signment of the chemisorbed cluster to structure **1**.

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Registry No. $Os_3(CO)_{12}$, 15696-40-9; silica, 7631-86-9.

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Electrochemical Redox Behavior of the Mononuclear Rhenium Heptahydride Complexes $ReH_7(PR_3)_2$: Evidence for the η^2-H_2 Ligand in This Class of Complex

Sir:

The question of the formulation of transition-metal hydrides as molecular hydrogen complexes ($M(\eta^2-H_2)$) or "classical" hydrides (H–M–H) has generated much interest and many important discoveries[1,2] since the isolation and structural characterization of the first molecular hydrogen complex by Kubas et al.[3] However, in spite of the existence of an extensive array of nonorganometallic mixed polyhydride–phosphine complexes of rhenium,[4] which are perhaps of a greater variety than for any other transition metal, the possibility that some of these might be formulated as containing the η^2-H_2 ligand has scarcely been addressed. The one very important exception is the study of $ReH_7(PPh_3)_2$ by Crabtree,[2] in which convincing evidence has been provided (via ^1H NMR spectroscopy) for its formulation as $Re(H_2)H_5(PPh_3)_2$. In contrast, the species $[ReH_8(PPh_3)]^-$ and $ReH_5(PPh_3)_3$ can be regarded as classical polyhydrides.[2] Upon examining the electrochemical properties of several complexes of the type $ReH_7(PR_3)_2$, we find evidence that they can all be formulated as $Re(H_2)H_5(PR_3)_2$. Furthermore, we believe that the electrochemical properties of such polyhydrides can, in certain instances, provide a quick and easy means of pointing to the presence of the η^2-H_2 ligand.

In an earlier report[5] we described the cyclic voltammetric (CV) properties of the complexes $ReH_5(PPh_3)_2L$ (L = PPh_3, PEt_2Ph, pyridine, piperidine, cyclohexylamine). Solutions of these complexes in 0.2 M TBAH–CH_2Cl_2 were found to exhibit an oxidation in the potential range +0.10–0.40 V vs SCE, with a coupled reduction wave ($E_{p,a} - E_{p,c} \simeq$ 70–140 mV, $i_{p,c}/i_{p,a} < 1$). Bulk electrolysis at a potential of +0.60 V led to decomposition of the complexes. A more recent reinvestigation of such systems in our laboratory has focused on the electrochemical properties of the complexes $ReH_5(PPh_3)_3$, $ReH_5(PMe_2Ph)_3$, $ReH_5(PMePh_2)_3$, and $ReH_5(PCyPh_2)_3$ (Cy = cyclohexyl).[6-9] A single-scan CV of $ReH_5(PPh_3)_3$ in 0.1 M TBAH–CH_2Cl_2 is shown in Figure 1a[10,11] and reveals that there are two oxidation processes ($E_{p,a}$ = +0.35 and +1.0 V vs Ag/AgCl), the first of which possesses a coupled reduction wave at $E_{p,c}$ = +0.22 V vs Ag/AgCl. The process at

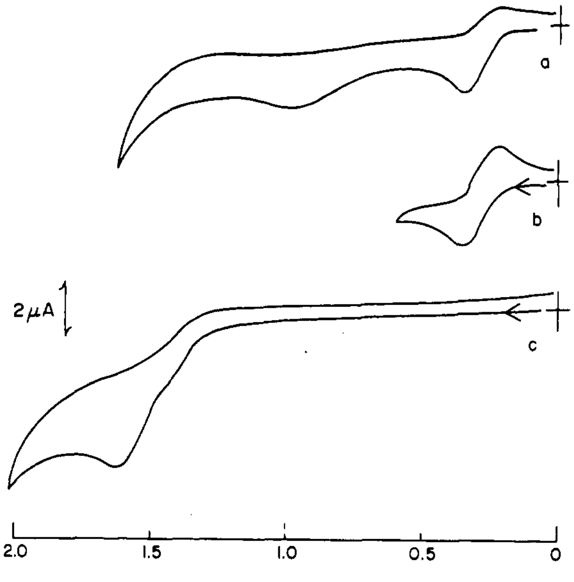

Figure 1. Single-scan cyclic voltammograms in 0.1 M TBAH–CH_2Cl_2: (a) $ReH_5(PPh_3)_3$ with a switching potential of +1.6 V; (b) $ReH_5(PPh_3)_3$ with a switching potential of +0.6 V; (c) $ReH_5(PPh_3)_3$ following bulk electrolysis at +0.5 V. All measurements are at a scan rate of 200 mV s^{-1}.

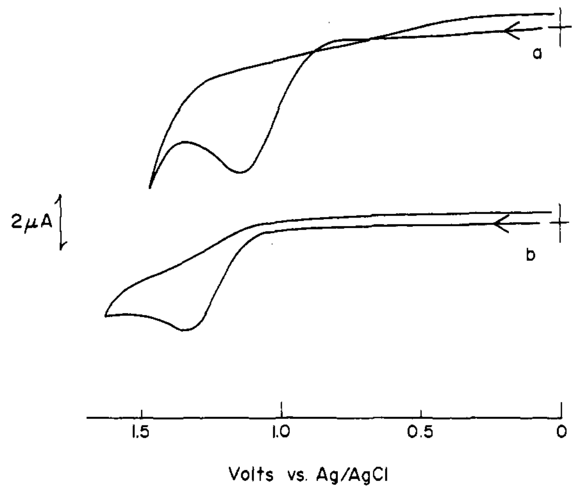

Figure 2. Single-scan cyclic voltammograms in 0.1 M TBAH–CH_2Cl_2: (a) $ReH_7(PPh_3)_2$; (b) PPh_3. All measurements are at a scan rate of 200 mV s^{-1}.

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(1) See, for example: (a) Kubas, G. J.; Ryan, R. R.; Unkefer, C. J. *J. Am. Chem. Soc.* **1987**, *107*, 8113. (b) Crabtree, R. H.; Lavin, M.; Bennevoit, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032. (c) Crabtree, R. H.; Hamilton, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 3124. (d) Morris, R. H.; Sawyer, J. F.; Shiralian, M.; Zubkowski, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5581. (e) Bautista, M.; Earl, K. A.; Morris, R. H.; Sella, A. *J. Am. Chem. Soc.* **1987**, *109*, 3780. (f) Clark, H. C.; Hampden Smith, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 3829. (g) Bianchini, C.; Mealli, C.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1987**, *109*, 5548.

(2) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299 and references cited therein.

(3) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451.

(4) Conner, K. A.; Walton, R. A. In *Comprehensive Coordination Chemistry*; Pergamon: Oxford, England, 1987; Chapter 43, pp 125–213.

(5) Allison, J. D.; Cameron, C. J.; Wild, R. E.; Walton, R. A. *J. Organomet. Chem.* **1981**, *218*, C62.

(6) These complexes were prepared by the usual methods[7-9] and their ^1H NMR and IR spectral properties found to be in agreement with literature data.[7-9] A sample of $ReH_5(PCyPh_2)_3$, which has not been reported before, was obtained as a product in the reaction of $ReOCl_3(PCyPh_2)_2$ with $NaBH_4$ in ethanol: yield 17%; IR (Nujol) 2388 (vw), 2294 (m–w), 2226 (w) cm^{-1}; ^1H NMR (CD_2Cl_2) δ −6.44 [quartet, J(P–H) = 18 Hz, Re–*H*]; $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ +35.8 (singlet).

(7) Chatt, J.; Coffey, R. S. *J. Chem. Soc. A* **1969**, 1963.

(8) Teller, R. G.; Carroll, W. E.; Bau, R. *Inorg. Chim. Acta* **1984**, *87*, 121.

(9) Skupinski, W. A.; Huffman, J. C.; Bruno, J. W.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 8128.

(10) Cyclic voltammetric measurements were made by using the instrumentation described elsewhere.[11] Potentials are referenced to the Ag/AgCl electrode, and measurements were conducted with the use of a Pt-bead electrode on 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH)–dichloromethane solutions of the complexes. Under our experimental conditions the ferrocenium/ferrocene couple has $E_{1/2}$ = +0.47 V vs Ag/AgCl.

(11) Zietlow, T. C.; Klendworth, D. D.; Nimry, T.; Salmon, D. J.; Walton, R. A. *Inorg. Chem.* **1981**, *20*, 947.

$E_{p,a}$ = +1.0 V is attributed to a chemical product wave. With a switching potential of +0.6 V the $i_{p,c}/i_{p,a}$ ratio for the couple at $E_{1/2}$ = +0.29 V becomes unity at v = 200 mV s^{-1}. This is shown by trace b in Figure 1. Similar behavior is exhibited by $ReH_5(PMe_2Ph)_3$, $ReH_5(PMePh_2)_3$, and $ReH_5(PCyPh_2)_3$ with $E_{1/2}$ = +0.27, +0.33, and +0.16 V vs Ag/AgCl, respectively, and product waves at +0.83, +1.02, and ~+0.95 V, respectively.

When a solution of $ReH_5(PPh_3)_3$ in 0.1 M TBAH–CH_2Cl_2 is bulk-electrolyzed at +0.5 V, the pentahydride complex decomposes as evidenced by the CV of the electrolyzed solution that results (Figure 1c). This is the same as the CV of a solution of an authentic sample of the complex $[ReH_6(PPh_3)_3]BF_4$[12] in 0.1 M TBAH–CH_2Cl_2, a result which signifies that the $[ReH_6(PPh_3)_3]^+$ cation is formed as the only identifiable electrochemically active species. It is formed, presumably, through the release of protons in the decomposition of unstable $[ReH_5(PPh_3)_3]^+$ and their subsequent reaction with unoxidized $ReH_5(PPh_3)_3$. A similar reaction ensues upon chemically oxidizing $ReH_5(PPh_3)_3$ with $[(\eta^5-C_5H_5)_2Fe]PF_6$ in THF.

One formulation of $[ReH_6(PPh_3)_3]^+$ is as a classical 18-electron hydride complex of Re(VII). However, the presence of the electrochemical oxidation at $E_{p,a}$ = +1.64 V (presumably metal-based) argues against this and suggests the alternative η^2-H_2 formulation $[Re(H_2)H_4(PPh_3)_3]^+$ (i.e. it is a derivative of Re(V)). This being the case, we might expect to see an accessible metal-based oxidation in the CV of the complex $ReH_7(PPh_3)_2$, if as suggested by Crabtree,[2] it is in reality $Re(H_2)H_5(PPh_3)_2$. This is indeed found to be the case, as shown by CV measurements on solutions of $ReH_7(PPh_3)_2$ in 0.1 M TBAH–CH_2Cl_2 (Figure 2a). A single-scan CV shows an oxidation at $E_{p,a}$ = +1.15 V vs Ag/AgCl when v = 200 mV s^{-1}. Note the hysteresis effect on the return scan due to the decomposition of the complex; this effect is probably caused by the evolution of $H_2(g)$. For the heptahydride complexes $ReH_7(PMePh_2)_2$, $ReH_7(PMe_2Ph)_2$, $ReH_7(PCy_3)_2$, and $ReH_7(dppe)$ (dppe = $Ph_2PCH_2CH_2PPh_2$)[13,14] similar well-defined oxidation processes are seen at $E_{p,a}$ = +1.25, +1.27, +1.10, and +1.37 V, respectively. For none of these complexes did we see evidence for a coupled reduction wave within the sweep rate range 100–900 mV s^{-1}. In the case of $ReH_7(PPh_3)_2$ this oxidation process is quite different from the oxidation of the free PPh_3 ligand at $E_{p,c}$ = +1.35 V vs Ag/AgCl (Figure 2b). When $ReH_7(PPh_3)_2$ is admixed with an approximately equimolar amount of PPh_3, the resulting CV shows the process at $E_{p,a}$ = +1.15 V, together with a product wave at $E_{p,a} \simeq$ +1.7 V due, we believe, to the formation of $[ReH_6(PPh_3)_3]^+$. We suggest that the generation of $[Re(H_2)H_5(PPh_3)_2]^+$ is followed by the loss of H_2 from the kinetically labile 17-electron cation and the capture of PPh_3 by $[ReH_5(PPh_3)_2]^+$ to give $[ReH_5(PPh_3)_3]^+$, which in turn abstracts H$^•$ from one of several hydrogen sources in the solution to form stable $[ReH_6(PPh_3)_3]^+$.

The preceding results not only point to the formulation of other members of the series $ReH_7(PR_3)_2$ (besides $ReH_7(PPh_3)_2$)[2] as the Re(V) complexes $Re(H_2)H_5(PR_3)_2$ but also suggest that the electrochemical behavior of "high"-oxidation-state transition-metal polyhydrides can be used as a guide to the presence of the η^2-H_2 ligand. Further work along these lines is in progress.

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(12) This complex is prepared by reacting $ReH_5(PPh_3)_3$ with $HBF_4 \cdot Et_2O$ in CH_2Cl_2; see: Moehring, G. A.; Walton, R. A. *J. Chem. Soc., Dalton, Trans.* **1987**, 715.

(13) The heptahydride complexes were prepared by literature methods[7-9,14] and identified on the basis of their ^{1}H NMR and IR spectral properties.

(14) Kelle Zeiher, E. H.; DeWit, D. G.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 7006.

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