energies of the metal dσ^* orbitals (d_{z^2}, $d_{x^2-y^2}$), in which such transitions would terminate, are expected to be moderately sensitive to X. However, the energies of the metal dπ orbitals (d_{xz}, d_{yz}, d_{xy}) should not be as dependent on such changes in the nature of the coordinated halide, and a metal-to-ligand charge transfer (MLCT) transition originating from these orbitals fits the observations satisfactorily. It may be noted that the absorption spectra of the square-planar $[IrX(CO)L_2]$ complexes, where the low energy bands are also believed to be MLCT in nature, show little X dependence.[22,24]

If the proposed MLCT assignment is correct, the metal atom becomes electron poor in the excited state

$$\mathrm{Ir^{III}P_4} \xrightarrow{h\nu} \mathrm{Ir^{IV}P_4^{\cdot}}$$

Oxidation of the electron-rich adduct fragments [O_2^{2-}, (H^-)(Cl^-), or (H^-)(H^-)] by this "Ir(IV)" center should be highly likely, yielding diatomic product molecules. However, the detailed pathway of photoelimination is unknown. Turning to the specific case of H_2 elimination, the most probable stepwise mechanism would involve homolysis of a single bond, producing Ir(II) and a hydrogen atom. We were initially persuaded against this mechanism, because irradiation of [$H_2IrCl(CO)(Ph_3P)_2$] in toluene does not produce any bibenzyl.[25] If hydrogen atoms were produced, one would expect them to react with toluene to produce benzyl radicals, which might ultimately couple. However, the argument is not compelling, because it is conceivable that the metal hydride is a very reactive hydrogen donor and that benzyl radicals would be efficiently scavenged by reaction 3.

$$\mathrm{PhCH_2\cdot} + [\mathrm{H_2IrCl(CO)(Ph_3P)_2}] \longrightarrow \mathrm{PhCH_3} + [\mathrm{HIrCl(CO)(Ph_3P)_2}] \quad (3)$$

Concerted elimination of diatomic product molecules also represents a possible nonradiative decay pathway. None of our experimental observations rules out such a pathway, and the simplicity of a concerted process is attractive. Experiments on isotopically labeled adduct complexes will be required to probe the mechanistic details of photoelimination. Such experiments are now in progress in our laboratories.

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(19) Heating a sample of [$O_2Ir(2\text{-phos})_2$]ClO_4 at 150° for 24 hr under vacuum results in loss of O_2 and formation of [$Ir(2\text{-phos})_2$]ClO_4 (J. Gordon, private communication).

(20) It should be noted, however, that [$O_2Co(2{=}phos)_2$]$^+$ does not deoxygenate cleanly upon irradiation. No evidence of reaction was observed upon 436-nm irradiation of this complex in solution, even with a strong inert gas purge. Irradiation at 366 nm induces decomposition of the complex, but [$Co(2{=}phos)_2$]$^+$ is not formed.

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