DEFINITIVE EXAMPLES OF POLYHYDRIDE COMPLEXES WHICH DO NOT ELIMINATE H_2 IN THE PRIMARY PHOTOCHEMICAL REACTION. PHOTODISSOCIATION OF PR_3 FROM [$ReH_3(PR_3)_4$] AND [$ReH_5(PR_3)_3$] COMPLEXES

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Summary

Irradiation of the complexes [ReH_5L_3] (L = PMe_2Ph, $PMePh_2$, PPh_3) and [$ReH_3(PMe_2Ph)_4$] gives efficient loss of phosphine in the primary photochemical reaction, in contrast to most monomeric polyhydride complexes which lose H_2 upon photolysis. The 366 nm quantum yields for the [ReH_5L_3] complexes range from 0.13—0.18; the 366 nm quantum yield for PMe_2Ph loss from [$ReH_3(PMe_2Ph)_4$] is 0.4. Under an H_2 atmosphere, [$ReH_3(PMe_2Ph)_4$] is converted into [$ReH_5(PMe_2Ph)_3$] upon photolysis; the pentahydrides in turn lose another equivalent of phosphine to give the corresponding [ReH_7L_2] complexes. The heptahydrides are themselves photosensitive and react to give a mixture of [$Re_2H_8L_4$] and [$Re_2H_6L_5$] dimers. Photolysis of degassed solutions of the [ReH_5L_2] complexes leads to a complex mixture of [ReH_7L_2], [ReH_3L_4], [$Re_2H_8L_4$], and [$Re_2H_6L_5$]. The efficient photoelimination of L from the [ReH_3L_4] complexes is discussed in view of the reported photochemistry of [$ReH_3(Ph_2PCH_2CH_2PPh_2)_2$] which loses H_2 upon irradiation.

A number of studies of di- and polyhydride complexes of the transition metals have shown that photoinduced loss of H_2 is the dominant photoreaction for this class of compounds [1,2]. For example, we recently reported that photolysis of [$ReH_3(dppe)_2$] (dppe = $Ph_2PCH_2CH_2PPh_2$) leads to H_2 elimination and formation of highly reactive [$ReH(dppe)_2$] which adds N_2, CO_2, C_2H_4, and C_2H_2 to yield adduct complexes and which also inserts into the C—H bonds of aromatic hydrocarbons, eq. 1 [3].

$$[ReH_3(dppe)_2] \overset{h\nu}{\to} H_2 + [ReH(dppe)_2] \overset{L}{\to} [ReH(L)(dppe)_2] \qquad (1)$$
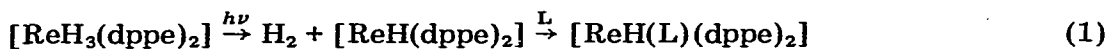
The reaction of [$ReH(dppe)_2$] with CO_2 was particularly interesting since the

TABLE 1

SPECTRAL DATA

Complex	^{1}H NMR [a]		IR [b]	UV-VIS
	δ(Re–H) (ppm)	J(P–H) (Hz)	ν(Re–H) (cm^{-1})	λ_{max} (nm) (ϵ, M^{-1} cm^{-1})
[ReH$_3$(PMe$_2$Ph)$_4$]	–6.74 (qt)	20.2	1952m, 1890m, 1784s, 1750m(sh)	323 (4770), 380sh (1730)
[ReH$_3$(PPh$_3$)$_4$]	–7.56 (qt)	40.7	1983m(sh), 1962m	–
[ReH$_5$(PMe$_2$Ph)$_3$]	–6.08 (q)	18.7	1949w(sh), 1931m, 1905m, 1852m	338 (4225)
[ReH$_5$(PMePh$_2$)$_3$]	–5.50 (q)	18.3	1935w(sh), 1953m(sh), 1982m, 1890m(sh), 1876m	327 (5270)
[ReH$_5$(PPh$_3$)$_3$]	–4.66 (q)	18.4	1952s, 1891s	332 (5900)
[ReD$_5$(PMe$_2$Ph)$_3$]	–	–	1395w(sh), 1380m, 1371m, 1335m	–
[ReH$_7$(PMe$_2$Ph)$_2$]	–5.11 (t)	20.4	1983w, 1965w(sh), 1893m(sh), 1862m, 1750vw(sh)	–
[ReH$_7$(PMePh$_2$)$_2$]	–4.72 (t)	20.0	–	–
[ReH$_7$(PPh$_3$)$_2$]	–4.20 (t)	18.6	–	–
[Re$_2$H$_8$(PMe$_2$Ph)$_4$]	–6.31 (qt)	9.5	–	–
[Re$_2$H$_8$(PMePh$_2$)$_4$]	–5.78 (qt)	8.9	–	–
[Re$_2$H$_8$(PPh$_3$)$_4$]	–5.01 (qt)	8.2	–	–

[a] Benzene-d_6 solution; t = triplet; q = quartet; qt = quintet; h = hextet. [b] KBr pellet.

product actually isolated was a formate derivative in which the hydride had migrated to CO_2. This led us to consider whether multiple hydrogen migration to a bound CO_2 or N_2 ligand might occur if the photogenerated intermediate possessed two or more hydrides. Photoinduced loss of H_2 from $[ReH_5(PR_3)_3]$, for example, would give $[ReH_3(PR_3)_3]$ with three hydrides which could potentially transfer. However, as reported herein, we find that these pentahydrides do not undergo elimination of H_2 in the primary photochemical event but instead efficiently lose a PR_3 ligand. These compounds thus constitute the first class of monomeric di- and polyhydride complexes in which the dominant photoreaction has definitely been shown to be something other than H_2 loss. The trihydride complex $[ReH_3(PMe_2Ph)_4]$ has also been examined and found to undergo efficient PR_3 elimination. These latter results are discussed in view of those noted above for $[ReH_3(dppe)_2]$ which loses H_2, eq. 1.

Experimental

The complexes $[ReH_3(PPh_3)_4]$ [4], $[ReH_5(PMe_2Ph)_3]$ [5], $[ReH_5(PMePh_2)_3]$ [5], $[ReH_5(PPh_3)_3]$ [6], $[ReH_7(PMe_2Ph)_2]$ [5] and $[Re_2H_8(PMe_2Ph)_4]$ [6] were prepared according to literature procedures. $[ReD_5(PMe_2Ph)_3]$ was prepared by a procedure similar to that reported for $[ReH_5(PMe_2Ph)_3]$ [5] except that $NaBD_4$ in methanol-d_4 was used in place of $NaBH_4$ in ethanol. $[ReH_3(PMe_2Ph)_4]$ was prepared by Bau's previously unreported procedure summarized below [7]. $[Re_2H_8(PMePh_2)_4]$, $[Re_2H_8(PPh_3)_4]$, $[ReH_7(PPh_3)_2]$, and $[ReH_7(PMePh_2)_2]$ were generated during the course of the photolysis experiments but were not isolated as pure compounds. They were identified on the basis of spectral evidence, particularly ^1H NMR data. The ^1H NMR, IR, and UV-VIS spectral data for the Re polyhydride complexes relevant to this study are summarized in Table 1. All materials employed in this work were reagent grade or better. Solvents were dried by standard methods and freshly distilled under vacuum prior to use.

Preparation of [ReH₃(PMe₂Ph)₄] [7]

To a solution containing 0.5 g of mer-$[ReCl_3(PMe_2Ph)_3]$ [5] in 20 ml of dry THF was added 0.5 ml of PMe_2Ph. The resulting orange solution was stirred under an N_2 atmosphere for 15 min and $LiAlH_4$ (0.2 g) was added. The resulting mixture was stirred at room temperature for 15 min and then heated to reflux for an additional 30 min. The reaction mixture was cooled to −20°C, the excess $LiAlH_4$ hydrolyzed with wet THF, and the solvent removed under vacuum. Extraction of the residue with 60 ml of benzene gave, upon removal of the solvent, a yellow oil. Dissolution of the latter in petroleum ether followed by cooling to −20°C precipitated the product as a bright yellow powder.

General irradiation procedures

Samples were irradiated with a 450 W Hanovia medium pressure Hg arc lamp, a 100 w Black-Ray B100A lamp equipped with a 366 nm filter, or on an optical bench equipped with a water-cooled lamp housing (Photochemical Research Associates, Inc., Model ALH215), a 100 W high-pressure Hg arc lamp (Osram HBO 100 w/2), a monochromator (Photochemical Research Associates,

Inc., Model B102), and a thermostated cell holder. Quantum yields were determined using the latter apparatus, and light intensities were measured using ferrioxalate actinometry [8]. Samples were irradiated in 1-cm quartz UV-VIS spectrophotometer cells sealed to Kontes 4 mm quick-release teflon valves for attachment to a vacuum line. Samples were degassed by several freeze-pump-thaw cycles and then placed under 1 atm of H_2. After irradiation at 366 nm, samples were transferred to 0.1 cm quartz UV-VIS spectrophotometer cells, and the decrease in intensity of the absorption band maximum, Table 1, was measured. All determinations were performed in triplicate. Samples for NMR experiments were prepared either in standard NMR tubes sealed under vacuum or in a degassable NMR tube equipped with a stopcock and a 17/25 female ground glass joint to allow solutions to be degassed and then placed under an H_2 atmosphere. Gases above irradiated solutions were quantitated by standard Toepler pump techniques and were analyzed by mass spectrometry.

Spectral measurements

The following instruments were employed in this study: UV-VIS-Cary 17 or Hewlett-Packard HP 8450A; IR-Perkin-Elmer 580; Mass spectra-AEI-MS-902; NMR-Varian A-60A, JEOL PS-100 FT, Bruker WH 200. ^1H NMR spectra were referenced externally to TMS or internally to the solvent, generally benzene. ^{31}P NMR spectra were referenced to external 85% H_3PO_4 and downfield chemical shifts are reported as positive.

Results

[ReH$_5$(PMe$_2$Ph)$_3$]

[ReH$_5$(PMe$_2$Ph)$_3$] is thermally quite stable, showing no detectable reaction when heated in a degassed isooctane solution for 15 h at 80°C. However, 366 nm photolysis of an isooctane solution of the complex results in a rapid decrease in intensity of its electronic absorption band at 338 nm. However, as the photolysis proceeds the spectral changes become more complex, as secondary photochemical and/or thermal reactions occur. Irradiation of concentrated solutions of the complex gives an initial change from colorless to pale orange and the formation of an orange precipitate, identified as [Re$_2$H$_8$(PMe$_2$Ph)$_4$] as indicated by its ^1H NMR spectrum which shows a quintet at δ —6.31 ppm with J(P—H) = 9.5 Hz. For comparison, [Re$_2$H$_8$(PEt$_2$Ph)$_4$] shows a quintet at δ —6.59 ppm with J(P—H) = 9.3 Hz [9]. Upon continued photolysis this precipitate redissolves to give a dark red solution. This coloration persists until one mole of H_2 per mole of initial [ReH$_5$(PMe$_2$Ph)$_3$] has been released. Exhaustive photolysis then results in a green coloration and eventually, after 1.5 equivalents of H_2 have been evolved, a white floculant precipitate deposits. Evaporation of solvent at this point gives a green oil which has a strong odor of free PMe$_2$Ph.

The metal-hydride region ^1H NMR spectrum of a sample that had been irradiated up to the point of the red coloration is shown in Fig. 1a. This spectrum shows the formation of [ReH$_7$(PMe$_2$Ph)$_2$] (δ(ReH) —5.11 ppm t, J(P—H) = 20.2 Hz), a trace amount of [ReH$_3$(PMe$_2$Ph)$_4$] (δ(ReH) —6.74 qt, J(P—H) = 20.2 Hz), and a broad hextet at δ —8.23 ppm (J(P—H) = 10.8 Hz) which may
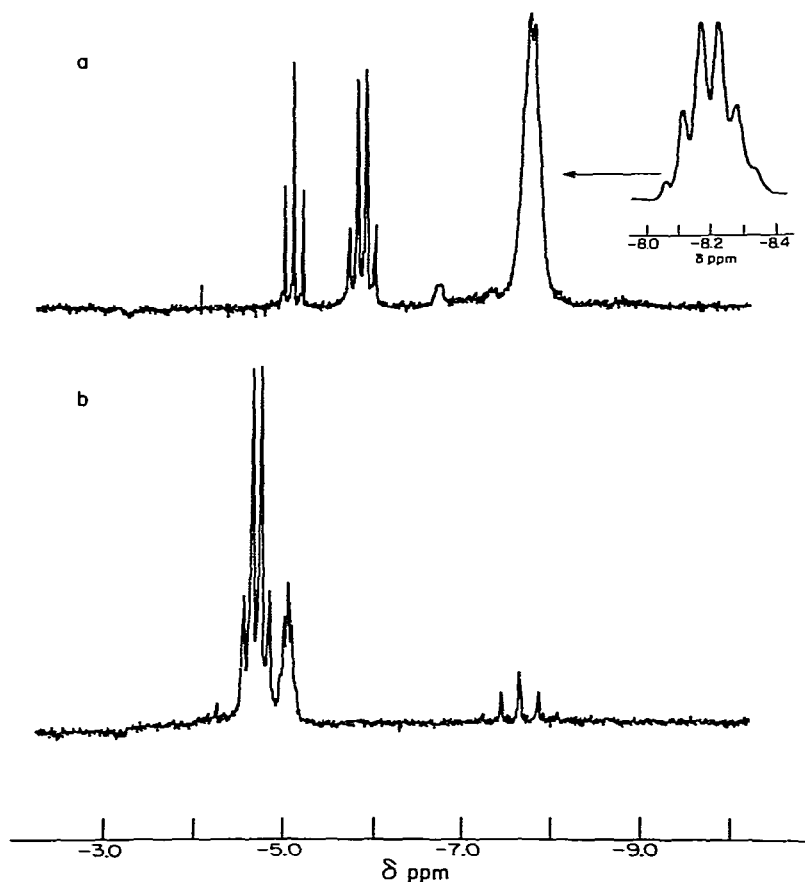
Fig. 1. Comparixon of the ^{1}H NMR spectra after 366 nm photolysis of a) [ReH$_5$(PMe$_2$Ph)$_3$] in cyclo-hexane-d_{12} solution, and b) [ReH$_5$(PPh$_3$)$_3$] in benzene-d_6 solution.

be attributed to the [Re$_2$H$_6$(PMe$_2$Ph)$_5$] dimer which has been structurally char-acterized by Caulton et al. [10]. The [ReH$_7$(PMe$_2$Ph)$_2$] and [ReH$_3$(PMe$_2$Ph)$_4$] products were identified by comparison to spectra of authentic samples. A doublet at δ 1.05 ppm (J(P—H) = 2.9 Hz) due to uncoordinated PMe$_2$Ph is also present in the spectrum but not shown in Fig. 1a.

The photoreaction is markedly inhibited by the presence of excess PMe$_2$Ph. For example, photolysis of [ReH$_5$(PMe$_2$Ph)$_3$] in the presence of a 100-fold excess of PMe$_2$Ph gave no detectable reaction after 8 h although a similarly pre-pared control sample without excess PMe$_2$Ph showed substantial reaction after 1 h irradiation.

The suppression of the rate of photoreaction by excess PMe$_2$Ph strongly argues for loss of PMe$_2$Ph from [ReH$_5$(PMe$_2$Ph)$_3$] in the primary photochemical event, eq. 2.

$$[ReH_5(PMe_2Ph)_3] \xrightarrow{h\nu} [ReH_5(PMe_2Ph)_2] + PMe_2Ph \qquad (2)$$
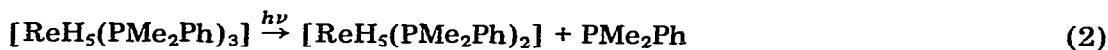
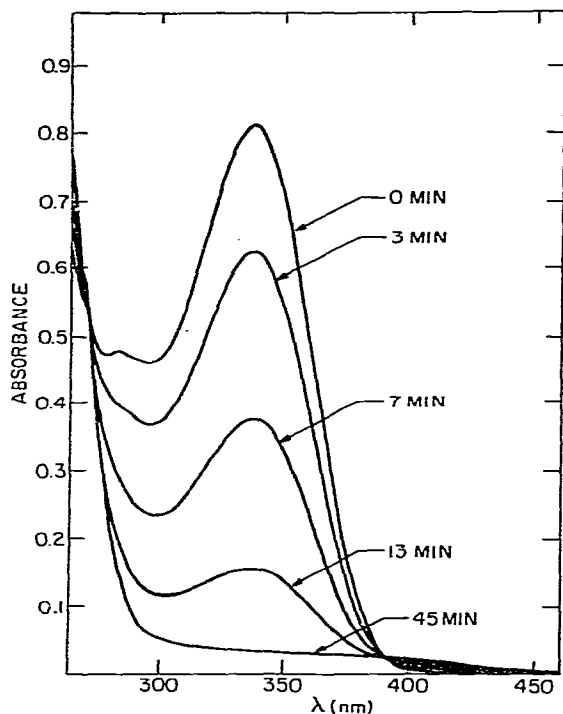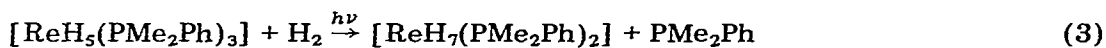This notion is supported by the observation of free PMe$_2$Ph in ^{1}H NMR sam-

Fig. 2. Electronic absorption spectral changes during 366 nm irradiation of an isooctane solution of [ReH$_5$(PMe$_2$Ph)$_3$] under an H$_2$ atmosphere.

ples of the irradiated solution. However, the presumed [ReH$_5$(PMe$_2$Ph)$_2$] intermediate must then undergo further reaction to give the mix of products described above. The overall reaction is much cleaner when the irradiation is conducted in the presence of H$_2$ as evidenced by the UV-VIS spectral changes, Fig. 2, which show a smooth, rapid decrease in the 338 nm absorption band as the irradiation proceeds. No suppression of the rate of disappearance of [ReH$_5$(PMe$_2$Ph)$_3$] is observed under an H$_2$ atmosphere, in direct contrast to the situation found for those hydride complexes where the primary photoreaction is H$_2$ loss [1,2].

The initial product of photolysis under an H$_2$ atmosphere is [ReH$_7$(PMe$_2$Ph)$_2$], eq. 3.

$$[\text{ReH}_5(\text{PMe}_2\text{Ph})_3] + \text{H}_2 \overset{h\nu}{\rightarrow} [\text{ReH}_7(\text{PMe}_2\text{Ph})_2] + \text{PMe}_2\text{Ph} \qquad (3)$$

Consistent with the spectral changes shown in Fig. 2, [ReH$_7$(PMe$_2$Ph)$_2$] shows no absorption maximum below 272 nm, Table 1. ^{1}H NMR spectra from low conversion ($\sim$35%) photolyses experiments showed resonances attributable to [ReH$_5$(PMe$_2$Ph)$_3$], [ReH$_7$(PMe$_2$Ph)$_2$], a trace of [Re$_2$H$_6$(PMe$_2$Ph)$_5$], and free PMe$_2$Ph. Furthermore, irradiation of 0.5 g of [ReH$_5$(PMe$_2$Ph)$_3$] under an H$_2$ atmosphere, led to the isolation of a mixture of [ReH$_7$(PMe$_2$Ph)$_2$] and [Re$_2$H$_8$(PMe$_2$Ph)$_4$]. The latter is a known thermal degradation product of [ReH$_7$(PMe$_2$Ph)$_2$] [6] and this [ReH$_7$(PMe$_2$Ph)$_2$] → [Re$_2$H$_8$(PMe$_2$Ph)$_4$] conversion has also been shown to be photoaccelerated [10]. The quantum yield of

PMe$_2$Ph loss from [ReH$_5$(PMe$_2$Ph)$_3$] under an H$_2$ atmosphere is 0.16 ± 0.02.

As noted above, photolysis in degassed solutions does lead to evolution of H$_2$ and formation of [Re$_2$H$_8$(PMe$_2$Ph)$_4$] and [Re$_2$H$_6$(PMe$_2$Ph)$_5$]. An attempt was made to determine the mechanism of this transformation by carrying out crossover experiments with [ReH$_5$(PMe$_2$Ph)$_3$] and [ReD$_5$(PMe$_2$Ph)$_3$]. However, 10 min 366 nm photolysis of [ReD$_5$(PMe$_2$Ph)$_3$] in hexane solution gave an approximate 1 : 4.1 : 4.4 ratio of D$_2$/HD/H$_2$ as determined by mass spectral analysis of the gases above the irradiated solution. Photolysis of [ReH$_5$(PMe$_2$Ph)$_3$] in cyclohexane-d_{12} gave <2% HD and no detectable D$_2$. These two experiments indicate that extensive scrambling of hydrogen between the hydride and PMe$_2$Ph ligands occurs upon photolysis, and thus these cross-over experiments would not be meaningful. ^{1}H NMR spectra also demonstrated that photolysis of [ReH$_5$(PMe$_2$Ph)$_3$] in benzene-d_6 leads to H/D exchange between solvent and ligand phenyl hydrogens. Surprisingly, the ^{1}H NMR spectra showed that exchange occurs almost exclusively at the *meta* and *para* positions of the phenyl substituents. For example, 30 min 366 nm irradiation of a benzene-d_6 solution of [ReH$_5$(PMe$_2$Ph)$_3$] showed near complete disappearance of the resonances in the δ 7.00—7.08 ppm chemical shift region due to the *meta* and *para* PMe$_2$Ph hydrogens whereas the δ 7.55 ppm resonance due to the *ortho* hydrogens did not show any appreciable loss of integrated intensity. Although incompletely resolved, there were changes in the multiplet structure of this resonance which can be attributed to the introduction of deuterium onto the *meta* and *para* positions. These results are in direct contrast to those obtained with [ReH$_3$(dppe)$_2$] which shows photoassisted H/D exchange with benzene-d_6 exclusively at the *ortho* positions of the dppe phenyl substituents [3]. These results indicate an intermolecular exchange path for [ReH$_5$(PMe$_2$Ph)$_3$] whereas exchange with [ReH$_3$(dppe)$_2$] is intramolecular [3].

[ReH$_5$(PMePh$_2$)$_3$]

The photochemistry observed for this complex is similar to that discussed above for [ReH$_5$(PMe$_2$Ph)$_3$], except that all reactions were carried out in benzene solution to increase compound solubility. The UV-VIS spectral changes which occur upon 366 nm photolysis under an H$_2$ atmosphere show a smooth decrease in intensity of the 327 nm absorption band as the [ReH$_7$(PMePh$_2$)$_2$] complex forms. A ^{1}H NMR spectrum of a sample irradiated in degassed solution showed resonances attributable to [ReH$_7$(PMePh$_2$)$_2$] (δ —4.72 ppm t, J(P—H) = 20.0 Hz), [ReH$_5$(PMePh$_2$)$_3$] (δ —5.50 ppm q, J(P—H) = 18.31 Hz), and [ReH$_2$H$_8$(PMePh$_2$)$_4$] (δ —5.78 ppm qt, J(P—H) = 8.85 Hz). A broad resonance at δ —7.59 ppm is also apparent and may be attributed to [Re$_2$H$_6$(PMePh$_2$)$_5$] on the basis of its spectral similarities to [Re$_2$H$_6$(PMe$_2$Ph)$_5$] [10]. No resonances attributable to [ReH$_3$(PMePh$_2$)$_4$] were observed in this spectrum. The 366 nm quantum yield for PMePh$_2$ loss from [ReH$_5$(PMePh$_2$)$_3$] is 0.13 ± 0.02.

[ReH$_5$(PPh$_3$)$_3$]

As indicated in Fig. 1b, the product mixture obtained upon photolysis of [ReH$_5$(PPh$_3$)$_3$] in degassed solution is different from that observed for the PMe$_2$Ph derivative. Resonances due to [Re$_2$H$_8$(PPh$_3$)$_4$] (δ —5.01 ppm qt,

J(P—H) = 8.16 Hz) are observed but no upfield resonance which might be attributable to [$Re_2H_6(PPh_3)_5$] is seen nor is there any evidence for [$ReH_7(PPh_3)_2$]. Instead, a quintet at —7.56 ppm (J(P—H) = 40.7 Hz) is present. We attribute the latter to [$ReH_3(PPh_3)_4$], although our ^{1}H NMR data for this compound differs from that previously reported in a review [11] of Re hydride complexes. However, following Freni et al.'s [4] recipe for the preparation of this compound, we obtained a yellow microcrystalline product which shows a quintet at —7.56 ppm (J(P—H) = 40.7 Hz) in its ^{1}H NMR spectrum and a corresponding quartet at 24.4 ppm (J(P—H) = 40.7 Hz) in its ^{31}P NMR spectrum in which the C_6H_5 hydrogens were decoupled. We are thus confident of the [$ReH_3(PPh_3)_4$] formulation for this compound and suggest that the data in the review [11] is in error. Although difficult to resolve, the resonance patterns in the δ 6—8 ppm region of the ^{1}H NMR spectrum of an irradiated [$ReH_5(PPh_3)_3$] solution indicated that little, if any, uncoordinated PPh$_3$ is present. This, of course, is consistent with the presence of [$ReH_3(PPh_3)_4$]. As with the other [$ReH_5(PR_3)_3$] complexes, the rate of photoreaction is suppressed by the presence of excess PPh$_3$ and clean UV-VIS spectral changes occur upon photolysis under an H$_2$ atmosphere as [$ReH_7(PPh_3)_2$] is formed. Taken together, all these results point to PPh$_3$ elimination in the primary photoreaction, and the 366 nm quantum yield for this process is 0.18 ± 0.02.

[ReH$_3$(PMe$_2$Ph)$_4$]

When irradiated in the presence of H$_2$, [ReH$_3$(PMe$_2$Ph)$_4$] smoothly converts to the corresponding [ReH$_7$(PMe$_2$Ph)$_2$] complex via the intermediacy of
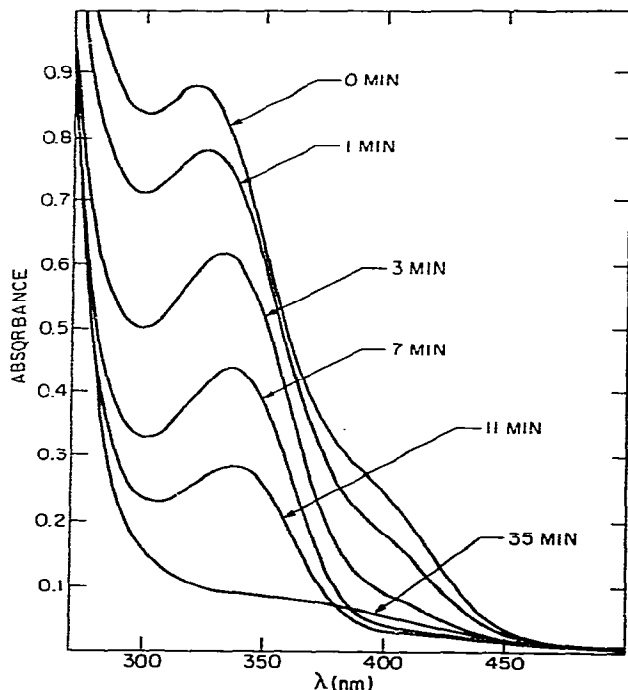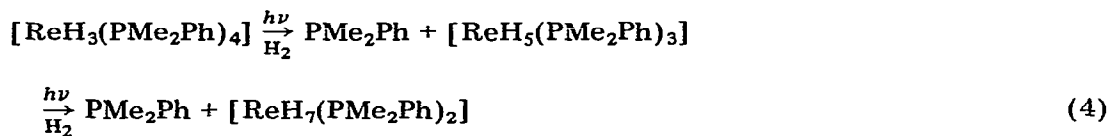

Fig. 3. Electronic absorption spectral changes during 366 nm irradiation of an isooctane solution of [ReH$_3$(PMe$_2$Ph)$_4$] under an H$_2$ atmosphere.

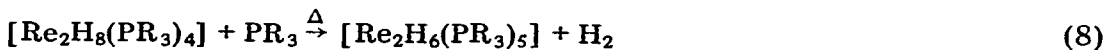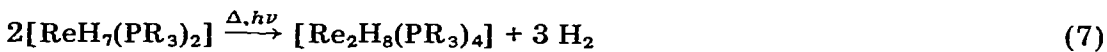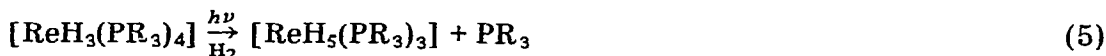$[ReH_5(PMe_2Ph)_3]$, eq. 4.

$$[ReH_3(PMe_2Ph)_4] \xrightarrow[H_2]{h\nu} PMe_2Ph + [ReH_5(PMe_2Ph)_3]$$

$$\xrightarrow[H_2]{h\nu} PMe_2Ph + [ReH_7(PMe_2Ph)_2] \tag{4}$$

This is clearly illustrated by the UV-VIS spectral changes shown in Fig. 3. As the irradiation proceeds, the 323 nm absorption maximum of $[ReH_3(PMe_2Ph)_4]$ shifts to 338 nm, the maximum of $[ReH_5(PMe_2Ph)_3]$. Continued photolysis then causes disappearance of all absorption bands below 270 nm as ReH_7-$(PMe_2Ph)_2]$ forms. This sequence of reactions is also evidenced by the ^{1}H NMR changes observed for 366 nm photolysis of $[ReH_3(PMe_2Ph)_4]$ under an H_2 atmosphere. These spectra show a progressive decrease in the δ −6.74 quintet due to $[ReH_3(PMe_2Ph)_4]$ and the growth of the δ −6.08 ppm quartet due to $[ReH_5(PMe_2Ph)_3]$. Free PMe_2Ph is also observed. The 366 nm quantum yield for PMe_2Ph loss from $[ReH_3(PMe_2Ph)_4]$ is 0.40 ± 0.05.

## Discussion

The results presented herein clearly demonstrate that photolysis of the $[ReH_5(PR_3)_3]$ and $[ReH_3(PR_3)_4]$ complexes studied gives relatively efficient loss of a PR_3 ligand in the primary photoreaction. In the presence of H_2 the complexes are initially converted to $[ReH_7(PR_3)_2]$, although the latter is thermally and photochemically unstable with regard to conversion to $[Re_2H_8(PR_3)_4]$ [6,10]. The $[Re_2H_8(PR_3)_4]$ compounds in turn can react with the photoreleased PR_3 to give the corresponding $[Re_2H_6(PR_3)_5]$ complexes, an example of which has been characterized by Caulton, et al. [10]. However, the extent of this latter transformation appears to be dependent upon the nature of PR_3; as shown in Fig. 1b, no evidence for a $[Re_2H_6(PPh_3)_5]$ dimer was obtained upon photolysis of $[ReH_5(PPh_3)_3]$. The sequence of events which occur under an H_2 atmosphere is summarized in eqs. 5—8.

$$[ReH_3(PR_3)_4] \xrightarrow[H_2]{h\nu} [ReH_5(PR_3)_3] + PR_3 \tag{5}$$

$$[ReH_5(PR_3)_3] \xrightarrow[H_2]{h\nu} [ReH_7(PR_3)_2] + PR_3 \tag{6}$$

$$2[ReH_7(PR_3)_2] \xrightarrow{\Delta,h\nu} [Re_2H_8(PR_3)_4] + 3\ H_2 \tag{7}$$

$$[Re_2H_8(PR_3)_4] + PR_3 \xrightarrow{\Delta} [Re_2H_6(PR_3)_5] + H_2 \tag{8}$$

The reactions are more complicated when the irradiation is conducted in the absence of H_2. Here the products observed are $[ReH_3(PR_3)_4]$, $[ReH_7(PR_3)_2]$, $[Re_2H_8(PR_3)_4]$ and $[Re_2H_6(PR_3)_5]$ with the relative amount of each varying significantly with the nature of PR_3. The experimental evidence again points to PR_3 loss in the primary photoreaction, although net H_2 loss does eventually obtain as the $[Re_2H_8(PR_3)_4]$ and $[Re_2H_6(PR_3)_5]$ dimers are produced. Scheme 1 illustrates one possible route to $[ReH_7(PR_3)_2]$ and the dimeric products.

SCHEME 1

(L = PR$_3$)
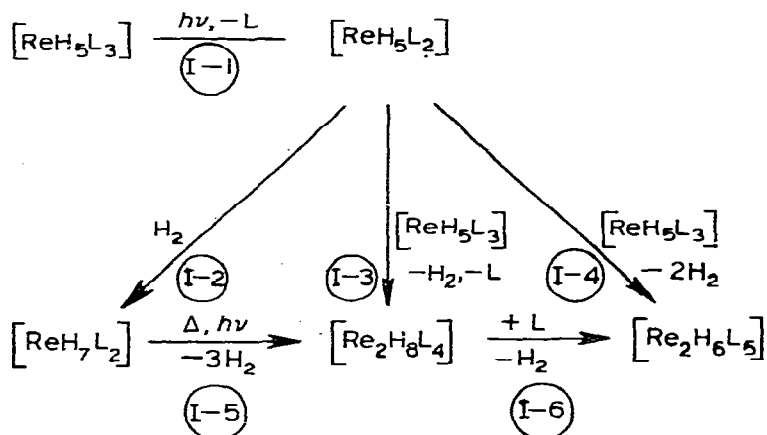
The photogenerated [ReH$_5$(PR$_3$)$_2$] complex could undergo binuclear reactions with [ReH$_5$(PR$_3$)$_3$], I-3 and I-4 in Scheme 1, to directly give the [Re$_2$H$_8$(PR$_3$)$_4$] and [Re$_2$H$_6$(PR$_3$)$_5$] dimers. Consistent with this proposal is the immediate observation of these dimers at the onset of photolysis and Norton's [12] studies of the dimerization of H$_2$Os(CO)$_4$ which proceeds by a similar bimolecular pathway. Reaction of the photogenerated [ReH$_5$(PR$_3$)$_2$] with H$_2$, released in the course of reactions I-3 and I-4, would yield [ReH$_7$(PR$_3$)$_2$]. [ReH$_7$(PR$_3$)$_2$] thermally and photochemically decomposes to give the respective [Re$_2$H$_8$(PR$_3$)$_4$] dimers which in turn are known to react with excess PR$_3$ [6] to yield the [Re$_2$H$_6$(PR$_3$)$_5$] dimers [10]. In our hands this latter conversion occurs at room temperature immediately upon combining the reagents.

Another possible route to [ReH$_7$(PR$_3$)$_2$] is via the disproportionation of photogenerated [ReH$_5$(PR$_3$)$_2$] with [ReH$_5$(PR$_3$)$_3$], eq. 9.

$$[ReH_5(PR_3)_2] + [ReH_5(PR_3)_3] \rightarrow [ReH_7(PR_3)_2] + [ReH_3(PR_3)_3] \qquad (9)$$
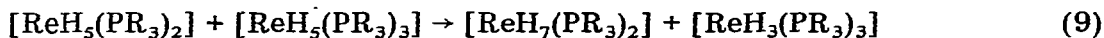
This reaction would also yield [ReH$_3$(PR$_3$)$_3$] which could add the photoreleased phosphine to give [ReH$_3$(PR$_3$)$_4$], a product observed in significant quantity for L = PPh$_3$, eq. 10.

$$[ReH_3(PR_3)_3] + PR_3 \rightarrow [ReH_3(PR_3)_4] \qquad (10)$$

It is significant that [ReH$_3$(PMe$_2$Ph)$_4$] loses PMe$_2$Ph in its primary photoreaction, whereas for [ReH$_3$(dppe)$_2$] the observed reaction is clearly H$_2$ elimination [3]. Note, however, that the quantum yields for these processes are vastly different. Elimination of H$_2$ from [ReH$_3$(dppe)$_2$] occurs with a quantum yield of 0.07 whereas loss of PMe$_2$Ph from [ReH$_3$(PMe$_2$Ph)$_4$] occurs with ϕ = 0.4. We now believe that phosphine loss is the preferred reaction for all the Re-trihydride complexes but that in the case of [ReH$_3$(dppe)$_2$] the chelating dppe ligands prevent net phosphine elimination, and hence H$_2$ elimination with a low quantum yield obtains.

Acknowledgements

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