THE PHOTOCHEMISTRY OF RHENIUM HYDRIDES. A FLASH PHOTOLYTIC INVESTIGATION OF THE TRANSIENTS IN THE PHOTOCHEMISTRY OF TRIS(DIMETHYLPHENYLPHOSPHINE)PENTAHYDRIDORHENIUM(V)

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Summary

The photochemistry of ReH_5P_3, (P $\equiv$ PMe$_2$Ph) has been investigated by laser and conventional flash photolysis. The first species observed in laser flash photolysis of the rhenium complex in saturated hydrocarbons has been assigned as an heptacoordinated 16-electron complex, ReH_5P_2, which is found to react with P at the diffusion-controlled rate. However, for photolysis in benzene such species is replaced by another metastable product, $ReH_5P_2(C_6H_6)$, which is proposed to be a η^2-C_6H_6 complex. At 10^{-5} M Re, isomerization and possibly elimination of hydrogen in subsequent unimolecular steps can precede dimerization, which has also been observed. The observed transient transformations have been correlated with previous observations during continuous photolysis, including coordination of simple olefins and H/D exchange of arenes. Kinetic measurements reveal that the transient ReH_5P_2 forms a dimetallic species by reaction with ReH_5P_3 and not with another (unsaturated) transient.

Introduction

Previous studies on the photochemistry of complexes of rhenium with hydride and phosphine as ligands have demonstrated that ultraviolet irradiations can induce either the elimination of hydrogen or phosphine [1–7]. The photoelimination of hydrogen is the process detected in photolysis of rhenium hydrides with bidentate phosphines, e.g.: $ReH_3(dppe)_2$ with dppe = $Ph_2CH_2CH_2PPh_2$. It has been claimed that a species with a reduced coordination number, $ReH(dppe)_2$, mediates the hydrogen photoelimination. Such assignment is based on the response of the
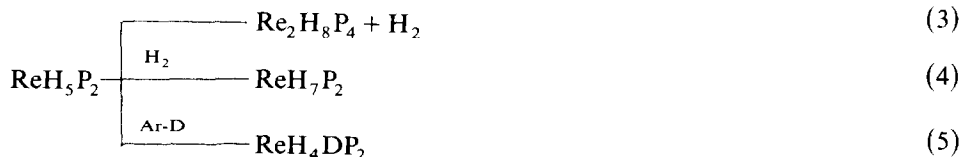
reaction to various scavengers, namely N_2, CO_2, C_2H_4 and C_2H_2 [1,5,6a]. The observed reactivity can be described by means of eq. 1, where L is a given scavenger

$$ReH_3(dppe)_2 \xrightarrow{-H_2} ReH(dppe)_2 \xrightarrow{L} ReHL(dppe)_2 \qquad (1)$$
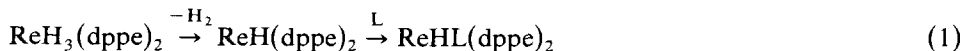
[6b]. This photochemical behaviour contrasts with the photoelimination of phosphine observed in photolyses of rhenium hydrides containing monodentate phosphine ligands [3,4]. It is interesting to observe that the photoelimination of hydrogen involves both the formation of a species with a reduced coordination number and a change in the oxidation state of the rhenium. However, the photoelimination of phosphine requires only the photogeneration of a species with reduced coordination number, as in eq. 2 where L is a given scavenger [8]. The formation of an

$$ReH_5P_3 \xrightarrow{h\nu} ReH_5P_2 \xrightarrow{L} ReH_5P_2L \qquad (2)$$

intermediate species with a reduced coordination number has been probed with scavengers that induce the formation of characteristic products, eq. 3–5 [3,4].

$$
ReH_5P_2
\begin{cases}
\rule{0pt}{1.2em}\text{———— } Re_2H_8P_4 + H_2 & (3) \\
\xrightarrow{H_2} ReH_7P_2 & (4) \\
\xrightarrow{Ar\text{-}D} ReH_4DP_2 & (5)
\end{cases}
$$

Questions remain to be answered concerning the mechanistic photochemistry of rhenium hydride complexes with monodentate phosphines and also the excited states involved in such photochemistry. Indeed, the studies indicated above, mainly oriented toward the isolation and characterization of the reaction products, have not dwelled upon the possible participation of other reaction intermediates that, in addition to possibly escaping chemical traps, have a significant role in the formation of the products. In this regard, we have investigated the mechanistic photochemistry of ReH_5P_3 by laser and conventional flash photolysis.

Of particular interest were two questions which appeared to be answerable by a detailed kinetic study in the short time domain of flash photolysis. First, it had been deduced solely from the observation that phosphine was dissociated that the phototransient could be written as the unsaturated species ReH_5P_2 [3,4,7]. We sought support for this by attempting to measure rate constants for scavenging of this species. In addition, dimerization and the formation of metal–metal bonds (eq. 3) are processes whose kinetics have been little studied. We therefore sought to learn whether eq. 3 was occurring by dimerization of two transient ReH_5P_2, or by attack of ReH_5P_2 on the thermally quite stable ReH_5P_3.

Experimental

Photochemical procedures and apparatus

The equipment used for laser and conventional flash photolysis has been previously described [9,10]. However, some features of the experimental setup are indicated below. Two FP-8D-100C Xenon Corporation flash lamps were flashed in series at stored electrical energies between 50 and 250 J/pulse. The photolyte was

irradiated at preselected wavelengths by using appropriate cutoff filters. These filters, in general aqueous solutions of thermally and photochemically stable compounds, served also the purpose of insulating the photolyte's solution from heating by the light pulse. Particular effort was also expended in order to minimize the creation of concentration gradients. Radiative heating of the solution and concentration gradients create diffusive transients which appear as sharp increases or decreases in absorbance in the longest portion of the millisecond time scale. The needle-like thermal transients (total duration of each spike ~ 30 msec) can be of considerable magnitude in organic solvents with a low heat capacity. Although such transients can be highly reproducible for a given solvent, they were insignificant in the present study.

Laser flash experiments were carried out by exciting with light pulses from a Molectron 400 nitrogen laser. Transients were monitored with the focused light of a 500 W Xenon lamp which was pulsed to around 10^4 times the steady state intensity.

Materials

The rhenium complexes ReH_5P_3 and $Re_2H_8P_4$ were available from previous work [3,4].

Spectroquality solvents, n-hexane and cyclohexane, were treated with a $1/1$ mixture of nitric and sulfuric acids, followed by treatment with concentrated sulfuric acid. They were then distilled under an atmosphere of nitrogen in an all-glass apparatus provided with a 40 theoretical plate fractionating column. The distillate was washed with H_2O under an Ar atmosphere and later dried over anhydrous Na_2SO_4 and molecular sieves. They were further dried by stirring with activated alumina under Ar before carrying out the photolysis experiments. Spectroquality benzene was distilled in an all-glass apparatus with a fractionating column. The fraction within $\pm 0.1°C$ of the benzene boiling point was used for photochemical experiments.

All flash measurements were carried out with solvents purified as described above and under an argon atmosphere, unless otherwise noted (e.g. H_2). We have observed that less attention to solvent purification and deoxygenation markedly altered the transient kinetics by impurity scavenging.

Results

The photochemical transformations of ReH_5P_3 are mediated by a considerable number of reactive intermediates. These species have been investigated by laser and conventional flash photolysis.

Laser flash photolysis

Irradiations (λ_{excit} 337 nm) of ReH_5P_3 in cyclohexane and in n-hexane produce a spectrum with $\lambda_{max} \sim 400$ nm at zero reaction time (Fig. 1). A subsequent increase of the 400 nm absorbance with a first order dependence on transient concentration was observed in a period of 30 μsec (Fig. 1a); this growth is characterized by a first order rate constant, $k_1 = 1.4 \times 10^5$ sec^{-1}. This increase in absorbance is assigned to an intramolecular transformation of the primary generated species, I_1, into second reactive intermediate, I_2. See Scheme 1. The reactivity of I_1 and I_2 was probed with added phosphine (PMe_2Ph) and also with H_2. The scavenging of the intermediate I_2
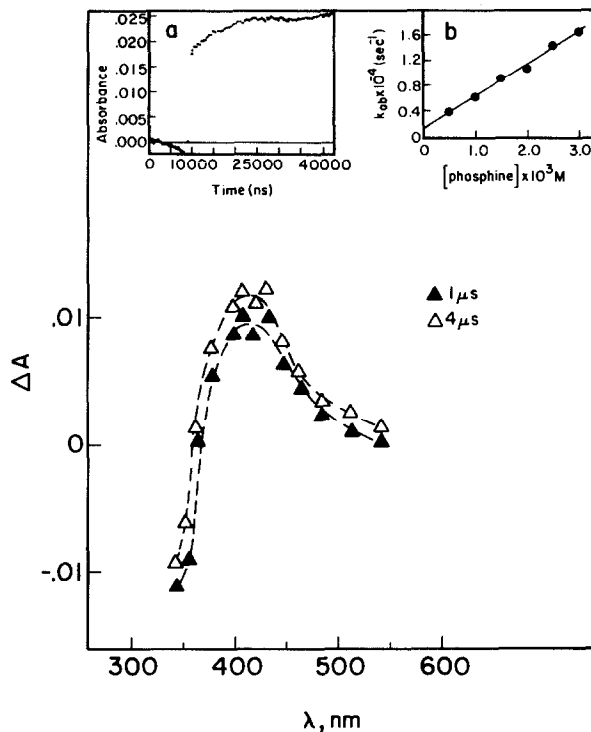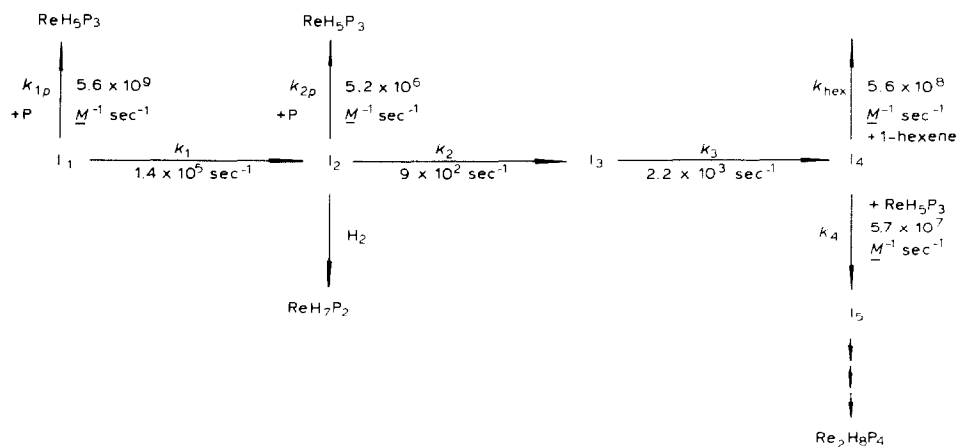
Fig. 1. Transient spectra recorded in laser flash irradiations of ReH_5P_3 in n-hexane. Insets show (a) typical trace obtained at $\lambda_m = 400$ nm corresponding to the formation of the intermediate I_2. (b) Rate constants for the phosphine scavenging of the intermediate I_2.

SCHEME 1. Observed rate processes (aliphatic solvents).

was observed at concentrations of phosphine larger than 10^{-4} M (Fig. 1b) and also under 1 atm H_2 (see conventional flash results). A second order rate constant, $k_{2p} = 5.2 \times 10^6$ $M^{-1}sec^{-1}$, was obtained from pseudo-first-order rate constants
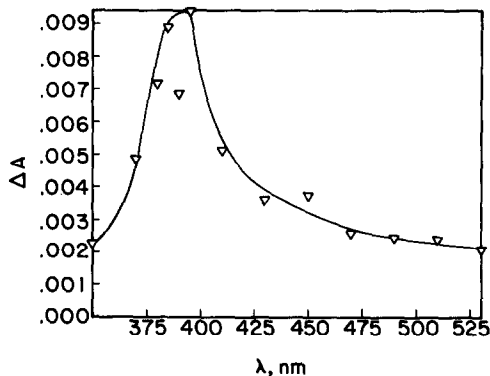
Fig. 2. The difference spectrum obtained in laser flash irradiations of ReH_5P_3 in benzene. Measurements are at 100 ns reaction time.

measured in the presence of added phosphine. A rate constant, $k_2 = 9.0 \times 10^2 \ \mathrm{sec}^{-1}$, for a concurrent phosphine-independent decay mode of I_2 was obtained by extrapolating to zero phosphine concentration. Such a process is related to a conversion of I_2 into another intermediate, I_3 (see below). The yield of transient I_1, produced during the duration of the flash in these experiments, did not change when phosphine was added up to concentrations of $5.0 \times 10^{-2} \ M$; phosphine scavenging of precursors of I_1 is thus not kinetically detectable. On the other hand, added PMe_2Ph scavenges I_1 itself with a rate constant of $k_{1p} = 5.6 \pm 0.3 \times 10^9 \ M^{-1} \ \mathrm{sec}^{-1}$.

In contrast to the above results in saturated hydrocarbons, irradiations of ReH_5P_3 in benzene produced a species (Fig. 2) that is found to be stable through the nanosecond time scale. Moreover, such species exhibits a spectrum with $\lambda_{max} \sim 390$ nm, which is very similar to that of the species I_2 (or I_3) detected in cyclohexane.

Conventional flash photolysis

The spectral transformations, described above for photolysis of ReH_5P_3 in n-hexane or cyclohexane, are followed by several transformations in a microsecond/ millisecond timescale. Indeed, flash photolysis of ReH_5P_3 in deaerated cyclohexane or n-hexane produced a species with $\lambda_{max} \sim 390$ nm, I_3, which undergoes a slow transformation into another species, I_4 (Fig. 3). In spite of the spectroscopic similarity of this I_3 with the laser-flash-detected I_2, their reactivity shows differences which indicate that they are distinct species. That the precursor of I_3 is the species I_2, generated in laser flash photolysis, was confirmed by scavenging with phosphine. Thus the yields of I_3, measured by means of the 390 nm absorbance at a zero reaction time, reveal that I_3 is formed in a process that competes with the scavenging of its precursor, I_2, by phosphine (see Appendix and Fig. 4). The ratio of the rate constant for the formation of I_3 to that for scavenging of its precursor by phosphine is $k_{2p}/k_2 = 5.2 \times 10^3 \ M^{-1}$. Such a value from the conventional flash experiments is in good agreement with the value, $5.7 \times 10^3 \ M^{-1}$, obtained in laser flash photolysis experiments.

These results thus confirm the phosphine scavenging observed under continuous photolysis conditions. To complete this comparison, we find that, at appropriate
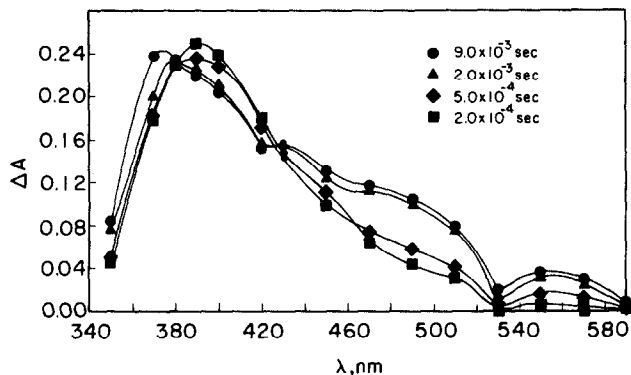
Fig. 3. Microsecond-millisecond spectral transformations obtained for flash irradiations of ReH_5P_3 in n-hexane. Excitations at $\lambda_{excit} \geq 320$ nm with 160 J/pulse. No phosphine has been added in these experiments.

concentrations of added PMe_2Ph, it is possible to create a system which is observed to be entirely photoreversible; i.e. $\Delta A_\infty = 0$ over the course of as many as 100 flashes. This result establishes the absence of reactive impurities in the solvents employed. At still higher concentrations of added PMe_2Ph, we create a system which is photostable (i.e. $\Delta A = 0$ at all conventional flash observation times).

In addition, flash photolyses of ReH_5P_3 in cyclohexane under one atmosphere of H_2 prevents the generation of the transient I_3. The observed transient spectra, which remain constant over the first 20 sec of observation, are consistent with the formation of ReH_7P_2.

As mentioned above, intermediate I_3 (λ_{max} 390 nm) is itself kinetically active on the millisecond timescale (Fig. 3). A rate constant for the decay of I_3, $k_3 = 2.2 \times 10^3$
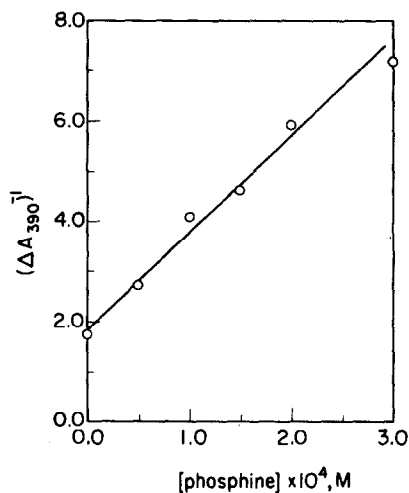

Fig. 4. Absorbance change, ΔA_{390}, recorded at zero reaction time for flash photolysis of ReH_5P_3 under conditions of added phosphine in n-hexane. For other conditions see Fig. 3.

TABLE 1

ReH_5P_3 CONCENTRATION DEPENDENCE OF THE RATE CONSTANTS FOR (A) THE DISAP-
PEARANCE OF I_3 (λ_{obs} 400 nm), AND (B) THE APPEARANCE OF I_5 (λ_{obs} 500 nm)

$[ReH_5P_3] \times 10^{5\ a}$ (M)	$k \times 10^{-3}$ (sec^{-1})
A. λ_{obs} 400 nm	
0.5	2.2 ±0.1
2.3	1.9 ±0.2
5.0	2.2 ±0.2
5.8	2.4 ±0.1
6.2	2.4 ±0.2
13.0	2.6 ±0.3
B. λ_{obs} 500 nm	
2.3	0.91±0.03
4.6	1.15±0.05
5.2	1.35±0.07
6.2	1.50±0.03
7.0	1.71±0.04

^{a} In n-hexane.

sec^{-1}, was obtained from measurements under various experimental conditions
(Table 1). Although no single spectral band is associated with the growth of I_4, the
400 nm decay is independent of ReH_5P_3 concentration (Table 1A) and is first order
in transient concentration, excluding the possibility that I_3 decay initiates the
dimerization observed in continuous photolysis.

With the unimolecular character of the production of I_4 from I_3 established, it
was possible to examine the reactivity of I_4. In particular, the growth of the band at
500 nm, associated with I_5, was shown (Table 1B) to be first order in transient (I_4)
and also in ReH_5P_3 concentration. A second order rate constant, $k_4 = 5.7 \times 10^7$
$M^{-1}sec^{-1}$ was obtained from the pseudo-first-order rate constants reported in Table
1B. The intermediate I_4 was shown to be reactive towards an olefin. Thus, although
addition of 1-hexene (2.0×10^{-5} M–3.0×10^{-6} M), fails to change the rate of

TABLE 2

SCAVENGING OF I_4 BY 1-HEXENE

[1-hexene]^a (M)	ΔA_{500}^{b}	$k_4 \times 10^{-3\ c}$ (sec^{-1})
0.0	0.190	1.3±0.1
3.3×10^{-6}	0.120	1.6±0.2
8.7×10^{-6}	0.080	1.6±0.2
1.3×10^{-5}	0.062	1.6±0.1
1.7×10^{-5}	0.051	1.5±0.1

^{a} Solutions were 5.8×10^{-5} M ReH_5R_3 in cyclohexane. ^{b} Yield of the transient I_5, measured by means of
the 500 nm absorbance change, at various 1-hexene concentrations. ^{c} Rate constant for conversion of I_4
into I_5 evaluated from ΔA_{500}. Compare Table 1B.

conversion of I_3 to I_4, it changes both the rate of formation and the yield of I_5, the product of the reaction of I_4 with ReH_4P_3 (Table 2). This observation can be interpreted as a competition between the scavenging of I_4 by 1-hexene with $k_{hex} = 5.6 \times 10^8 \ M^{-1}sec^{-1}$ and the scavenging of I_4 by ReH_5P_3. The analysis of these data is identical to that in the appendix with I_5 and I_4 replacing I_3 and I_2, respectively.

Finally, we have observed that the difference spectrum (Fig. 5), determined after a time lapse of 10 to 20 sec in the absence of added scavengers, is consistent with formation of $Re_2H_8P_4$ as the final reaction product, well downstream from I_5 in the kinetic scheme. This completes the association of the results of the current rapid kinetic study with those of the continuous photolysis work [3]. In the latter, $Re_2H_8P_4$ was shown to be a product, but to also be susceptible (on a timescale of minutes to hours) to reaction with photodissociated PMe_2Ph to give H_2 and $Re_2H_6P_5$.

The microsecond-millisecond timescale kinetics of the ReH_5P_3 photosystem were also investigated in benzene solvent. Flash photolysis of ReH_5P_3 in benzene produces transient spectra (Fig. 6) similar to those described above for irradiations in saturated hydrocarbons. A growth of the 390 nm peak was observed (Fig. 6a) with a half life $t_{1/2} \sim 8.0 \times 10^{-6}$ sec, and its rate exhibited a first order dependence in transient concentration, namely $k = 8.7 \times 10^4$ sec^{-1}. Such a growth is followed by a decrease (Fig. 6b) of the absorbance at 370 nm with $t_{1/2} \sim 3.3 \times 10^{-3}$ sec and a rate that exhibited a first order dependence in transient concentration. The rate of the two processes, namely the growth and the decrease of the absorbance, were not affected by phosphine in concentrations equal to or smaller than $5.0 \times 10^{-3} \ M$. This reduced reactivity of transients in benzene is attributed to the participation of benzene as a ligand capable of saturating coordination positions after the thermal or photochemical ejection of PMe_2Ph.
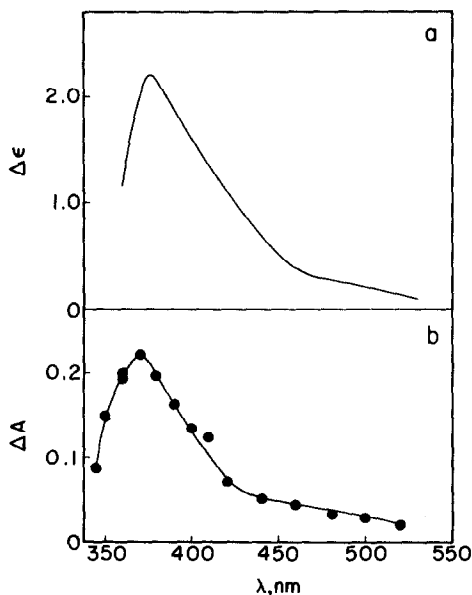

Fig. 5. A comparison between (a) the difference spectra of ReH_5P_3 and $Re_2H_8P_4$ in n-hexane and (b) the difference spectra at 20 sec elapsed time after conventional flash photolysis of ReH_5P_3 in n-hexane.
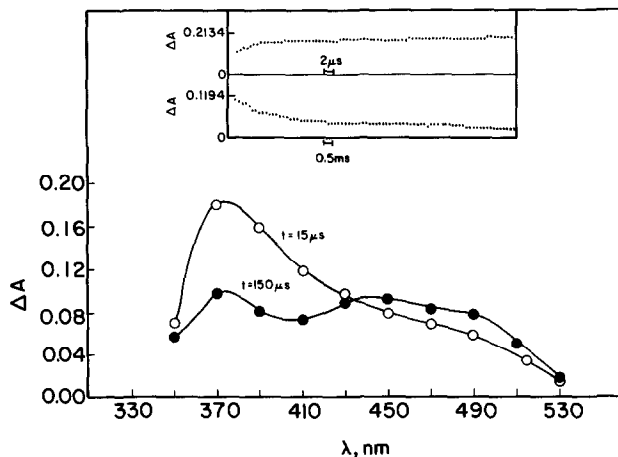
Fig. 6. Spectral transformations observed in flash photolysis of ReH_5P_3 in benzene. Insets show two typical traces at different reaction times for $\lambda_{obs} \sim 370$ nm. Excitation at $\lambda_{excit} \geq 320$ nm with 160 J/pulse.

Discussion

Equations 6–8 represent some of the earliest chemical events (i.e. bond breaking and making processes) subsequent to light absorption; curly brackets enclose

$$ReH_5P_3 \xrightarrow{h\nu} \{ReH_5P_2, P\} \tag{6}$$

$$\{ReH_5P_2, P\} \rightarrow ReH_5P_3 \tag{7}$$

$$\{ReH_5P_2, P\} \rightarrow ReH_5P_2 + P \tag{8}$$

geminate (i.e. solvent-caged) fragments. These events (recombination, eq. 7, and diffusion, eq. 8) are expected to be complete in the sub-nanosecond time domain. Chemical scavenging was employed in an attempt to probe whether there are further intermediates hidden in the recovery time from the laser flash. Added phosphine was found to have no effect on the yield of I_1. This failure to accomplish scavenging of any precursor to I_1 can be associated with both the short intrinsic lifetime ($t_{1/2} \leq 20$ ns) of such a precursor and to the relatively low concentration of phosphine which could be employed.

The earlier investigation of the primary photoproduct from 360 nm irradiation of ReH_5P_3 employed a variety of scavengers and showed photoejection of phosphine to be the primary process [3,4,7]. Consequently, I_1, whose formation is observed to be complete at the earliest acquisition times in laser flash photolysis of ReH_5P_3 in aliphatic hydrocarbons, is assigned as the heptacoordinate and unsaturated complex ReH_5P_2. Consistent with this assignment is the observation that I_1 reacts with added PMe_2Ph at the diffusion-controlled rate.

The full range of kinetic studies reported here demonstrate that the path from ReH_5P_2, I_1, to $Re_2H_8P_4$ is mediated by thermal reactions of an unexpectedly large

number of reactive intermediates. This process is far more complex than originally envisioned. As summarized in the Scheme, transients I_2, I_3 and I_4 intervene before the detection of the first process which is second order in rhenium. Dimerization begins [11] with an encounter of ReH_5P_3 with I_4, a transient of probable composition "ReH_5P_2". This indicates that transient I_4 is sufficiently reactive to react with ReH_5P_3 at 25°C. This is a significant accomplishment since previous work [3,12] has demonstrated the resistance of ReH_5P_3 to thermal reaction with a variety of two-electron donor reagents. More impressive is the fact that the second order rate constant for formation of the Re_2 species is as large as 5.7×10^7 M^{-1} sec^{-1}. Finally it was possible to merge the flash photolysis results to the continuous photolysis work by showing that the ultimate (20 s) product of flash photolysis has the electronic spectrum of $Re_2H_8P_4$. Although the detailed sequence of loss of H_2 and PMe_2Ph from the resulting "$Re_2H_{10}P_5$" to give $Re_2H_8P_4$ remains unknown, it is significant that PMe_2Ph is lost at all; $Re_2H_6P_5$ is a known species [3]. Transient I_4 was also observed to be scavenged by 1-hexene at near the diffusion-controlled rate. It is reasonable that k_{hex} is greater than the rate constant for reaction of I_4 with the bulkier and more inert reagent ReH_5P_3.

The origin of the unexpectedly complex kinetic system reported here lies in the fact that I_1, ReH_5P_2, undergoes a unimolecular "reorganization" on the microsecond timescale. Because the concentration of ReH_5P_3 is nearly five orders of magnitude lower in flash photolysis (as low as 5.10^{-6} M) than in the earlier continuous photolysis study ($\sim 10^{-1}$ M), I_1 is comparatively immune to bimolecular collisions which would lead to prompt dimer formation. The flash study is therefore capable of detecting the evolution of I_1 along a complex array of unimolecular transformations.
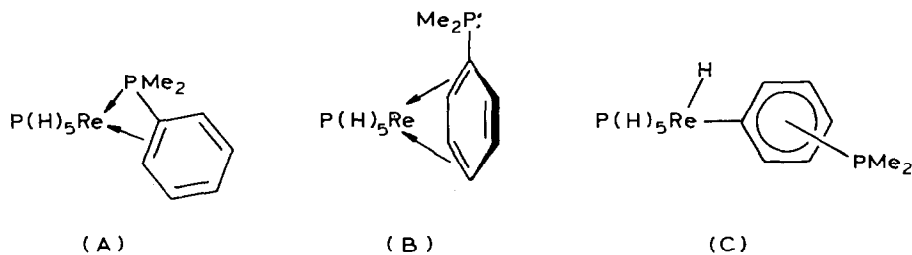
The elemental composition of I_2 is concluded to be ReH_5P_2 since it is scavenged by phosphine to give ReH_5P_3 and by H_2 to give ReH_7P_2. The rate constant for scavenging by phosphine, 5.2×10^6 M^{-1} sec^{-1}, is consistent with I_2 being reactive, but less so than I_1. I_2 also undergoes phosphine-independent unimolecular "reorganization" to I_3, but at a modest rate. In turn, I_3 isomerizes to I_4, again at a modest rate, but it is not scavenged effectively by either hex-1-ene or ReH_5P_3.

This series of observations confirms the preeminent reactivity of authentically heptacoordinate ReH_5P_2 (I_1). We must rely on allied results from organometallic chemistry for tentative structural identifications of the successor species I_2, I_3, and I_4.

The complex ReH_5P_3, like most polyhydrides, is termed "nonrigid" at the time resolution of the slower (e.g. NMR) spectroscopic techniques, with intramolecular rearrangement occurring rapidly [12] at 25°C. This rearrangement serves to permute all five hydrogens, and also the three phosphines; the latter possess only mirror symmetry (one unique phosphorus) in the ground state structure [13]. Typical values for the rate of such rearrangements are $\sim 10^2$ sec^{-1} for MH_4P_4 (M = Mo or W) at 25°C [14]. The electronic spectral detection employed in flash photolysis is of course unaffected by the above degenerate rearrangements. However, allied nondegenerate rearrangements (e.g. from a non-ground-state 7-coordinate polyhedron to the ground state) warrant consideration. Such isomerization will probably occur with little or no activation energy (the entire energy surface for angular deformation of high coordination number hydride complexes is characterized by small barriers). Consequently, we assume that I_1 has relaxed completely with respect to geometrical isomerization

and that none of the transformations to I_2, I_3 and I_4 involve simple isomerizations. Structures A, B, and C warrant consideration for I_2, I_3 and I_4. All involve

$$Me_2P \cdot$$

PMe₂ structure (A): P(H)₅Re ... PMe₂ — benzene ring
structure (B): Me₂P⋮ — P(H)₅Re — cyclohexadiene ring
structure (C): H — P(H)₅Re — benzene ring — PMe₂

(A)   (B)   (C)

sufficient reorganization to justify activation energies appropriate to the observed values of k_2 and k_3. A and B are 18-electron complexes which should therefore be exergonic relative to I_1. Structure A is sufficiently closely related to heptacoordinate I_1 that it could form as rapidly as dictated by the observed k_1. It finds direct analogy to the observed structure of $Rh(PPh_3)_3{}^+$ [15,16]. Structure B should be reactive since η^4-arene complexes sacrifice benzene resonance energy. Structure C is preferred as the *meta*- or *para*-isomer, since it is known [3] that this photosystem exchanges Re–D with the *meta*- and *para*-protons of PMe_2Ph. The *ortho*-isomer (or even the *ortho*-metallated species D) is not rigorously excluded at 10^{-5} M Re, although we

H — P(H)₅Re — benzene ring — PMe₂

(D)
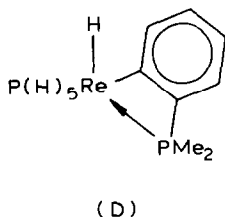
know it to be absent at 10^{-1} M Re from the continuous photolysis study. Recalling that phosphine loss is known to occur in the dimerization initiated from I_4, the rupture of one Re–P bond in forming structures B and C makes either attractive as the structure of I_4.

One more process warrants consideration for one of the transformations between I_2 and I_4: reductive elimination of dihydrogen. This must be accepted as possible within the available kinetic spectroscopic data [17,18]. If I_4 is in fact a trihydride, its substantial bimolecular reactivity is explained, and the dimeric product I_5 is an octahydride at the moment of its production: "$Re_2H_8P_5$".

The above results in saturated hydrocarbons contrast to those in benzene. This study provides evidence for active participation of benzene solvent with the earliest phototransient. In particular, the nanosecond time domain is simplified in benzene compared to alkane solvent and the product of enhanced stability (lifetime) has an absorbance maximum not unlike that of I_2 [19]. We suggest that this is due to rapid capture and η^2-coordination of benzene by authentic heptacoordinate ReH_5P_2. Such a process will be extremely rapid in neat benzene, and the product more stable than the strained "chelated" PMe_2Ph portrayed as A for I_2. This coordination quite naturally accounts for the Re–H/arene-*d* isotopic exchange reported earlier [3,4] under continuous photolysis conditions for the ring protons of benzene, toluene,

naphthalene and PMe_2Ph. Available examples indicate that η^2-coordination of arenes is possible [20,21].

Conclusion

We have pursued our study of ReH_5P_3 photochemistry in recognition of the fact that phosphine photodissociation is unusual in such a complex [22]. This study establishes the high (diffusion-controlled) reactivity of the photoproduct ReH_5P_2 and also that dimerization proceeds by thermal reaction of a phototransient with a ground state saturated species, ReH_5P_3. The complexity of the time evolution of the primary product ReH_5P_2 in the absence of added scavengers and at $[ReH_5P_3] \approx 10^{-5}$ is a consequence of the inefficiency of bimolecular processes. Bimolecular capture of the primary photoproduct ReH_5P_2 is of course the main path to product in the continuous photolysis work, where $[ReH_5P_3] \approx 10^{-1}$ and scavenger concentrations are even higher. Nevertheless, the complex set of unimolecular transformations from I_1 to I_4 focus attention on the fact that aryl ligand substituents provide an intramolecular scavenging option which can diminish the reactivity of the primary photoproduct. Noteworthy in this context is the fact that irradiation of a 3/1 mole ratio of $PMe_2Ph/ReH_5(PMe_2Ph)_3$ in cyclohexane-d_{12} gives no H/D scrambling (or any new metal complexes). Trialkylphosphines may therefore be preferable as ligands [23].

Acknowledgment

Appendix

The generation of I_3 is conventional flash photolysis can be described by the following scheme.

$$ReH_5P_3 \xrightarrow[\varphi]{h\nu} I_2 \longrightarrow \left\{ \begin{array}{l} \xrightarrow{k_{2p}} \quad P \quad ReH_5P_3 \\ \xrightarrow{k_2} \quad I_3 \end{array} \right. \tag{9, 10}$$

The precursor I_2 can either rearrange into I_3 or be scavenged by phosphine, P. A steady state treatment, based on a constant concentration of I_2 during the irradiation, gives the rate of formation of I_3 indicated in eq. 11.

$$\frac{d[I_3]}{dt} = \varphi \langle I_{abs} \rangle \frac{k_2}{k_2 + k_{2p}[P]} \tag{11}$$

($\langle I_{abs} \rangle$ = average light intensity absorbed during the flash).

Hence the yield of I_3, $\Phi(I_3)$, can be expressed as in eq. 12.

$$\Phi(I_3) = \frac{1}{\langle I_{abs} \rangle} \frac{d[I_3]}{dt} = \varphi \frac{k_2}{k_2 + k_{2p}[P]} \tag{12}$$

Equation 12 predicts a linear dependence of the reciprocal of the I_3 yield, $1/\Phi(I_3)$, on phosphine concentration. Figure 4 confirms the validity of eq. 12 with a ratio $k_{2p}/k_2 = 5.2 \times 10^3 \ M^{-1}$. Moreover the two processes, namely the rearrangement of I_2 to I_3 and the scavenging of I_2 by phosphine, can be observed in laser flash photolysis with rate constants $k_{2p} = 5.2 \times 10^6 \ M^{-1} \ sec^{-1}$ and $k_2 = 9.0 \times 10^2 \ sec^{-1}$. These rate constants gave a ratio $k_{2p}/k_2 = 5.7 \times 10^3 \ M^{-1}$ which is in agreement with the value obtained in conventional flash photolysis.

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