

Preliminary communication

MECHANISTIC STUDIES ON THE OXIDATION OF AN ANIONIC RHENIUM POLYHYDRIDE COMPLEX: GENERATION AND REACTIVITY OF THE TRANSIENT RADICAL $[\text{ReH}_6(\text{PMePh}_2)_2]$

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(Received June 20th, 1986)

Summary

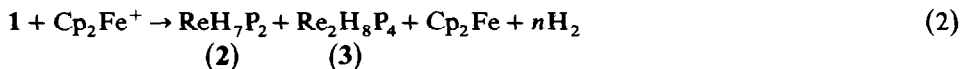
The anionic polyhydride $[\text{ReH}_6\text{P}_2][\text{K}]$ (1) ($\text{P} = \text{PMePh}_2$) undergoes facile one-electron oxidation when treated with either ferricinium ion or $[\text{Fe}(\text{bpy})_3]^{3+}$; the ultimate products are ReH_7P_2 (2) and dimer $\text{Re}_2\text{H}_8\text{P}_4$ (3). Mechanistic studies are consistent with the initial production of the 17-electron intermediate $[\text{ReH}_6\text{P}_2]$; while the proposed intermediate is not trapped by added phosphines, it reacts with an added hydrogen atom source (1,4-cyclohexadiene) to form 2 at the expense of 3. The $[\text{ReH}_6\text{P}_2]$ is proposed to proceed in the absence of trapping reagents to 2 and 3 via two distinct pathways, hydrogen abstraction and condensation with another rhenium hydride species. This competition is concentration dependent; while 2 is always observed as the major product, the percentage of 3 formed is greater at higher concentrations.

We have been interested in the generation of odd electron transition metal polyhydrides in the belief that they should show greater reactivity than their diamagnetic counterparts. Examples of paramagnetic hydrides have been observed [1] and even isolated [2] for early transition metals, but monomeric derivatives of the later transition metals are few in number [3-5]. An obvious synthetic approach is the oxidation of diamagnetic hydrido compounds, and this proceeds readily with triply bonded $\text{Re}_2\text{H}_8\text{P}_4$ [6]. However, reaction of monomeric hydrides with aggressive oxidants leads to rapid two-electron oxidation in the case of MoH_4P_4 [7], while use of weaker oxidants/electrophiles has been found to yield hydride-bridged adducts in a number of cases [8-10]. Recently we reported that deprotonation of ReH_7P_2 ($\text{P} = \text{PMePh}_2$) constitutes a convenient, high yield preparation of anionic $[\text{ReH}_6\text{P}_2][\text{K}]$ (1) (eq. 1) [11]; herein we report studies on the oxidation of this anion,



including evidence for the intermediacy of the short-lived 17-electron transient $[\text{ReH}_6\text{P}_2]$.

Addition of THF to an equimolar (8 mM each) mixture of **1** and $[(\text{C}_5\text{H}_5)_2\text{Fe}][\text{BF}_4]$ [12] results in a blue-green suspension which gradually (30–45 min at ambient temperature) turns orange-red as the ferricinium salt dissolves and is consumed; gas evolution is discernable, but is more evident at higher concentrations (see below). Proton NMR (and the absence of the blue color of ferricinium) indicates the complete consumption of both reactants with formation of known compounds ReH_7P_2 (**2**), $\text{Re}_2\text{H}_8\text{P}_4$ (**3**), and $(\text{C}_5\text{H}_5)_2\text{Fe}$ (eq. 2); the rhenium-containing products are present in a ratio of $2/3 = 4/1$ as determined by integration of their phosphine



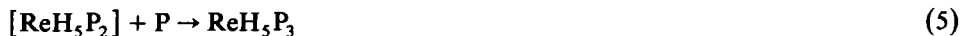
methyl resonances (also verified by ^{31}P NMR). Additionally, ^1H NMR indicates the production of 0.9 ± 0.1 equivalents of ferrocene per equivalent of **1** converted.

Although the NMR evidence indicated that ferricinium was ultimately reduced to ferrocene in this reaction, we were concerned with the possibility that ferricinium could also function as a hydrogen atom acceptor. This would lead to the known 18-electron species $(\text{C}_5\text{H}_5)_2\text{FeH}^+$ [13]. As such, we sought verification of the redox pathway by employing the outer sphere oxidant $[\text{Fe}(\text{bpy})_3][\text{PF}_6]_3$ [14]. Reaction of this species with **1** under conditions identical to those employed in eq. 2 resulted in conversion of the blue Fe^{III} compound to red $[\text{Fe}(\text{bpy})_3]^{2+}$, as well as the production of **2** and **3** in the same 4/1 ratio observed with ferricinium.

The data discussed above are consistent with an initial process involving single electron oxidation of **1** to the 17-electron species $[\text{ReH}_6\text{P}_2]$, but indicate little about the mechanism by which this transient results in **2** and **3**. Previous work [15] had shown that $\text{Re}_2\text{H}_8\text{P}_4$ can be formed from the 16-electron intermediate $[\text{ReH}_5\text{P}_2]$. This was generated from either ReH_7P_2 (via thermal H_2 loss) or ReH_5P_3 (via photochemical P loss); once formed the transient either reacts with ReH_7P_2 result-



ing in **3** and H_2 (eq. 3), or is scavenged by H_2 to regenerate **2** (eq. 4). However, both of these processes were shown to be quenched by the addition of 5 equivalents of free phosphine, which served to trap the $[\text{ReH}_5\text{P}_2]$ with unit efficiency (eq. 5). One

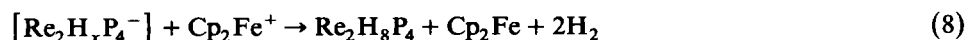


pathway, therefore, by which intermediate $[\text{ReH}_6\text{P}_2]$ could give rise to **2** and **3** in the present studies is via disproportionation to $[\text{ReH}_5\text{P}_2]$ and ReH_7P_2 . To test this possibility, we carried out the oxidation in the presence of 5–6 equivalents of PMePh_2 [16]. Under these conditions the reaction proceeded as before, with the exception that the $\text{Re}_2\text{H}_8\text{P}_4$ product was subsequently converted to $\text{Re}_2\text{H}_6\text{P}_5$ in a known follow-up reaction [15]. Fortunately, this latter process was considerably slower than the reaction of **1** and ferricinium ion and did not interfere with the spectral interpretation. Furthermore, there was less than 5% conversion to ReH_5P_3 ; this indicates that disproportionation of $[\text{ReH}_6\text{P}_2]$ to free $[\text{ReH}_5\text{P}_2]$ and ReH_7P_2 is

at most a very minor component of the reactions of this transient.

Two additional observations bear on the intermediacy and possible fate of the proposed transient $[\text{ReH}_6\text{P}_2]$. In an attempt to trap this 17-electron species, 1,4-cyclohexadiene was employed as a potential hydrogen atom source. When **1** and $[\text{Fe}(\text{bpy})_3]^{3+}$ ion reacted in the presence of 25 molar equivalents of this diene, monomer **2** made up nearly all ($96 \pm 2\%$) of the resulting products. Moreover, even in the absence of trapping reagents the product ratio shows a dependence on concentration. Thus, while the **2/3** product ratio is 4/1 at 8 mM reactant concentrations (THF solvent), it decreases to 3/2 at 35 mM and increases to ca. 6/1 at 4 mM; i.e., dimer **3** production is facilitated at higher transient concentration [17].

Since our results appear to rule out disproportionation of $[\text{ReH}_6\text{P}_2]$ and simultaneous (i.e. stoichiometrically linked) production of **2** and **3**, we favor a mechanism in which these products arise via different channels. We will first discuss the formation of dimer **3**. This could involve combination of two $[\text{ReH}_6\text{P}_2]$ intermediates (eq. 6), or a sequence involving combination of $[\text{ReH}_6\text{P}_2]$ and **1** followed by oxidation of the resulting dimeric radical anion (eqs. 7,8). Either process would require elimination of two equivalents of H_2 ; in the second sequence, the timing of this relative to oxidation (eq. 8) is unclear. We favor this latter process because



the first requires that two short-lived intermediates encounter each other. Moreover, such a condensation of an 18- and 17-electron species (with possible simultaneous H_2 loss) resembles the condensation of 18- and 16-electron fragments observed so frequently [15,18].

Monomer **2** is suggested to arise from a hydrogen atom abstraction process, with solvent the likely source of this hydrogen [19]. We have attempted to verify this with isotopic labelling studies, but these attempts have been frustrated by the statistical uncertainty involved in quantifying small amounts of label in a species with 7 hydrides. However, there is indirect evidence supporting the involvement of solvent. First, the trapping studies with 1,4-cyclohexadiene establish that $[\text{ReH}_6\text{P}_2]$ can lead exclusively to **2** via hydrogen abstraction. Also, production of hydrogen-rich **2** is favored by low reactant concentrations, arguing against the prospects that the hydrogen atom originates either from oxidant or from a rhenium hydride species.

In summary, the data presented here indicate that the anionic polyhydride **1** undergoes single electron oxidation with no obvious tendency toward a second oxidation. The 17-electron $[\text{ReH}_6\text{P}_2]$ does not disproportionate, but rather undergoes competitive abstraction and combination processes leading to monomer **2** and dimer **3**, respectively. Electrochemical studies designed to further characterize this and related systems are currently underway.

Acknowledgements. We thank Wesleyan University, Merck & Co., and NSF (grant CHE-83-05281) for partial support of this work. Rhenium Alloys Inc. is acknowledged for material support.

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