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Preliminary communication

REDOX REACTIONS OF POLYHYDRIDE COMPLEXES OF RHENIUM: ELECTROCHEMISTRY AND REACTIONS WITH ALKYL ISOCYANIDES

J.D. ALLISON, C.J. CAMERON, R.E. WILD and R.A. WALTON*
Department of Chemistry, Purdue University, West Lafayette, Indiana 47907 (U.S.A.)

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Summary

The dark red octahydride complex of dirhenium, $Re_2H_8(PPh_3)_4$, undergoes a reversible one-electron oxidation to the blue mono-cation $[Re_2H_8(PPh_3)_4]^+$ ($E_{1/2}$ −0.24 V vs. SCE by cyclic voltammetry). The X-band ESR spectrum of a dichloromethane glass (−160°C) containing the monocation is in accord with the HOMO being a delocalized metal-based orbital. Treatment of the heptahydrides $ReH_7(PR_3)_2$ (PR_3 = PPh_3 or $PEtPh_2$) with $C_6H_{11}NC$ or Me_3CNC in the presence of KPF_6 leads to the elimination of hydrogen and the formation of $[Re(CNR)_4(PR_3)_2]PF_6$. Electrochemical oxidation of $ReH_5(PPh_3)_2L$ (L = PPh_3, PEt_2Ph, pyridine, piperidine or cyclohexylamine) activates these molecules to attack by RNC to afford rhenium(I) species.

Polyhydride complexes of the transition metals are a well established class of molecule [1] for which there has been a recent resurgence of interest in their chemical reactivity [2—5]. Following our development of a high yield synthetic route to the dinuclear multiply-bonded complexes $Re_2H_8(PR_3)_4$ [6]* we have embarked upon a study of the reactions of these molecules and other polyhydride complexes of the second and third transition series. Preliminary results of certain aspects of the rich and varied redox chemistry of Re_2H_8(PPh (I), $ReH_7(PR_3)_2$ (IIa, PR_3 = PPh_3; IIb, PR_3 = $PEtPh_2$), $ReH_5(PPh_3)_3$ (III) and $ReH_5(PPh_3)_2L$ (IV, with L = PEt_2Ph, pyridine, piperidine or cyclohexylamine) are reported herein.

The octahydride $Re_2H_8(PPh_3)_4$ was originally formulated as the "agnohydride" $[ReH_x(PPh_3)_2]_2$ [7] but structural studies by Bau et al. [8] showed

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*Address any correspondence to this author.

**Recent improvements in the procedure by which $(Bu_4N)_2Re_2Cl_8$ is hydrogenated ($NaBH_4$) in the presence of PPh_3 [6], affords $Re_2H_8(PPh_3)_4$ in 80% yield.

that this class of molecule possessed the dinuclear hydrido-bridged structure $(R_3P)_2H_2Re(\mu\text{-}H)_4ReH_2(PR_3)_2$. The short Re—Re distance can be interpreted in terms of a Re—Re triple bond [6,8], although the bonding in such molecules is actually rather complicated [9]. Studies on the solution chemistry of the triphenylphosphine derivative were previously discouraged [6,7] by the poor solubility properties of this complex. However, in the present investigation we found I to be sufficiently soluble in CS_2 to permit measurement of its previously unobtained ^{1}H NMR spectrum. In the high field region, the resonance due to the hydride ligands in this fluxional molecule is seen as a symmetric quintet at δ −5.75 ppm (J(P—H) ~8.5 Hz), a result which is in accord with ^{1}H NMR spectral data for the corresponding PEt_2Ph and $PEtPh_2$ derivatives [6—8].

The electrochemical properties of I have been investigated in 0.2 M tetra-n-butylammonium hexafluorophosphate-dichloromethane solutions using cyclic voltammetry and coulometric techniques. The cyclic voltammogram consists of a reversible couple at −0.24 V vs. SCE, as well as an irreversible oxidation at $E_{p,a}$ = +0.55 V vs. SCE (Fig. 1). The oxidation at −0.24 V corresponds to a one-electron process; $[Re_2H_8(PPh_3)_4] \xrightarrow{-e} [Re_2H_8(PPh_3)_4]^+$. The peak current ratio $i_{p,a}/i_{p,c} \approx 1$, and values of $i_{p,c}/v^{1/2}$ were constant for scan rates (v) from 50 to 400 mV/s. For the −0.24 V couple, ΔE_p (90 mV at 200 mV/s) increased with increasing scan rate. These properties are (with our cell configuration and solvent system) [10] consistent with an electron transfer process which is reversible or approaches reversibility.

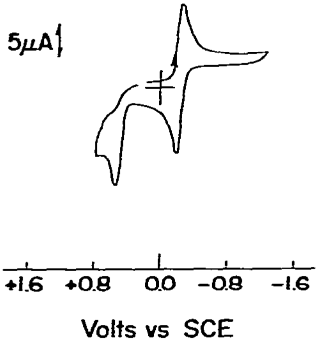

Fig. 1. Cyclic voltammogram of $Re_2H_8(PPh_3)_4$ in 0.2 M tetra-n-butylammonium hexafluorophosphate-dichloromethane recorded using a sweep rate of 200 mV/s and a platinum bead electrode.

Upon electrochemical oxidation at +0.1 V, solutions of I changed in color from orange-red to deep blue. At room temperature, $[Re_2H_8(PPh_3)_4]^+$ was found to be a short lived species, and within a few minutes following the completion of the oxidation the deep blue solution turned green. The cyclic voltammogram of the green solution showed the absence of significant quantities of $[Re_2H_8(PPh_3)_4]^{0,+1}$. If the electrolysis was carried out at 0°C, the complex was then quite stable for several hours (as monitored by C.V.) provided it was kept under a nitrogen atmosphere. Indeed, red $Re_2H_8(PPh_3)_4$ could be regenerated upon reducing (at −0.4 V) the solutions which contained the monocation.

The X-band ESR spectrum of a dichloromethane glass (−160°C) of the electrolyzed solution yielded an eleven-line spectrum centered at g = 2.16 (Fig. 2).

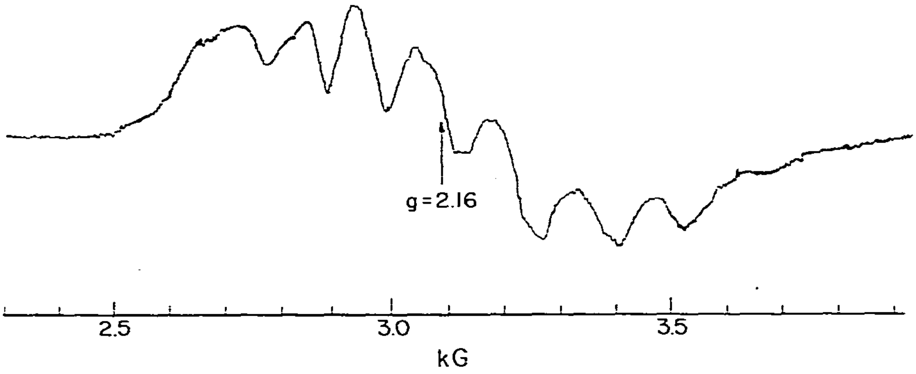

Fig. 2. X-Band ESR spectrum of a CH_2Cl_2 glass (−160°C) of electrochemically generated $[Re_2H_8(PPh_3)_4]$

Integration of the signal intensity showed it to arise from the majority species. A slight asymmetry in the signal (Fig. 2) may reflect a small difference in $g_{\parallel}$ and $g_{\perp}$ for the complex. This signal disappeared upon allowing the blue solution to decompose to the green solution. This eleven-line pattern is in accord with the HOMO being a delocalized metal-based orbital. If $Re_2H_8(PR_3)_4$ is correctly pictured as containing a Re—Re triple bond [6,8], then this result implies that in the monocations the formal Re—Re bond order is 2.5.

In a continuation of our studies of the isocyanide complexes of the Group VI and VII transition elements [11], we investigated the reactions of the hydride complexes II—IV with alkyl isocyanide ligands RNC (R = CMe_3 or C_6H_{11})*. Upon stirring suspensions of the heptahydrides IIa and IIb in methanol with an excess of RNC (R = C_6H_{11} or CMe_3) yellow solutions were formed which upon treatment with acetone solutions of KPF_6 precipitated $[Re(CNR)_4(PR_3)_2]PF_6$ in yields of 90—95%**. These reactions also proceed smoothly in tetrahydrofuran, but here the reaction time is shorter (30 min, vs. 2—3 h) because of the enhanced solubility of II in this solvent. The ^1H NMR and IR spectra (ν(NC) 2090—2040 cm^{-1}) of these complexes were normal and revealed the absence of coordinated hydride. These reactions are important since they demonstrate a further pathway for the reaction of II with organic substrates [4,5], namely, the reductive elimination of dihydrogen*** with the concomitant formal 6-electron reduction of the metal center and its stabilization by coordination of the π-acceptor ligands. Interestingly, although these complexes are phosphine substituted derivatives of $[Re(CNR)_6]^+$, they cannot be made readily by the reaction of $[Re(CNR)_6]^+$ with PR_3 due to the kinetic stability of these homoleptic cations. Electrochemical measurements on 0.2 *M* TBAH-dichloromethane solutions of $[Re(CNR)_4(PR_3)_2]PF_6$ reveal the presence of electrochemical oxidation at an $E_{1/2}$ of ca. +0.80 V vs. SCE, be-

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*The reaction of $Re_2H_8(PPh_3)_4$ with neat t-butyl isocyanide has also been investigated but yields a product we have not yet fully characterized.

**These complexes had satisfactory elemental microanalyses, e.g. Found: C, 56.44; H, 5.88; N, 4.70. $[Re(CNBu^t)_4(PPh_3)_2]PF_6$ calcd.: C, 56.60; H, 5.60; N, 4.71%.

***The release of dihydrogen was confirmed by a mass spectral analysis of the vapor above the reaction solution in a closed reaction vessel. At the present time we are also exploring the possibility that the isocyanide ligand can be hydrogenated by these polyhydride complexes.

havior which we find is similar to that which characterizes the electrochemistry of $[Re(CNR)_6]PF_6$ [12].

A characteristic thermal reaction of $ReH_7(PR_3)_2$ is that in which an excess of a phosphine or a nitrogen donor (e.g. pyridine or cyclohexylamine) produces $ReH_5(PR_3)_2L$ [7]. We have attempted to prepare $ReH_5(PR_3)_2(CNR)$ by the reaction of II with equi-molar quantities of RNC but under these conditions we isolate only $[Re(CNR)_4(PR_3)_2]^+$ and unreacted II. Apparently, coordination of CNR so activates the molecule to further attack that the intermediate $ReH_5(PR_3)_2(CNR)$, if it indeed forms, is extremely unstable. This behavior contrasts with the relative kinetic inertness of preformed $ReH_5(PPh_3)_3$ (III) [7] and $ReH_5(PPh_3)_2L$ (IV) [7] toward further reaction with σ-donors, such as phosphines, or even π-acceptors (e.g. carbon monoxide) since vigorous reaction conditions are necessary to persuade these latter reactions to proceed [7,13,14]. In accord with such observations we find that the thermal reactions of RNC with III and IV proceed extremely slowly.

In exploring the electrochemistry of III and IV we have now discovered a novel means of activating these molecules to attack by RNC. In contrast to II which exhibits no reversible electrochemistry in 0.2 *M* tetra-n-butylammonium hexafluorophosphate-dichloromethane, complex III and those of type IV possess an oxidation in the potential range of +0.10 to +0.40 vs. SCE. For each complex there is a coupled reduction wave ($E_{p,a} - E_{p,c} \simeq 70$—140 mV), but in all instances $i_{p,c}/i_{p,a} < 1$. The values of $E_{p,a}$ for this series of complexes $ReH_5(PPh_3)_2L$ appear to correlate quite nicely with the basicity of L since they decrease in the sequence PPh_3 (+0.37 V) > PEt_2P (+0.29 V) > py (+0.17 V) > $C_6H_{11}NH_2$ (+0.155 V) > $C_5H_{10}NH$ (+0.11 V), i.e., oxidation is easiest with the complex where the build-up of electron density at the metal is greatest. While bulk electrolysis at a potential of ca. +0.6 V leads to the decomposition of these complexes, in the presence of an excess of t-butyl isocyanide we find that these electrochemical oxidations result in the appearance of a new couple in the resulting cycle voltammograms. For example, in the case of $ReH_5(PPh_3)_3$ this couple is at +0.68 V, a value which when compared to that for $[Re(CNCMe_3)_4(PPh_3)_2]^+$ (+0.81 V vs. SCE), suggests that $[Re(CNCMe_3)_3(PPh_3)_3]^+$ may be the product which results from this coupled electrochemical-chemical reaction. Similar results were found upon oxidizing $ReH_5(PPh_3)_2L$ (L = cyclohexylamine or piperidine) in the presence of Me_3CNC. Further work is underway to further explore and exploit these findings.

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