bonding orbital (b_2) is delocalized (and may account for the peak in the PES at 10.07 eV). This orbital can interact with the πd orbital of the metal; it and its antibonding counterpart may play some role in the delocalization of electron density. If the contribution of the bonding level dominated, III would be expected to show a more intense band than II, because isonicotinamide, by making Ru(III) more oxidizing, would cause a stronger admixture of the Ru(III)·L^+·Ru(III) state into the ground state.

Since a significant fraction of the nominally [2.3] species is present in the isovalent forms, the extinction coefficient of the mixed-valence molecule may be as high as 60 or 70, suggesting that elecron transfer within the molecule, while nonadiabatic, is not markedly so.[15]

Acknowledgment. Support for this work through Grant GM13638-14 from the National Institutes of Health is gratefully acknowledged.

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Photochemistry of Transition-Metal Polyhydrides: Dimerization of $ReH_5(PMe_2Ph)_3$ Following Photodissociation of Phosphine†

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Among low-valent metals, those at the center of the transition series (groups 6, 7, and 8) constitute a group where the effective atomic number concept rules most firmly. Moreover, within a group it appears that the heavier representatives have the greatest aversion to coordinative unsaturation. It is thus predictable that monomeric 16-electron rhenium complexes should be (1) difficult to produce and, once formed, (2) highly reactive. We report here the photoassisted production of $H_5Re(PMe_2Ph)_2$ by an unprecedented photoextrusion of phosphine in preference to dihydrogen. We demonstrate a regioselective and catalytic activation of arene C–H bonds by 16-electron $H_5Re(PMe_2Ph)_2$ and also the efficient condensation of this fragment to a new class of rhenium polyhydride dimers.

Photolysis[1] of a benzene solution of colorless $H_5Re(PMe_2Ph)_3$[2] results in rapid appearance of a dark red color due to a new polyhydride dimer of formula $H_6Re_2P_5$ ($P \equiv PMe_2Ph$). In a closed vessel of limited head space, H_7ReP_2[2,3,4a] is also a detectable product, but it, unlike $H_6Re_2P_5$, is rather photosensitive (see below).

We have sought to establish the primary chemical product of irradiation, although the existing literature[5,6] indicates that L_mMH_n ($n \geq 2$) complexes generally undergo photoextrusion of dihydrogen. We consider the two processes shown in eq 1 and 2. Irradiation

$$H_5ReP_3 \overset{h\nu}{\rightleftharpoons} H_3ReP_3 + H_2 \tag{1}$$

$$H_5ReP_3 \overset{h\nu}{\rightleftharpoons} H_5ReP_2 + P \tag{2}$$

of a benzene solution of H_5ReP_3 in the presence of 3 equiv of PMe_2Ph completely quenches dimerization; no change is evident in the solution composition after irradiation. Additionally, irradiation of a C_6D_6 solution of D_5ReP_3 containing excess free

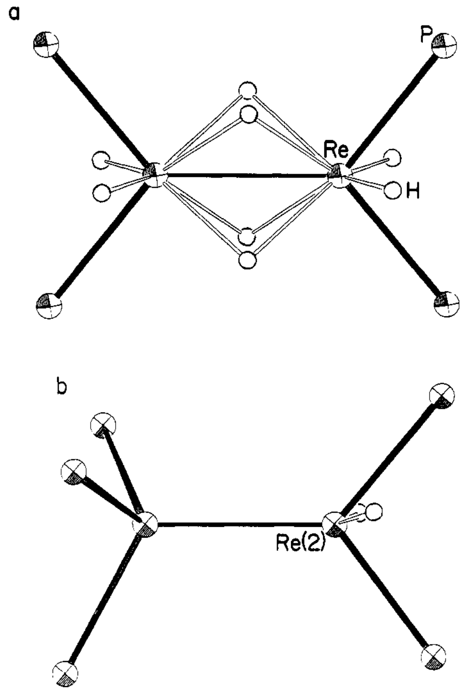
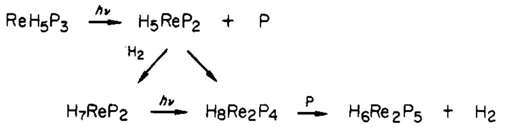


Figure 1. ORTEP drawings of the inner coordination spheres of (a) $H_8Re_2(PEt_2Ph)_4$[4] and (b) $H_6Re_2(PMe_2Ph)_5$, oriented to show the structural relationship between the two.[16] Note that only two of the six metal-bound hydrogens have been located in $H_6Re_2(PMe_2Ph)_5$. These yield a terminal ligand environment about Re(2) which closely mimics that in $H_8Re_2(PEt_2Ph)_4$.

Scheme I



PMe_2Ph under a purge of H_2 results in no incorporation of protium bound directly to rhenium. Finally, irradiation of a benzene solution of $H_5Re(PMe_2Ph)_3$ containing 6 equiv of PEt_2Ph shows (^{31}P NMR) production of all possible species of the type $H_5Re(PMe_2Ph)_{3-n}(PEt_2Ph)_n$, along with free PMe_2Ph. This photoinduced[7] phosphine exchange,[8] along with the preceding two experiments, indicates that irradiation effects dissociation of phosphine (eq 2). Photoextrusion of hydrogen (eq 1) is not viable even as a second, independent photodecay pathway. This result is highly significant in that the photoproduct thus conserves the inherently more interesting hydride ligand.

The photodimerization (eq 3) which occurs in the absence of added phosphine is enhanced in rate when carried out under a

$$2H_5ReP_3 \xrightarrow{h\nu} H_6Re_2P_5 + 2H_2 + P \tag{3}$$

purge of H_2. Under these conditions, H_7ReP_2 achieves considerably higher concentrations at intermediate stages of the photolysis. Conversely, an argon purge during photolysis slows (but does not completely prevent) dimer formation; this establishes the existence of a direct path from H_5ReP_2 to the dimer. We interpret these results in terms of Scheme I, which invokes both a direct route to dimer from H_5ReP_2 and also dimerization of H_7ReL_2 by a secondary photolysis.[9] If irradiation is carried out in hexane,

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† Contribution No. 3552.

(1) Hanovia 550-W medium-pressure Hg lamp, through Pyrex glass.

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(7) This same solution held at 80 °C for 3 h showed no evidence (^{31}P NMR) for phosphine exchange.

(8) We view this experiment as equivalent to an isotopic exchange. It is essentially entropically driven: when the mixture of complexes $H_5Re(PMe_2Ph)_{3-n}(PEt_2Ph)_n$, separated from free PEt_2Ph, is irradiated in the presence of added PMe_2Ph, complete regeneration of $H_5Re(PMe_2Ph)_3$ is effected.

(9) H_7ReP_2 is thermally stable to dimerization under our photochemical reaction conditions. The photodimerization of H_7ReP_2 has been verified independently.

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$H_8Re_2P_4$[3,4] may be intercepted since it precipitates. We have shown directly that the Re(IV) polyhydride $H_8Re_2P_4$ undergoes facile thermal phosphine-induced reductive elimination of H_2 at 25 °C in benzene, and therefore propose that it, and not $H_6Re_2P_5$, is the first stable dimeric product of photolysis. The reduced polyhydride $H_6Re_2P_5$, whose coordination sphere is shown[10,11] in Figure 1b, is unusual in being a mixed oxidation state species. The metal-metal separation [2.589 (1) Å] is similar to that in $H_8Re_2P_4$ [2.538 (4) Å],[4] in spite of ^1H NMR evidence[12] which indicates $H_6Re_2P_5$ to have one terminal hydride on Re(1), and thus only three μ_2-H ligands.

H_5ReP_2 activates arene C-H bonds. Any of the above irradiations of H_5ReP_3, when carried out in C_6D_6, effects deuteration of the metal in both H_5ReP_3 and the dimeric products. In a competitive process, the aryl ring of the phosphine also undergoes deuteration by D_5ReP_3 during irradiation. This is evident if the photoassisted phosphine exchange experiment described above is performed in C_6D_6: the liberated phosphine appears (^{31}P NMR) as at least two lines of unequal intensity, due to a deuterium isotope effect on the ^{31}P chemical shift (8-Hz upfield at 40 MHz for the ring-deuterated species).[13] Remarkably, ^1H NMR shows that arylphosphine deuteration occurs only at the meta and para positions; no ortho deuteration is detected. This suggests that deuteration of coordinated phosphine is an intermolecular process, in which D_5ReP_2 acts on the aryl ring of D_5ReP_3 as it would on more conventionally substituted arenes.[14]

We are continuing to explore the reactivity of H_5ReP_2 and $H_6Re_2P_5$ as well as the synthetic generality of the concept of photocondensation of polyhydride monomers to polyhydride dimers.

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Supplementary Material Available: A table of atomic positional and thermal parameters (1 page) for $H_6Re_2(PMe_2Ph)_5$. Ordering information is given on any current masthead page.

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(10) The two terminal hydride positions shown in Figure 1b were located in a difference Fourier map. We have suspended any search for the remaining four hydridic hydrogens pending a neutron diffraction study.

(11) Crystallographic data (−170 °C): $a = 11.737$ (3), $b = 13.031$ (4), $c = 15.238$ (5) Å; $\alpha = 73.39$ (1), $\beta = 90.76$ (2), $\gamma = 108.16$ (1)°; $V = 2114.8$ Å^3; $Z = 2$ in space group $P\bar{1}$; $R(F) = 3.7\%$, $R_w(F) = 4.1\%$ for 5020 observed [$F_o > 2.3\sigma(F_o)$] reflections using anisotropic thermal parameters for all nonhydrogen atoms; all hydrogens bound to carbon were refined isotropically.

(12) The 360-MHz ^1H NMR spectrum of $H_6Re_2(PMe_2Ph)_5$ in toluene-d_8 shows three hydride resonances at −90 °C: δ −6.30 (br s), −9.75 (t, $J = 44.5$ Hz), and −10.35 (quartet, $J = 45.0$ Hz) with intensities of 3:2:1 (integrated relative to the 30 methyl protons). At room temperature these collapse into a single broad resonance at −8.26 ppm.

(13) $P(2,6\text{-}D_2C_6H_3)_3$, kindly supplied by U. Klabunde and G. Parshall, experiences a ^{31}P deuterium isotope effect of 25 Hz (0.6 ppm).

(14) U. Klabunde has informed us of unpublished experiments in which he has observed exchange of D_2 with a variety of arenes catalyzed by $H_5Re(PMe_2Ph)_3$ at 108 °C. A detailed description of related thermal exchanges has been reported for other metal hydride catalysts.[15]

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(16) Selected distances: Re(1)-P: 2.317 (2), 2.327 (2), and 2.345 (2) Å; Re(2)-P: 2.313 (2) and 2.298 (2) Å. Selected angles: P-Re(1)-P, 102.1-111.6°; P-Re(2)-P, 103.4°; P-Re(1)-Re(2), 104.5-117.5°; P-Re(2)-Re(1), 126.5 and 129.6°.

On the Mechanism of T4 RNA Ligase[1]

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The bacteriophage T4 RNA ligase catalyzes the formation of a 5′-3′-phosphodiester linkage, thereby joining two oligoribonucleotides with the concomitant conversion of ATP to AMP and inorganic pyrophosphate (PP_i).[2] A plausible minimum reaction sequence constructed from the observation of an adenylated enzyme (AMP-ligase)[3] and under certain experimental conditions an adenylated pyrophosphoryl intermediate ($App(Np)_n$)[4] is given in Scheme I, where $p(Np)_n$ represents an oligoribonucleotide where $n \geq 1$ (the 5′-phosphoryl donor) and $(Np)_mN$ represents an oligoribonucleotide where $m \geq 2$ (the 3′-hydroxyl acceptor). We have sought the answers to two questions: (1) Is there, possibly for reasons of symmetry, an undetected reaction intermediate involving a covalent bond between the ligase and the donor in the last step of the above sequence? (2) Is there a preferred chirality at phosphorus maintained in the activation and transfer of the 5′-phosphoryl moiety in steps 2 and 3?

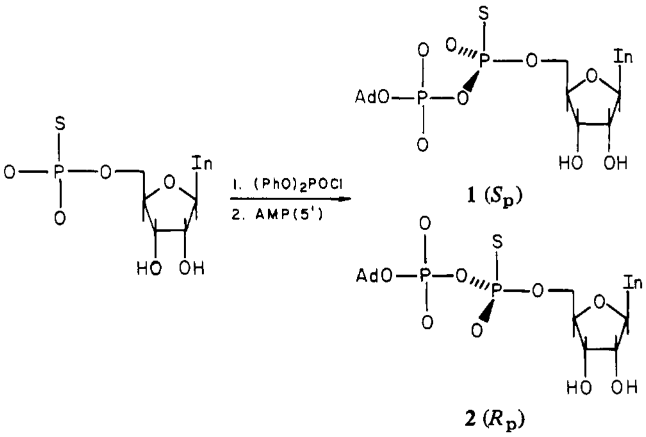
Scheme I

$$\text{ATP} + \text{ligase} \rightleftharpoons \text{AMP-ligase} + PP_i \qquad (1)$$

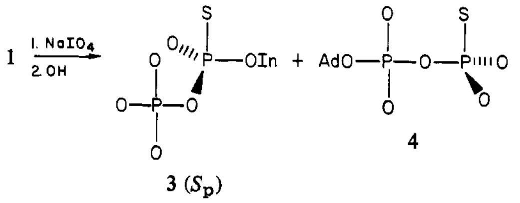
$$\text{AMP-ligase} + p(Np)_n \rightleftharpoons App(Np)_n + \text{ligase} \qquad (2)$$

$$App(Np)_n + (Np)_mN \xrightleftharpoons{\text{ligase}} (Np)_mNp(Np)_n \qquad (3)$$

Scheme II



Scheme III



The stereochemical course of step 3 with respect to phosphorus was investigated by using **1** and **2**, which were synthesized as outlined in Scheme II. Activation of inosine 5′-phosphorothioate[5] by diphenyl phosphorochloridate[6] was followed by coupling to adenosine monophosphate to yield **1** and **2** in 44% total yield. These were separated by column chromatography on DEAE-

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(1) Supported by Grant No. GM 13306 from the National Institutes of Health.

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