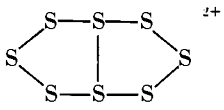
sition metals. Oxidation cyclooctasulfur produces the bicyclic cation 7.[46] Further examples of such transanular oxidations and oxidative-additions may be anticipated.



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References and Notes

(1) W. P. Griffith, "The Chemistry of the Rarer Platinum Metals", Interscience, New York, N.Y., 1967.
(2) B. R. James, "Homogeneous Hydrogenation", Wiley, New York, N.Y., 1973.
(3) K. R. Mann, J. G. Gordon II, and H. B. Gray, *J. Am. Chem. Soc.*, **97**, 3553 (1975).
(4) J. S. Miller and A. J. Epstein, *Prog. Inorg. Chem.*, **20**, 1 (1976).
(5) H. Isci and W. R. Mason, *Inorg. Chem.*, **13**, 1175 (1974).
(6) M. M. Olmstead and A. L. Balch, *J. Am. Chem. Soc.*, **98**, 2354 (1976).
(7) C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2956 (1970).
(8) F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc.*, **96**, 4422 (1974).
(9) A. Camus, G. Narding, and L. Randaccio, *Inorg. Chim. Acta*, **12**, 23 (1975).
(10) G. Nardin, L. Randaccio, and E. Zangrando, *J. Chem. Soc., Dalton Trans.*, 2566 (1975).
(11) F. H. Carré, F. A. Cotton, and B. A. Frenz, *Inorg. Chem.*, **15**, 380 (1976).
(12) J. T. Mague, *Inorg. Chem.*, 8, 1975 (1969).
(13) J. T. Mague and J. P. Mitchener, *Inorg. Chem.*, **8**, 119 (1969).
(14) F. A. Cotton and J. G. Norman, Jr., *J. Am. Chem. Soc.*, **93**, 80 (1971).
(15) K. G. Caulton and F. A. Cotton, *J. Am. Chem. Soc.*, **93**, 1914 (1971).
(16) J. Halpern, E. Kimura, J. Molin-Case, and C. S. Wong, *Chem. Commun.*, 1207 (1971).
(17) O. S. Mills and E. F. Paulus, *J. Organomet. Chem.*, **10**, 331, 337 (1967).
(18) O. S. Mills and E. F. Paulus, *J. Organomet. Chem.*, **11**, 587 (1968).
(19) E. R. Corey, L. F. Dahl, and W. Beck, *J. Am. Chem. Soc.*, **85**, 202 (1963).
(20) O. S. Mills and J. P. Nice, *J. Organomet. Chem.*, **10**, 337 (1967).
(21) C. H. Wei, G. R. Wilkes, and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 4792 (1967).
(22) E. O. Fischer, O. S. Mills, E. F. Paulus, and H. Wawersik, *Chem. Commun.*, 643 (1967).
(23) C. B. Dammann, P. Singh, and D. J. Hodgson, *J. Chem. Soc., Chem. Commun.*, 586 (1972).
(24) R. E. Schuster, J. E. Scott, and J. Casanova, Jr., *Org. Synth.*, **46**, 75 (1966).
(25) J. Casanova, Jr., N. D. Werner, and R. E. Schuster, *J. Org. Chem.*, **31**, 3473 (1966).
(26) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).
(27) A. L. Balch and J. Miller, *J. Organomet. Chem.*, **32**, 263 (1971).
(28) P. R. Branson and M. Green, *J. Chem. Soc., Dalton Trans.*, 1303 (1972).
(29) J. W. Dart, M. K. Lloyd, R. Mason, and J. A. McCleverty, *J. Chem. Soc., Dalton Trans.*, 2039 (1973).
(30) J. W. Dart, M. K. Lloyd, R. Mason, and J. McCleverty, *J. Chem. Soc., Dalton Trans.*, 2046 (1973).
(31) R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964).
(32) J. R. Boehm, D. J. Doonan, and A. L. Balch, *J. Am. Chem. Soc.*, **98**, 4845 (1976).
(33) J. R. Boehm and A. L. Balch, to be submitted for publication.
(34) G. L. Geoffroy, M. S. Wrighton, G. S. Hammond, and H. B. Gray, *J. Am. Chem. Soc.*, **96**, 3105 (1974).
(35) H. Isci and W. R. Mason, *Inorg. Chem.*, **14**, 913 (1975).
(36) J. P. Fackler, *Prog. Inorg. Chem.*, **21**, 55 (1976).
(37) L. F. Dahl, C. Martell, and D. L. Wampler, *J. Am. Chem. Soc.*, **83**, 1761 (1961).
(38) S. B. Piepho, P. N. Schatz, and A. J. McCaffery, *J. Am. Chem. Soc.*, **91**, 5994 (1973).
(39) L. V. Interrante and R. P. Messmer, *Chem. Phys. Lett.*, **26**, 225 (1974).
(40) L. F. Dahl, C. Martell, and D. L. Wampler, *J. Am. Chem. Soc.*, **83**, 1761 (1961).
(41) J. Coetzer and G. Gafner, *Acta Crystallogr., Sect. B*, **26**, 985 (1970).
(42) C. A. Tolman, P. Z. Meakin, D. L. Lindner, and J. P. Jesson, *J. Am. Chem. Soc.*, **96**, 2762 (1974).
(43) L. Dubicki and R. L. Martin, *Inorg. Chem.*, **9**, 673 (1970).
(44) H. Schmidbaur and R. Franke, *Inorg. Chim. Acta*, **13**, 85 (1975).
(45) H. Schmidbaur, J. R. Mandl, A. Frank, and G. Huttner, *Chem. Ber.*, **109**, 466 (1976).
(46) C. Davies, R. J. Gillespie, J. J. Park, and J. Passmore, *Inorg. Chem.*, **10**, 2781 (1971).

Photochemistry of Transition Metal Hydride Complexes. 1. Photoinduced Elimination of Molecular Hydrogen from $[IrClH_2(PPh_3)_3]$ and $[IrH_3(PPh_3)_3]$

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Abstract: Although $[IrClH_2(PPh_3)_3]$, *mer*-$[IrH_3(PPh_3)_3]$, and *fac*-$[IrH_3(PPh_3)_3]$ will not lose hydrogen under a variety of thermal conditions, irradiation with ultraviolet light readily induces elimination of H_2. Irradiation of $[IrClH_2(PPh_3)_3]$ with ultraviolet light or sunlight gives formation of $[IrCl(PPh_3)_3]$ with a 254-nm quantum yield of 0.56 ± 0.03. Irradiation of *mer*-$[IrH_3(PPh_3)_3]$ and *fac*-$[IrH_3(PPh_3)_3]$ leads to H_2 loss with subsequent formation of internally metallated $[\overline{Ir(C_6H_4P}Ph_2)(PPh_3)_2]$. The results reported herein suggest that photoinduced elimination of H_2 is a general process for di- and polyhydride complexes of iridium. The lack of production of HD upon photolysis of an $[IrClH_2(PPh_3)_3]$–$[IrClD_2(PPh_3)_3]$ mixture demonstrates that the photoelimination of H_2 from $[IrClH_2(PPh_3)_3]$ proceeds in a concerted fashion. A molecular orbital description of the complexes is proposed, and the photoactive excited state is believed to involve population of an iridium-H_2 antibonding orbital. The $[IrClH_2(PPh_3)_3]$–$[IrCl(PPh_3)_3]$ system is an attractive model for hydrogen storage and energy storage.

Transition metal hydride complexes have become an important class of compounds in inorganic and organometallic chemistry, and the field has expanded tremendously since the 1955 report[1] of the first thermally stable hydride complex, $[Re(\eta^5\text{-}C_5H_5)_2H]$. Many reviews have been published[2-7] describing the properties of metal hydrides, and in a recent literature survey[8] of the three catalytically important metals, ruthenium, rhodium and iridium, over 2000 known hydride complexes were uncovered. Transition metal hydrides play a key role in many homogeneous catalytic reactions, are useful synthetic intermediates, have promise as hydrogen and energy storage systems, and have been proposed[9] as important intermediates for obtaining molecular hydrogen from water.

In spite of the very large number of known hydride complexes and their importance in homogeneous catalysis, relatively few photochemical investigations have been conducted on these compounds. It is appropriate to briefly review those studies here. In 1968, Sacco and Aresta reported[10] that in sunlight $[FeH_2(N_2)(PEtPh_2)_3]$ undergoes reversible loss of hydrogen,

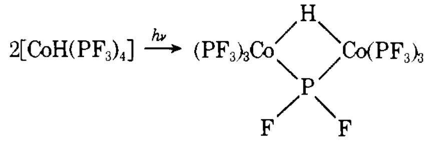
$$[FeH_2(N_2)(PEtPh_2)_3] \xrightarrow{h\nu} H_2 + [\overline{FeH(C_6H_4P}EtPh)(N_2)(PEtPh_2)_2] \quad (1)$$

It was proposed that irradiation induces formation of coordinatively unsaturated $[Fe(N_2)(PEtPh_2)_3]$ and in a subsequent step iron inserts into an ortho C–H bond of PPh_3 (ortho-metallation). In a separate report,[11] however, Koerner von Gustorf and co-workers present evidence that N_2 rather than H_2 is lost upon photolysis, but give relatively few details. Darensbourg[12] reported that irradiation of $[FeH_2(N_2)(PEtPh_2)_3]$ in the presence of excess carbon monoxide yields $[Fe(CO)_4(PEtPh_2)]$ and *trans*-$[Fe(CO)_3(PEtPh_2)_2]$,

$$[FeH_2(N_2)(PEtPh_2)_3] + CO \xrightarrow{h\nu} [Fe(CO)_4(PEtPh_2)] + trans\text{-}[Fe(CO)_3(PEtPh_2)_2] \quad (2)$$

Green and co-workers have shown[13-15] that UV irradiation of solutions of $[W(\eta^5\text{-}C_5H_5)_2H_2]$ results in formation of $[W(\eta^5\text{-}C_5H_5)_2H(R)]$ or $[W(\eta^5\text{-}C_5H_5)_2R_2]$, in which R is derived from the solvent. Irradiation of the dihydride complex in benzene, for example, produces $[W(\eta^5\text{-}C_5H_5)_2H(C_6H_5)]$,[14] and in methanol $[W(\eta^5\text{-}C_5H_5)_2H(OMe)]$ and $[W(\eta^5\text{-}C_5H_5)_2Me(OMe)]$ are formed.[15] These reactions presumably occur through photoinduced elimination of H_2, yielding reactive tungstenocene, which then inserts into a C–H or O–H bond of a solvent molecule.

In 1971 Kruck and co-workers showed[16] that UV irradiation of the monohydride $[IrH(PF_3)_4]$ produced H_2 and $[Ir_2(PF_3)_8]$. Although this reaction apparently occurs with a very low quantum yield, the system is particularly interesting, since $[Ir_2(PF_3)_8]$ reacts with water to regenerate $[IrH(PF_3)_4]$,[16] thus completing a cycle for the photochemical generation of H_2 from water. These same workers have also shown[17] that irradiation of the cobalt analogue, $[CoH(PF_3)_4]$, produces the hydride and phosphide bridged complex shown in eq 3. In 1972,

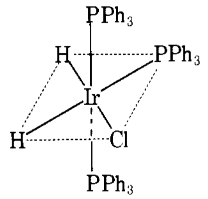


$$2[CoH(PF_3)_4] \xrightarrow{h\nu} (PF_3)_3Co(\mu\text{-}H)(\mu\text{-}PF_2)Co(PF_3)_3 \quad (3)$$

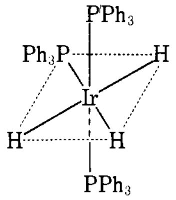
Camus and co-workers reported[18] that the elimination of hydrogen from $[CoH_2(Chel)(PR_3)_2]$ (Chel = 2,2′-bipyridine, 1,10-phenanthroline) is light accelerated.

In a study of the photochemical properties of several dihydride complexes of iridium, Geoffroy, Gray, and Hammond[19] observed that irradiation of argon-purged solutions of $[IrH_2(Ph_2PCH_2CH_2PPh_2)_2]^+$, $[IrH_2(Ph_2PCHCHPPh_2)_2]^+$, and $[IrClH_2(CO)(PPh_3)_2]$ leads to elimination of H_2 and formation of the stable Ir(I) complexes $[Ir(Ph_2PCH_2CH_2PPh_2)_2]^+$, $[Ir(Ph_2PCHCHPPh_2)]^+$, and $[IrCl(CO)(PPh_3)_2]$. Of the dihydrides studied only $[IrClH_2(CO)(PPh_3)_2]$ loses hydrogen thermally, and photolysis is the only known method for effecting elimination of H_2 from the diphosphine complexes. The nature of the active excited state in these complexes was not identified, and the mechanism of H_2 elimination was not unambiguously determined.

Because of the importance of transition metal hydride complexes in homogeneous catalysis and their possible role in the photoassisted production of H_2 from water, we have undertaken a systematic investigation into the photochemical properties of this class of compounds. Our first objective is to test the generality of the photoinduced elimination of molecular hydrogen from stable di- and polyhydride complexes of the transition elements, and we have chosen to initially examine the well characterized triphenylphosphine complexes, $[IrClH_2(PPh_3)_3]$, *mer*-$[IrH_3(PPh_3)_3]$, and *fac*-$[IrH_3(PPh_3)_3]$. $[IrClH_2(PPh_3)_3]$ was first prepared by Vaska,[20] who reported it to be an air stable, light-sensitive white solid, and it was subsequently shown by NMR and infrared analysis to have the configuration **1**.[21] The complex has also been prepared by Bennett and Milner[22] by the irreversible addition of H_2 to $[IrCl(PPh_3)_3]$. *mer*-$[IrH_3(PPh_3)_3]$ and *fac*-$[IrH_3(PPh_3)_3]$ are easily prepared[23] by heating $Na_2[IrCl_6]$, PPh_3, and $NaBH_4$ in ethanol, and have structures **2** and **3**.[24] All three complexes are quite resistant to thermal loss of hydrogen. For example, we have shown that no loss of H_2 occurs when solutions are purged with an inert gas or when solid samples are heated to 150 °C for 24 h under vacuum. The results reported herein, however, demonstrate that irradiation with ultraviolet light gives ready elimination of H_2.

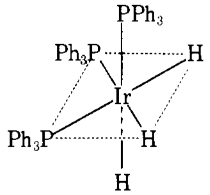


1



2

mer-$[IrH_3(PPh_3)_3]$



3

fac-$[IrH_3(PPh_3)_3]$

Experimental Section

The complexes $[IrClH_2(PPh_3)_3]$,[20] $[IrClD_2(PPh_3)_3]$,[22] *mer*- and *fac*-$[IrH_3(PPh_3)_3]$,[23] $[IrCl_2H(PPh_3)_3]$,[25] and $[IrCl(PPh_3)_3]$[26] were prepared according to published procedures. Pure *mer*-$[IrH_3(PPh_3)_3]$ was isolated by recrystallization from benzene–methanol. Solvents used for absorption spectra were Fisher spectroquality. All other chemicals and solvents used were reagent grade. All experiments and manipulations of compounds were performed under vacuum or under an N_2 atmosphere, unless otherwise specified.

General Irradiation Procedures. Irradiations were conducted at 366 nm using a 450-W Hanovia medium-pressure Hg lamp equipped with Corning glass 0-52 and 7-37 filters ($I \approx 10^{-8}$ einstein/min) or at 254 nm with a low-pressure Hg lamp ($I = 4.4 \times 10^{-7}$ einstein/min). The complex to be studied was dissolved in CH_2Cl_2 or benzene, and the solution was placed in either an evacuatable quartz UV cell which was subsequently degassed by three freeze–pump–thaw cycles, or under N_2 in a sealed 0.5-mm solution infrared cell with NaCl windows. The solution was then irradiated with the appropriate lamp, and the electronic and infrared spectra were periodically recorded. Lamp intensities were measured with ferrioxalate actinometry. The quantum yield of elimination of H_2 from degassed CH_2Cl_2 solutions of $[IrClH_2(PPh_3)_3]$ was determined by irradiating with 254 nm and monitoring the increase in absorbance at 460 nm due to formation of $[IrCl(PPh_3)_3]$.

Photolysis of $[IrClH_2(PPh_3)_3]$. Irradiation of degassed benzene or CH_2Cl_2 solutions of $[IrClH_2(PPh_3)_3]$ with $\lambda < 400$ nm induced an initial change from colorless to orange. Evaporation of the solvent from the orange solutions gave an orange solid with infrared and electronic absorption spectra identical with an authentic sample of $[IrCl(PPh_3)_3]$. Prolonged (1–5 h) photolysis of $[IrClH_2(PPh_3)_3]$ solutions induced a bleaching of the initially generated orange color and evaporation of the solvent from these solutions gave a cream-colored solid (Anal. Calcd for $[\overline{IrClH(C_6H_4P}Ph_2)(PPh_3)_2]$: Cl, 3.49; P, 9.14; C, 63.94; H, 4.44. Found: Cl, 3.62; P, 8.84; C, 63.76; H, 4.50.) which showed infrared bands (KBr) at 2050 (ν_{Ir-H}), 1575, 1560, 1550, and 717 cm^{-1} in addition to other coordinated PPh_3 vibrations. Addition

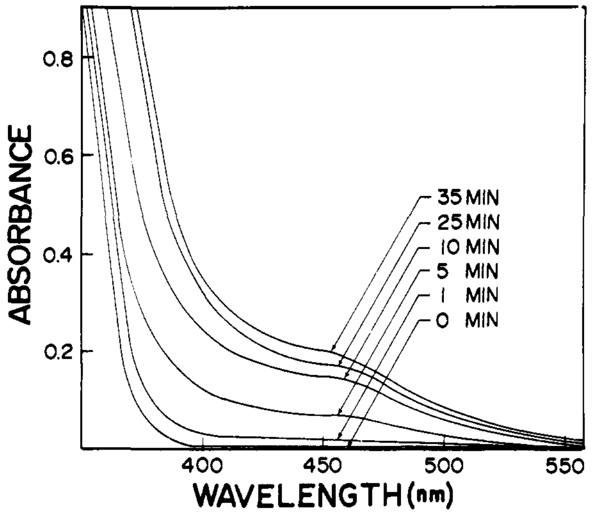


Figure 1. Electronic absorption spectral changes accompanying 366-nm photolysis of a 2.3×10^{-2} M degassed CH_2Cl_2 solution of $[IrClH_2(PPh_3)_3]$.

of H_2 to solutions containing either product readily regenerated $[IrClH_2(PPh_3)_3]$. Mass spectral analysis of the gases above 366 nm irradiated CH_2Cl_2 solutions of $[IrClH_2(PPh_3)_3]$ and $[IrClD_2(PPh_3)_3]$ showed the presence of H_2 and D_2, respectively. Prolonged photolysis (>2 h) of $[IrClD_2(PPh_3)_3]$ solutions produced small amounts of HD. Mass spectral analysis of the gases above a solution 6.77×10^{-3} M in $[IrClH_2(PPh_3)_3]$ and 7.05×10^{-3} M in $[IrClD_2(PPh_3)_3]$ irradiated with 366 nm for 15 min showed only H_2 and D_2, with no HD detected.

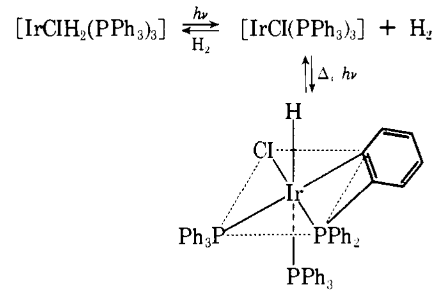
Photolysis of $[IrH_3(PPh_3)_3]$. Photolysis of degassed CH_2Cl_2 or benzene solutions of *mer*-$[IrH_3(PPh_3)_3]$ or of a mixture of *mer*- and *fac*-$[IrH_3(PPh_3)_3]$ with 366 or 254 nm induced a color change from colorless to orange. Mass spectral analysis of the gases above these irradiated solutions showed the presence of large amounts of H_2. Evaporation of solvent from solutions irradiated for 3 h gave an orange solid which showed no metal hydride vibrations in the infrared spectrum (KBr), but which showed bands at 1579, 1561, 1556, and 715 cm^{-1} not present in the spectra of *mer*-$[IrH_3(PPh_3)_3]$ or *fac*-$[IrH_3(PPh_3)_3]$. Reproducible elemental analyses of the photoproduct were not obtained, but the mass spectrum of the orange solid (70 eV) was virtually identical in mass number and relative intensity with that reported by Schwartz and Cannon[27] for $[\overline{Ir(C_6H_4P}Ph_2)(PPh_3)_2]$, with principal mass peaks at 978 ($M^+[^{193}Ir]$), 977, 976 ($M^+[^{191}Ir]$), 975, 715, 714, 713, 712, 711, 637, 636, 635, 634, 633, and 632. Addition of H_2 to a benzene solution of the photoproduct reversed the photoreaction, yielding a mixture of *mer*-$[IrH_3(PPh_3)_3]$ and *fac*-$[IrH_3(PPh_3)_3]$. Irradiation of benzene solutions of *mer*- and *fac*-$[IrH_3(PPh_3)_3]$ under an H_2 atmosphere gave precipitation of a white solid that was insoluble in water, acetone, benzene, $CHCl_3$, and CH_2Cl_2, and which showed in the infrared (KBr) a strong ν_{Ir-H} at 1948 cm^{-1}. Irradiation under a CO atmosphere produced $[IrH(CO)(PPh_3)_3]$, as evidenced by its characteristic[25] $\nu_{C\equiv O}$ at 1915 cm^{-1}.

Spectral Measurements. Infrared spectra were recorded on a Perkin-Elmer 621 grating infrared spectrophotometer using KBr disks prepared from IR spectroquality powder (MCB) or 0.5-mm path length NaCl solution infrared cells. Electronic absorption spectra were recorded with a Cary 17 spectrophotometer using 1-cm quartz spectrophotometer cells. Mass spectra were recorded with an AEI MS902 mass spectrometer.

Results

We have observed that $[IrClH_2(PPh_3)_3]$ is quite photosensitive, and when solid samples or solutions of the complex are irradiated with sunlight or fluorescent room light a rapid color change from white to orange occurs. Mass spectral analyses of the gases above irradiated solid samples show the presence of large amounts of hydrogen. The electronic absorption spectral changes which occur during 366-nm photolysis of a degassed 2.3×10^{-2} M CH_2Cl_2 solution are shown in Figure 1. The spectrum of $[IrClH_2(PPh_3)_3]$ is featureless below 300 nm, and as the irradiation proceeds a new band appears and grows in at 449 nm. This band is identical in position and shape with that displayed by an authentic sample of $[IrCl(PPh_3)_3]$, prepared by the reaction of $[IrCl(N_2)(PPh_3)_2]$ with PPh_3.[26] When the photolysis is followed in the infrared spectral region, solutions show a steady decrease in intensity of the metal hydride vibrations at 2215 and 2110 cm^{-1}, and no new bands appear between 1800 and 2300 cm^{-1}.

Scheme I

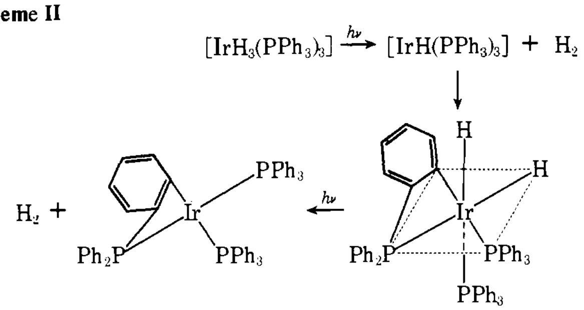


The mass spectral analysis and the electronic and infrared spectral changes detailed above demonstrate that hydrogen is eliminated from $[IrClH_2(PPh_3)_3]$ upon photolysis and that $[IrCl(PPh_3)_3]$ is the primary photoproduct. If the photolysis is not prolonged (<30 min), $[IrCl(PPh_3)_3]$ can be isolated as an orange solid from the irradiated solutions by evaporation of the solvent. However, under continuous irradiation the initially generated orange color slowly bleaches, and after 2-3 h of irradiation the solution is again colorless. Evaporation of the solvent from these colorless solutions gives a cream-colored solid which analyzes for $[IrCl(PPh_3)_3]$, but which shows a metal-hydride vibration at 2050 cm^{-1}. Additional weak bands at 1575, 1560, 1550, and 717 cm^{-1}, not present in the spectra of either $[IrClH_2(PPh_3)_3]$ or $[IrCl(PPh_3)_3]$, are also observed. The infrared spectrum suggests an ortho-metallated derivative similar to that which has been show by Bennett and Milner[22] to result from heating $[IrCl(PPh_3)_3]$ solutions. A similar bleaching and product are obtained when a degassed solution of $[IrCl(PPh_3)_3]$ is irradiated with 366 nm. The ortho-metallated product obtained in these experiments may be a different isomer than that initially reported by Bennett and Milner,[22] as evidenced by the different IR spectrum (ν_{M-H}: 2050 vs. 2160 cm^{-1}) and by the observation that the color bleaching is greatly enhanced by photolysis.

The entire photolysis sequence can be readily reversed by H_2, as summarized in Scheme I. A sealed degassed benzene solution of $[IrClH_2(PPh_3)_3]$, from which the photoreleased H_2 is not allowed to escape, can be recycled repeatedly (>50 cycles) through the photoinduced H_2 elimination-thermal H_2 addition reactions without any observable loss of complex. Elimination of H_2 can be induced by irradiation with $\lambda < 400$ nm, and the quantum yield of elimination measured at 254 nm by monitoring the growth of the 449-nm band of $[IrCl(PPh_3)_3]$ is 0.56 ± 0.03.

Preparation of $[IrH_3(PPh_3)_3]$ according to literature procedures[23] gives a mixture of facial and meridional isomers which are separated by recrystallization from benzene-methanol. Irradiation of a degassed benzene solution of the synthetic mixture yields a rapid decrease in intensity of the 1740-cm^{-1} ν_{Ir-H} of the meridional isomer and a much slower decrease of the 2080-cm^{-1} ν_{Ir-H} of the facial isomer and no new ν_{Ir-H} vibrations are observed. Formation of H_2 was verified by mass spectral analysis of the gases above irradiated solutions. Irradiation of a degassed benzene solution of pure *mer*-$[IrH_3(PPh_3)_3]$ leads to electronic absorption spectral changes similar to those observed for photolysis of $[IrClH_2(PPh_3)_3]$, with new absorption shoulders appearing at 375 and 430 nm.

Scheme II



The expected primary photoproduct from both isomers, $[IrH(PPh_3)_3]$, should be more reactive toward ortho-metallation than $[IrCl(PPh_3)_3]$. Indeed, evaporation of solvent from irradiated solutions of *mer*-$[IrH_3(PPh_3)_3]$ yields an orange solid, **4**, which shows no iridium-hydride vibrations, but which does show bands at 1579, 1561, 1556, and 715 cm^{-1}. We have been unable to obtain satisfactory and reproducible elemental analyses on this very air-sensitive material, but its mass spectrum is virtually identical with that reported by Swartz and Cannon[27] for a complex formulated as internally-metallated $[\overline{Ir(C_6H_4P}Ph_2)(PPh_3)_2]$. A complex of similar formulation has also been isolated by Bresadola and co-workers,[28] who reported an infrared spectrum quite similar to that of **4**. The formation of **4** suggests occurrence of ortho-metallation followed by photoelimination of a second molecule of H_2 (Scheme II). Further support for the formulation of **4** comes from our observation that the photoproduct can be converted quantitatively into $[IrH_3(PPh_3)_3]$ simply by stirring a benzene solution of the complex under an H_2 atmosphere. Evidence for the initial photoproduction of $[IrH(PPh_3)_3]$ comes from our finding that irradiation of *mer*- and *fac*-$[IrH_3(PPh_3)_3]$ under a CO atmosphere leads to formation of $[IrH(CO)(PPh_3)_3]$. This reaction does not occur thermally and $[IrH(CO)(PPh_3)_3]$ must thus be formed by the scavenging of $[IrH(PPh_3)_3]$ with CO.

If photolysis of *mer*- or *fac*-$[IrH_3(PPh_3)_3]$ is conducted under a hydrogen atmosphere, a different product is obtained. Prolonged photolysis of $[IrH_3(PPh_3)_3]$ in benzene under an H_2 purge yields a white precipitate with a single ν_{Ir-H} at 1948 cm^{-1} (KBr). This white solid is insoluble in water, acetone, benzene, chloroform, and dichloromethane, and further characterization proved impossible. A complex of similar color and solubility and with an identical infrared spectrum was prepared by Chatt and co-workers,[24] originally formulated as $[IrH_3(PPh_3)_2]$, but later proposed[29] to be $[IrH_5(PPh_3)_2]$. Irradiation under H_2 thus suppresses the principal photoreaction pathway (loss of H_2) and allows a second pathway (loss of PPh_3) to be observed

$$[IrH_3(PPh_3)_3] \xrightarrow[H_2]{h\nu} [IrH_5(PPh_3)_2] + PPh_3 \qquad (4)$$

The poor spectral properties of *mer*- and *fac*-$[IrH_3(PPh_3)_3]$ have thus far precluded quantum yield measurements, although the infrared spectral changes and the results obtained by monitoring the photolysis with high-pressure liquid chromatography[30] indicate that the meridional isomer is more photosensitive than the facial isomer.

Discussion

The results reported herein demonstrate that elimination of molecular hydrogen from these iridium di- and trihydride complexes is photoinduced. Furthermore, it is becoming evident that this is a general photoreaction pathway for polyhydride complexes of iridium.[31] The exact mechanism of the photoelimination reaction is of some importance. It has been shown[32] that the thermal elimination of molecular hydrogen from $[IrH_2(CO)_2(PMePh_2)_2]^+$ proceeds in a concerted fashion, and it is likely that thermal elimination of H_2 from other polyhydride complexes of iridium also occurs by a similar mechanism. We have conducted experiments directed toward determining the mechanism of the *photoinduced* elimination of H_2. Irradiation of degassed CH_2Cl_2 solutions of $[IrClH_2(PPh_3)_3]$ and of $[IrClD_2(PPh_3)_3]$ yields H_2 and D_2, respectively. However, prolonged photolysis (>2 h) of $[IrClD_2(PPh_3)_3]$ solutions eventually leads to detectable amounts of HD, which presumably arises from scrambling through ortho-metallation. Photolysis (λ 366 nm; 15 min irradiation) of a degassed CH_2Cl_2 solution containing equimolar amounts of $[IrClH_2(PPh_3)_3]$ and $[IrClD_2(PPh_3)_3]$ gave only H_2 and D_2, with no HD detected by mass spectrometry. The absence of HD in the gases above the irradiated solution of the mixture indicates that the photoinduced elimination of H_2 is also concerted, since elimination of $H^-(D^-)$, $H\cdot(D\cdot)$, or $H^+(D^+)$ would certainly lead to detectable amounts of HD. Further evidence of the concerted pathway for the photoinduced elimination comes from previous studies,[19] in which it was observed that irradiation of $[IrClH_2(CO)(PPh_3)_2]$ in toluene did not yield any bibenzyl, a product expected if hydrogen atoms were formed in the photoprocess.

Table I. Electronic Absorption Spectra of Some Iridium Hydride Complexes in CH_2Cl_2 Solution

Complex	λ_{max}, nm	μm^{-1} (ε)
$[IrCl_2H(PPh_3)_3]$	435	2.30 (140)
	360	2.78 (2120)
	276 sh	3.62 (19 240)
	270 sh	3.70 (20 800)
$[IrClH_2(PPh_3)_3]$	325 sh	3.08 (2700)
	260 sh	3.85 (24 900)
mer-$[IrH_3(PPh_3)_3]$	308 sh	3.25 (4450)
	265 sh	3.77 (14 500)

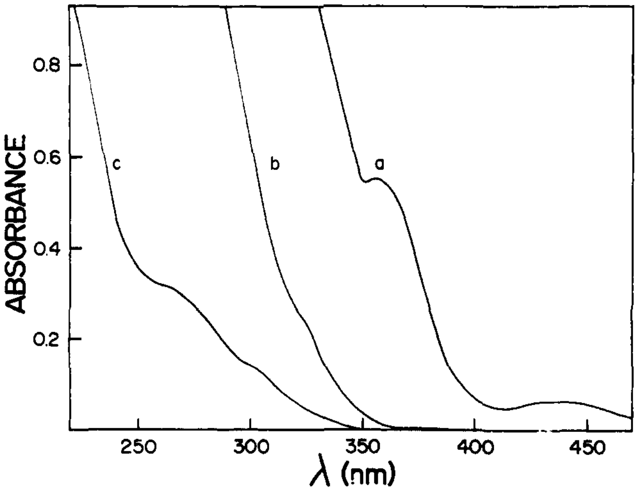


Figure 2. Electronic absorption spectra of iridium hydride complexes in CH_2Cl_2 solution: (a) $[IrCl_2H(PPh_3)_3]$ (2.5×10^{-4} M); (b) $[IrClH_2(PPh_3)_3]$ (8.3×10^{-5} M); (c) *mer*-$[IrH_3(PPh_3)_3]$ (1.4×10^{-5} M).

In an effort to determine the nature of the photoactive excited state in these hydride complexes, we have carefully examined their electronic absorption spectra. Spectral data for *mer*-$[IrH_3(PPh_3)_3]$, $[IrClH_2(PPh_3)_3]$, and $[IrCl_2H(PPh_3)_3]$ are set out in Table I, and the spectra are shown in Figure 2. The spectra of *mer*-$[IrH_3(PPh_3)_3]$ and $[IrClH_2(PPh_3)_3]$ are virtually featureless below 350 nm, whereas $[IrCl_2H(PPh_3)_3]$ shows a distinct band at 435 nm with ε 140. This latter band can readily be assigned to a ligand-field transition and analogous interpretations[33] have been made for similar bands in the

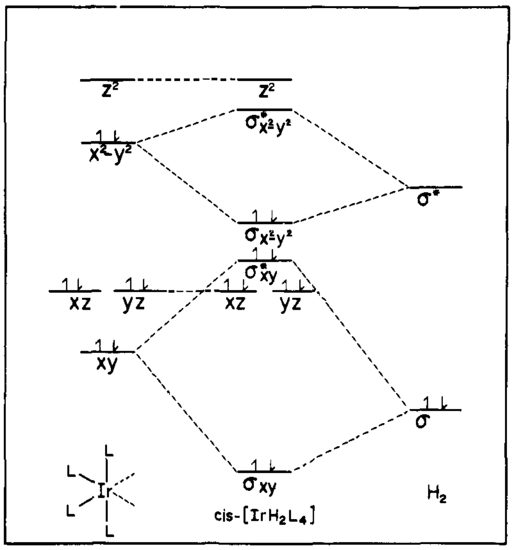


Figure 3. Molecular orbital energy level diagram for six-coordinate cis-dihydride complexes of iridium. The metal d orbitals for an IrL_4 complex in octahedral geometry with vacant cis sites are shown on the left side of the diagram, and the H_2 molecular orbitals are indicated on the right.

spectra of $[IrCl_2(Ph_2PCH_2CH_2PPh_2)_2]^+$ and $[IrCl_2(Ph_2AsCH_2CH_2AsPh_2)_2]^+$. The absence of analogous bands in the spectra of *mer*-$[IrH_3(PPh_3)_3]$ and $[IrClH_2(PPh_3)_3]$ is not surprising due to the very high position of hydride in the spectrochemical series and indicates that the ligand-field bands are shifted above 3.0 μm^{-1} in these complexes. The active excited state leading to elimination must come from one of the transitions, which appear as shoulders in the 3.0-3.3 μm^{-1} spectral region, since elimination can be induced by irradiation into this region. However, the ill-defined spectra of the photoactive complexes preclude positive assignment of these shoulders.

A molecular orbital diagram which can be drawn for an iridium dihydride complex is shown in Figure 3. The orbitals on the left side of the diagram are the d orbitals in the proper ordering for an IrL_4 complex, which is distorted to form an octahedron with vacant cis sites. The σ and σ^* orbitals of molecular hydrogen are shown on the right side of the diagram. In a *cis*-$[IrH_2L_4]$ complex, bonding of hydrogen occurs through interaction of the H_2-σ orbital with d_{xy} and through interaction of the H_2-σ^* orbital with $d_{x^2-y^2}$, and bonding and antibonding combinations are formed in each case. The exact positioning of the H_2-σ and H_2-σ^* orbitals relative to the metal d orbitals greatly influences the final molecular orbital ordering, although the positioning given in Figure 3 appears reasonable in view of the low electronegativity of H_2. A similar molecular orbital picture results if hydrogen is added as two distinct H atoms rather than as an H_2 molecule. An electronic transition which depopulates $\sigma_{x^2-y^2}$ or populates $\sigma^*_{x^2-y^2}$ should lead to a weakening of the metal H_2 bonding. The transition $\sigma_{x^2-y^2} \rightarrow \sigma^*_{x^2-y^2}$ leaves the complex with zero net bonding between H_2 and iridium, and elimination of H_2 is predicted. Although the exact nature of the photoactive excited state has not been elucidated from spectral measurements, it is attractive to view the complex in terms of the MO diagram shown in Figure 3, and we propose that $\sigma^*_{x^2-y^2}$ is populated in the photoactive state. A similar molecular orbital diagram based on semiempirical calculations has been drawn for analogous O_2, S_2, and Se_2 adducts of iridium,[34] and electrochemical studies on these complexes suggest that in the reduction of the adducts the electron goes into an orbital of the $\sigma^*_{x^2-y^2}$ type.[35] It is worthy to note that irradiation of these dioxygen[19] and disulfur[36] adducts leads to efficient elimination of O_2 and S_2.

Bennett and Milner[22] have reported that $[IrCl(PPh_3)_3]$ dehydrogenates ethanol to produce acetaldehyde and $[IrClH_2(PPh_3)_3]$. We have attempted to cycle this dehydrogenation reaction by irradiating $[IrClH_2(PPh_3)_3]$ in the presence of ethanol with the aim of catalytically dehydrogenating primary alcohols through continuous photolysis. Irradiation of $[IrClH_2(PPh_3)_3]$ in refluxing ethanol leads only to less than stoichiometric amounts of CH_3CHO and not the catalysis that was expected. It was subsequently discovered that both $[IrCl(PPh_3)_3]$ and $[IrClH_2(PPh_3)_3]$ react with acetaldehyde to produce catalytically inactive species, including *trans*-$[IrCl(CO)(PPh_3)_2]$.

The $[IrClH_2(PPh_3)_3]$-$[IrCl(PPh_3)_3]$ system serves as a model system for hydrogen storage and energy storage. $[IrCl(PPh_3)_3]$ readily takes up H_2 to store it as $[IrClH_2(PPh_3)_3]$ and then easily releases it on demand by irradiation with ultraviolet light or with sunlight. Further, when hydrogen adds to $[IrCl(PPh_3)_3]$, approximately 15-20 kcal/mol of energy is released[37]

$$[IrCl(PPh_3)_3] + H_2 \rightarrow [IrClH_2(PPh_3)_3] + 15\text{-}20\ \text{kcal/mol}$$

Irradiation of $[IrClH_2(PPh_3)_3]$ with 366 nm (78 kcal/mol) gives H_2 and $[IrCl(PPh_3)_3]$, which can be separately stored. When the components are later allowed to react to re-form $[IrClH_2(PPh_3)_3]$, approximately 15-20 kcal/mol of energy is given off and this amount of energy was then stored. Because of the high cost of iridium, a system like this can only serve as a model. Experiments are currently in progress to explore the potential of using hydride complexes of less expensive metals for hydrogen storage and energy storage.

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References and Notes

(1) G. Wilkinson and J. M. Birmingham, *J. Am. Chem. Soc.*, **77**, 3421 (1955).
(2) J. Chatt, *Science*, **160**, 723 (1968).
(3) A. P. Ginsberg, *Transition Met. Chem.*, **1**, 111 (1965).
(4) M. L. H. Green, *Endeavour*, **26**, 129 (1967).
(5) M. L. H. Green and D. J. Jones, *Adv. Inorg. Chem. Radiochem.*, **7**, 115 (1965).
(6) H. D. Kaesz and R. B. Saileant, *Chem. Rev.*, **72**, 231 (1972).
(7) D. M. Roundhill, *Adv. Organomet. Chem.*, **13**, 273 (1975).
(8) G. L. Geoffroy and J. R. Lehman, *Adv. Inorg. Chem. Radiochem.*, in press.
(9) V. Balzani, L. Moggi, M. F. Manfrin, F. Bolletta, and M. Gleria, *Science*, **189**, 852 (1975).
(10) A. Sacco and M. Aresta, *Chem. Commun.*, 1223 (1968).
(11) E. Koerner von Gustorf, I. Fischler, J. Leitish, and H. Dreeskamp, *Angew. Chem., Int. Ed. Engl.*, **11**, 1088 (1972).
(12) D. J. Darensbourg, *Inorg. Nucl. Chem. Lett.*, **8**, 529 (1972).
(13) K. Elmitt, M. L. H. Green, R. A. Forder, I. Jefferson, and K. Prout, *J. Chem. Soc., Chem. Commun.*, 747 (1974).
(14) C. Giannotti and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 1114 (1972).
(15) L. Fairugia and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 416 (1975).
(16) T. Kruck, G. Sylvester, and I. P. Kunau, *Angew. Chem., Int. Ed. Engl.*, **10**, 725 (1971).
(17) T. Kruck, G. S. Sylvester, and I. P. Kunau, *Z. Naturforsch B*, **28**, 38 (1973).
(18) A. Camus, C. Cocevar, and G. Mestroni, *J. Organomet. Chem.*, **39**, 355 (1972).
(19) G. L. Geoffroy, H. B. Gray, and G. S. Hammond, *J. Am. Chem. Soc.*, **97**, 3933 (1975).
(20) L. Vaska, *J. Am. Chem.,Soc.*, **83**, 756 (1961).
(21) R. C. Taylor, J. F. Young, and G. Wilkinson, *Inorg. Chem.*, **5**, 20 (1966).
(22) M. A. Bennett and D. L. Milner, *J. Am. Chem. Soc.*, **91**, 6983 (1969).
(23) N. Ahmad, S. D. Robinson, and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, 843 (1972).
(24) J. Chatt, R. S. Coffey, and B. L. Shaw, *J. Chem. Soc.*, 7391 (1965).
(25) J. J. Levison and S. D. Robinson, *J. Chem. Soc. A*, 2947 (1970).
(26) J. P. Collman, M. Kubota, F. D. Vastine, J. Y. Sun, and J. W. Kang, *J. Am. Chem. Soc.*, **90**, 5430 (1968).
(27) J. Schwartz and J. B. Cannon, *J. Am. Chem. Soc.*, **94**, 6226 (1972).

(28) B. Longato, F. Morandini, and S. Bresadola, *J. Organomet. Chem.*, **88**, C7 (1975).
(29) M. G. Clerici, S. Di Gioacchino, F. Maspero, E. Perrotti, and A. Zanobi, *J. Organomet. Chem.*, **84**, 379 (1975).
(30) C. T. Enos, G. L. Geoffroy, and T. H. Risby, *Anal. Chem.*, **48**, 990 (1976).
(31) For other examples, see ref 19.
(32) M. J. Mays, R. N. F. Simpson, and F. P. Stefanini, *J. Chem. Soc. A*, 3000 (1970).
(33) G. S. Arnold, W. L. Klotz, W. Halper, and M. K. DeArmond, *Chem. Phys. Lett.*, **19**, 546 (1973).
(34) A. P. Ginsberg and B. K. Teo, presented at the 169th American Chemical Society National Meeting, Philadelphia, Pa., April 1975.
(35) B. K. Teo, A. P. Ginsberg, and J. C. Calabrese, *J. Am. Chem. Soc.*, **98**, 3027 (1976).
(36) A. P. Ginsberg, private communication.
(37) Estimated from data given by L. Vaska and M. F. Werneke, *Trans. N.Y. Acad. Sci.*, **33**, 70 (1971).

Applications of X-Ray Photoabsorption Spectroscopy to the Determination of Local Structure in Organometallic Compounds

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Abstract: Curve fitting methods have been developed which promise to be of considerable utility in extracting structural information from x-ray absorption spectra. In principle, the extended x-ray absorption fine structure (EXAFS) for a given atom can be analyzed to reveal the radial distances and atomic numbers of those atoms surrounding the absorber. The requisite high-quality x-ray absorption spectra can now be easily and rapidly obtained on solid or solution samples, using synchrotron radiation from the Stanford electron-positron storage ring SPEAR at the Stanford Linear Accelerator Center. In order to provide the basis for an understanding of metalloprotein absorption fine structure, data for ferrocene, $Co(NH_3)_6{}^{3+}$, $Co(OH_2)_6{}^{2+}$, and a variety of iron porphyrins have been analyzed. The procedure used was to fit the EXAFS of known structures with a parameterized, semiempirical function: $\sum_i C_i k^{-\beta_i} \exp(-2(\sigma_i{}^2)k^2) \sin(2R_i k + \alpha(k))$; where the sum is over all neighboring atoms, the distance information R_i is contained in the phase term, and the other variables account for the amplitude behavior as described in detail in the text. These parameters are then used in fits on other known structures, and the accuracy of the calculated distances (R_i) is used as a test for the validity of the method. The results of fits on $Fe^{II}TPP$, $Fe^{III}TPP(SC_6H_5)$, and FeTpivPP(N-MeIm)O_2 indicate that radial distances out to four coordination shells in iron porphyrins can be determined to better than 0.1 Å. For cases where the interest is only in changes in coordination, difference methods of analysis have been developed which allow accurate determination of the geometry and distances to small molecules such as dioxygen which can reversibly bind to the metal ion. For oxy and deoxy FeTpivPP(N-MeIm), the Fe–O distances are determined to better than 0.03 Å. At present, the interpretation of the EXAFS from an unknown structure relies heavily on comparison with model compound data. However, the present results suggest that a library of transferable phase shift and amplitude functions may be eventually compiled, and that curve-fitting analysis of the extended fine structure will be useful for determining the local structure around specific atomic constituents in metalloproteins and other complex materials.

The recent availability of a stable, intense x-ray source using synchrotron radiation from high energy (GeV) electron storage rings[1] has generated a renaissance of interest in x-ray absorption spectroscopy. Following the absorption edge, where the photon energy equals the binding energy of a core electron, simple models of x-ray photoabsorption predict a gradual monotonic decrease in the absorption coefficient with increasing photon energy.[2] Although such behavior is approximately observed for noble gas spectra, the presence of other atoms around the absorber causes the appearance of a periodic modulation in the absorption coefficient. This modulation contains information about the nature of the surrounding atoms and their distances to the absorber. The absorption coefficient oscillations have been termed EXAFS (Extended X-ray Absorption Fine Structure) or alternatively Kronig structure, and until recently they were more a theoretical curiosity than a useful structural tool.[3] It is the purpose of this paper to illustrate the application of x-ray absorption spectroscopy to the study of the local environments around specific metal centers in complex molecules. Specifically, in an earlier communication[4] we suggested that x-ray absorption spectroscopy might be useful for structural investigation of molecules such as metalloporphyrins. We consider herein detailed application of this method to the study of the molecular environment of the iron in porphyrins.

While it is easy to show that the extended fine structure is related to the radial distribution of atoms around the absorbing atom, there is considerable difficulty in interpreting the data in a quantitative manner. The extended fine structure was first treated theoretically by Kronig in the 1930's.[5] More recent theoretical treatments of EXAFS by Ashley and Doniach,[6] Lee and Pendry,[7] and Sayers and Stern[8] have emphasized the effect of short-range photoelectron backscattering on the transition probabilities to the continuum states. Multiple scattering effects have also been treated by these authors. While theoretical calculations cannot as yet produce perfect agreement with experimental results, they provide a useful foundation upon which to base empirical methods.

Since EXAFS is essentially a result of the photoelectron backscattering from the surrounding atoms, it contains information about the nature of these atoms and their distances from the absorbing atom. Unfortunately, this information is veiled by the energy dependence of the electron-atom backscattering function. Inelastic processes may also complicate the fine structure. Recent attempts to unravel the structural information from EXAFS have involved three types of approaches: (1) ab initio calculations, (2) Fourier transformation, and (3) curve-fitting.

Using a short-range-order electron-atom backscattering approach as a starting point, Kincaid and Eisenberger[9] have