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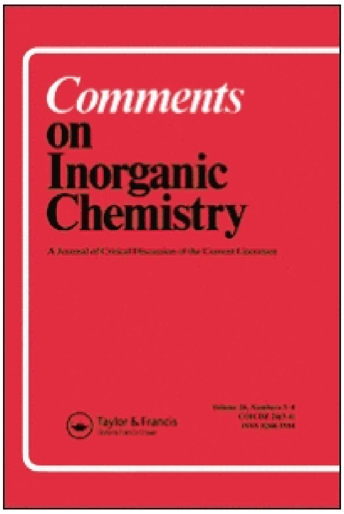

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Can Electrochemistry Distinguish Classical from Nonclassical Transition-Metal Polyhydrides?

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Can Electrochemistry Distinguish Classical from Nonclassical Transition-Metal Polyhydrides?

The present article intends to propose electrochemistry as a tool to distinguish classical hydride coordination to metal centers from nonclassical dihydrogen complexation. The successful application to a series of Group VIII metal–polyhydride complexes of the type $[(XP_3)MH_2]^+$ (XP_3 = $X(CH_2CH_2PPh_2)_3$ (X = P, N); M = Co, Rh, Ir), in which classical and nonclassical hydrides are present, induces us to think that such a technique, notably less demanding of sophisticated instrumentations than established crystallographic, NMR and IR techniques, might play some role in the future for what concerns the yet elusive characterization of dihydrogen complexes. The limitations of such an electrochemical approach are put in evidence. The scattered and sometimes disputed data in the literature are also discussed.

Key Words: *electrochemistry as a tool to discriminate classical from nonclassical polyhydride metal complexes*

INTRODUCTION

A few overview articles have recently focused on a theme of much current interest in coordination chemistry: the coordination of molecular hydrogen in transition-metal complexes.[1–3] It is generally accepted that the interaction of dihydrogen with transition-metal centers occurs via a two-electron three-center bonding, in which electron donation from the filled σ-bonding orbital of dihydrogen to an empty d_σ orbital of the metal cooperatively works with back-donation from filled d_π orbitals of the metal into the empty σ^*-antibonding orbital of dihydrogen. A delicate balance between

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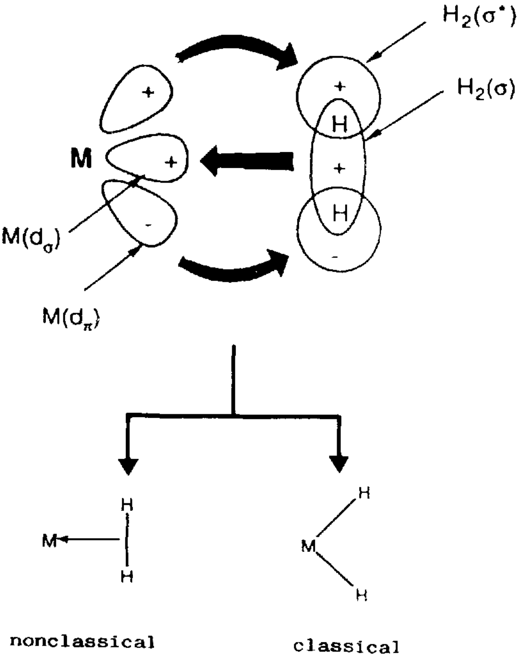
electron depopulation of the H–H bonding orbital and electron population of the H–H antibonding orbital governs the formation of classical or nonclassical hydride complexes (Scheme 1).

Since the conclusive evidence reported by Kubas *et al.* for "side on" bonding of dihydrogen in $W(CO)_3(PPr^i_3)_2$ (η^2–H_2) (Fig. 1),[1] a variety of physico-chemical tools have been proposed to authenticate the coordination mode of dihydrogen in polyhydride complexes.

There is little doubt that X-ray and neutron diffraction techniques are the best choice, but their use can present severe limitations (small dimensions of the hydrogen atoms, need for large crystals, rotational disorder of H_2). On the other hand, spectroscopic techniques based either on the temperature dependence of the spin-lattice relaxation time, T_1 (NMR),[3] or on the vibration modes of the M–H_2 moiety (IR, Raman and Inelastic Neutron Scattering)[1] also suffer from some drawbacks.



SCHEME 1

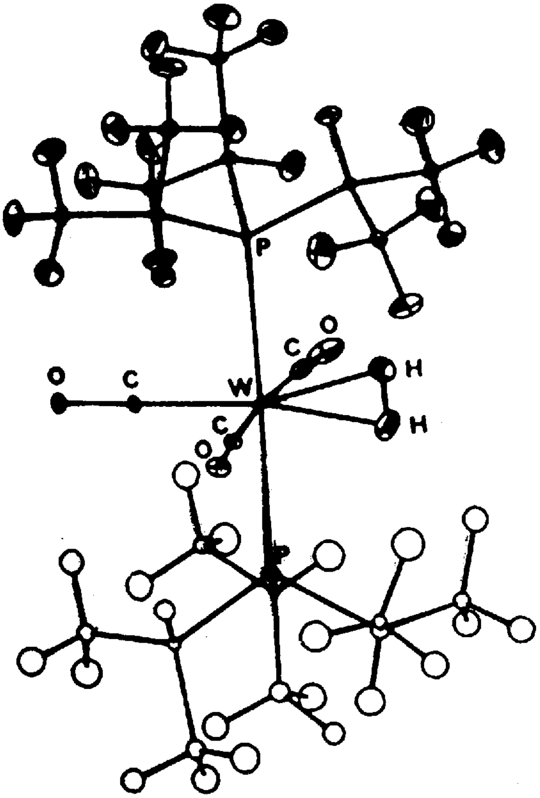


FIGURE 1 Perspective view of $W(CO)_3(PPr^i_3)_2(H_2)$. W–H, 1.95 Å; H–H, 0.75 Å (X-ray) and 0.84 Å (neutron) (from Ref. 1).

In this picture, we have recently presented[4] an electrochemical approach to discriminate between classical and nonclassical structures of polyhydride metal complexes in solution. Our idea stems from the simple (and unoriginal) consideration that dihydrogen withdraws less electron density from the metal when it coordinates in the intact form than when it oxidatively adds. In other words, for the two limiting cases, the oxidation state of the metal is expected to vary by two units, from n^+ to $(n + 2)^+$ (Scheme 2).

Since electrochemistry is a specific technique to ascertain the oxidation state of the metal in coordination compounds, it seems

SCHEME 2

likely that it may contribute discrimination between the different coordination modes of dihydrogen.

Honestly, the existence of a correlation between the formal oxidation state of the metal and the bonding mode of H_2 has already been proposed in terms of $\nu_{(CO)}$ stretching frequencies in hydrido–carbonyl complexes.[5–7] As is shown in Fig. 2, a comparison of the $\nu_{(CO)}$ frequencies of the dihydride $(cp)Re(CO)_2(H)_2$ and the dihydrogen $(cp)Mn(CO)_2(H_2)$ complexes ($cp = C_5H_5$) with those of the corresponding dinitrogen complexes $(cp)Re(CO)_2(N_2)$ and $(cp)Mn(CO)_2(N_2)$ makes evident the change of the metal oxidation state.[5]

For the rhenium complexes, $\nu_{(CO)}$ of the hydride–Re(III) species are evidently shifted to higher wavenumbers as compared with those of the dinitrogen–Re(I) derivative; in contrast, the dihydrogen–Mn(I) complex and the dinitrogen–Mn(I) congener display substantially similar $\nu_{(CO)}$ frequencies.

The circle closes if one considers that redox potentials and C–O stretching frequencies are quite correlated with each other within isostructural series[8–10]: the higher the basicity of the metal (as measured by its propensity to lose electrons) the lower the CO force constant (and hence its frequency, because of the increasing d–π* backdonation). An analogous trend is observed for the N–N stretching frequencies in dinitrogen complexes.[8]

AN HISTORICALLY RECENT FLASHBACK

The first attempt to solve by electrochemical tests the dilemma between classical or nonclassical polyhydride complexes was pro-

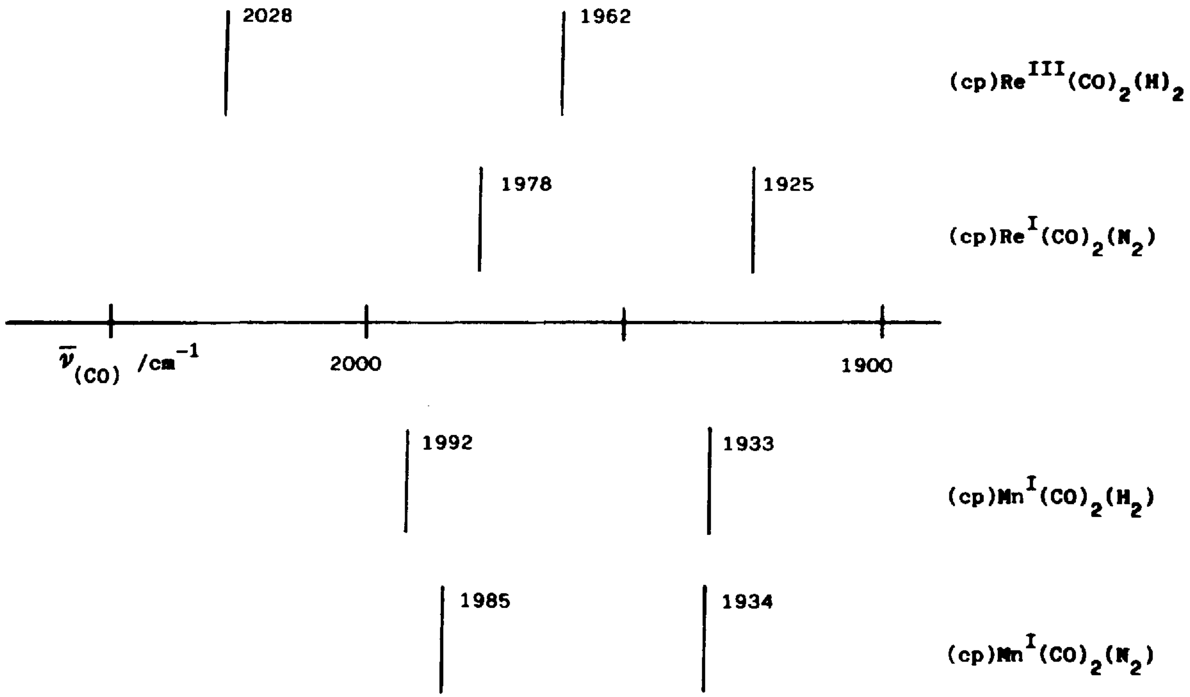


FIGURE 2 Schematic comparison of the $\nu_{(CO)}$ frequencies in $(cp)Re(CO)_2(H)_2$ vs. $(cp)Re(CO)_2(N_2)$, and $(cp)Mn(CO)_2(H_2)$ vs. $(cp)Mn(CO)_2(N_2)$ (from Ref. 5).

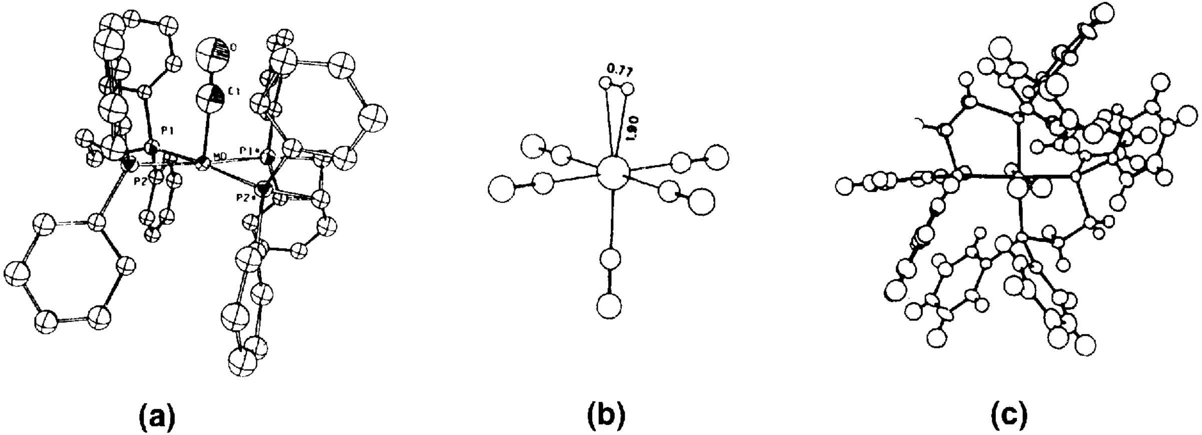


FIGURE 3 Perspective view of: (a) Mo(CO)($Ph_2PCH_2CH_2PPh_2$)$_2$(H_2). The H_2 fragment has not been directly located (from Ref. 11); (b) Cr(CO)$_5$(H_2). Computer aided image (from Ref. 12); (c) [Fe(H)($Ph_2PCH_2CH_2PPh_2$)$_2$(H_2)](BPh_4). H–H, 0.87 Å (X-ray) and 0.82 Å (neutron) (from Ref. 13).

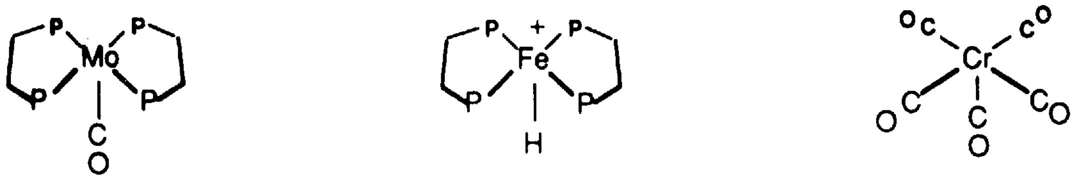
posed by Morris *et al.* for octahedral d^6 species.[8] In effect, this is an "indirect" electrochemical method, as it considers the electrochemical response of the potential coordination site of dihydrogen rather than that of authentic hydrogen complexes. Three dihydrogen complexes, the structure of which is shown in Fig. 3, were fundamentally considered: $Mo(CO)(Ph_2PCH_2CH_2PPh_2)_2(H_2)$,[11] $Cr(CO)_5(H_2)$,[12] $[Fe(H)(Ph_2PCH_2CH_2PPh_2)_2(H_2)]^+$.[13]

The metal fragments of the molibdenum and chromium derivatives represent the extreme cases of electronic control favoring dihydrogen coordination, while the iron fragment possesses intermediate electronic properties (Fig. 4).

Examination of about fifty complexes led to the conclusion that those compounds which form dinitrogen and/or carbonyl adducts displaying $\nu_{(N-N)}$ in the range from 2060 to 2150 cm^{-1} and/or $\nu_{(CO)}$ from 1860 to 1960 cm^{-1}, coupled to redox potentials ranging from 0 to +1.2 V (vs. SCE), are expected to form nonclassical hydrides. Dinitrogen or carbonyl derivatives exhibiting lower values of both stretching frequencies and redox potentials possess very basic metal centers, so that their strong metal-to-ligand backdonation leads to oxidative addition of dihydrogen. Complexes showing higher IR–$E^{0\prime}$ indexes easily lose dihydrogen because backdonation is almost totally inhibited by the electron poorness of their metal sites.[8]

A more direct approach has been proposed by Walton's group,[14] and is based on the ability of polyhydride complexes to undergo redox changes only consistent with nonclassical formulations. Unfortunately, this study was directed towards rhenium–phosphine polyhydrides. This means having a metal center whose oxidation state can range from zero to seven; accordingly, the appearance of redox processes for intermediate oxidation states cannot unambiguously help in elucidating the nature of hydride coordination. This is the case for the one-electron oxidation exhibited by $ReH_5(PPh_3)_3$ in dichloromethane solution, which, as shown in Fig. 5, displays marked features of chemical reversibility ($E^{0\prime}$ = +0.29 V, vs. Ag/AgCl).

This process is alternatively attributable either to the Re(III)/Re(IV) step in a nonclassical $Re(H)_3(PPh_3)_3(H_2)$ formulation, or to the Re(V)/Re(VI) redox change in the classical pentahydride formulation. The relative stability of the oxidized product in the short timescale of cyclic voltammetry does not allow one to disregard preliminarily the nonclassical structure, in that dihydrogen



electron-rich metal center, whose electron density is diminished by the "trans" w-accepting CO group

electron-poor metal center, whose electron density is increased by the "trans" σ-donating H^- ligand

electron-poor metal center, whose electron density is further diminished by the "trans" w-accepting CO group

FIGURE 4 Electronic properties of the coordination fragment of d^6 metal complexes able to bind dihydrogen in the sixth position of the octahedral geometry.

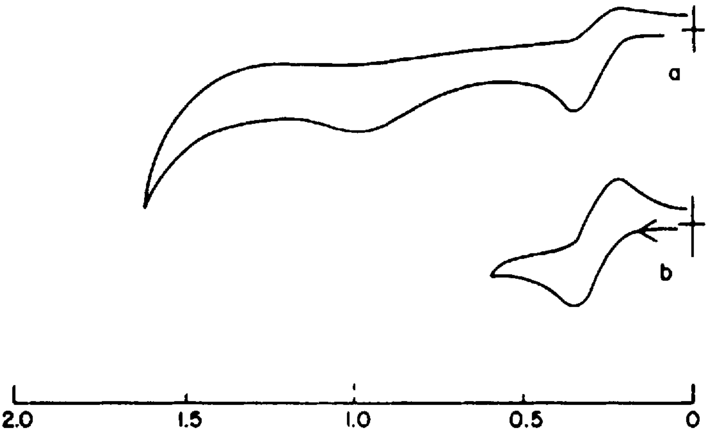


FIGURE 5 Cyclic voltammograms exhibited by $ReH_5(PPh_3)_3$, in CH_2Cl_2 solution, at different switching potentials. Platinum working electrode. Scan rate 0.2 Vs^{-1} (from Ref. 14).

complexes stable in two oxidation states of the metal have been recently reported.[15] Hence, it is evident that this datum cannot throw light on the conflicting results obtained by X-ray (classical structure)[16] and NMR (nonclassical structure)[3,16] experiments. Further ambiguity arises from the fact that also $ReH_5(PMe_2Ph)_3$, which, in the solid state, is certainly a classical pentahydride,[17] is oxidized at similar potential values ($E^{0\prime} = +0.27$ V).[14] Speculatively, in keeping with a possible $(H)_3(H_2)$ coordination in solution, this redox potential is even less positive than the Re(III)/Re(IV) oxidation of $ReCl_3(PMe_2Ph)_3$ ($E^{0\prime} = +0.63$ V, vs. SCE, in MeCN solution).[18] Less ambiguous information seemed provided by the redox behavior of $[ReH_6(PPh_3)_3]^+$, $ReH_7(PR_3)_2$ (PR_3 = PPh_3, $PMePh_2$, PMe_2Ph, PCy_3) and $ReH_7(Ph_2PCH_2CH_2PPh_2)$. As illustrated in Fig. 6 for $ReH_7(PPh_3)_2$, these formally Re(VII) complexes display an oxidation step (at potentials apparently different from that relevant to the free phosphine; see Table I), which suggested their formulation as nonclassical Re(V) species of the type $[Re(H)_4(PPh_3)_3(H_2)]^+$, $Re(H)_5(PR_3)_2(H_2)$ and $Re(H)_5(Ph_2PCH_2CH_2PPh_2)(H_2)$, respectively.

This conclusion at first seemed to be supported by NMR results,[3]

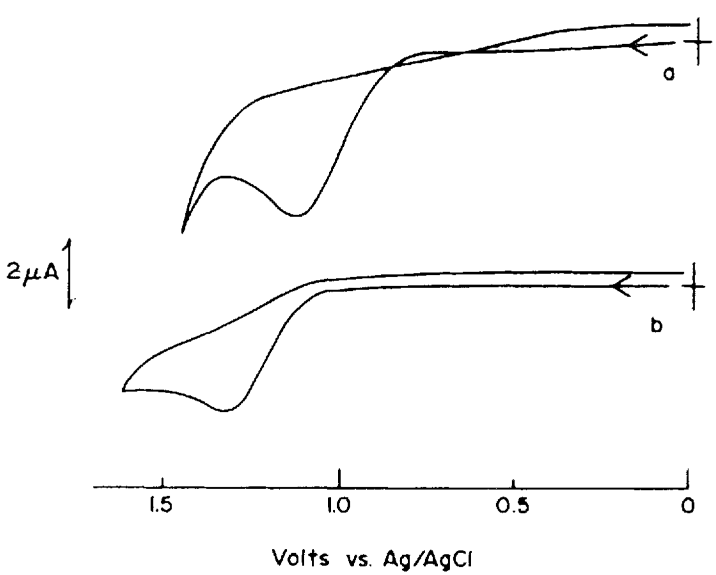


FIGURE 6 Cyclic voltammograms recorded at a platinum electrode on CH_2Cl_2 solutions of: (a) $ReH_7(PPh_3)_2$; (b) PPh_3. Scan rate 0.2 Vs^{-1} (from Ref. 14).

TABLE I

Peak potential values (in volts, vs Ag/AgCl) for the irreversible oxidation step exhibited by a series of polyhydride–rhenium complexes in dichloromethane solution.[14]

Complex	E_p
$ReH_7(PPh_3)_2$	$+1.15^a$
$ReH_7(PMePh_2)_2$	$+1.25$
$ReH_7(PMe_2Ph)_2$	$+1.27$
$ReH_7(PCy)_2$	$+1.10$
$ReH_7(Ph_2PCH_2CH_2PPh_2)$	$+1.37$
$[ReH_6(PPh_3)_3]^+$	$+1.64^a$

[a] Under the same experimental conditions, the free PPh_3 ligand oxidizes at $E_p = +1.35$ V.

but the subsequent neutron diffraction structure of $Re(H)_7(Ph_2PCH_2CH_2PPh_2)$[19] (Fig. 7) induced us to reject this hypothesis.

Nevertheless, the recently reported X-ray structure[20] of $[Re(H)_4\{PhP(CH_2CH_2CH_2PCy_2)_2\}(H_2)]^+$ (Fig. 8) seems to provide again some reliability to the electrochemical test.[21]

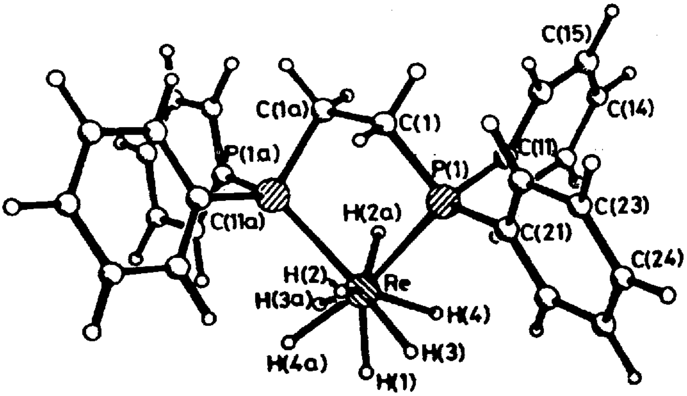


FIGURE 7 Molecular structure of $ReH_7(Ph_2PCH_2CH_2PPh_2)$ (from Ref. 19).

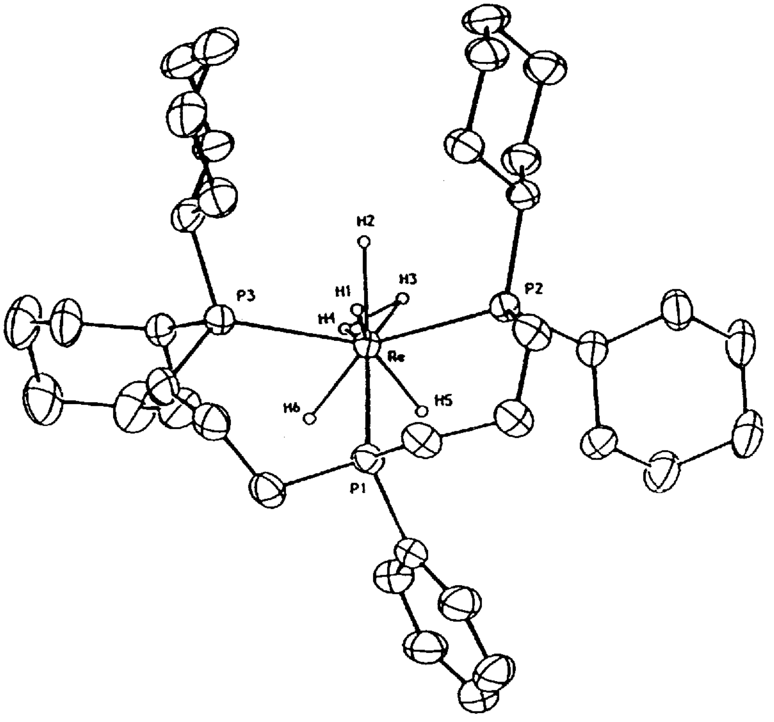


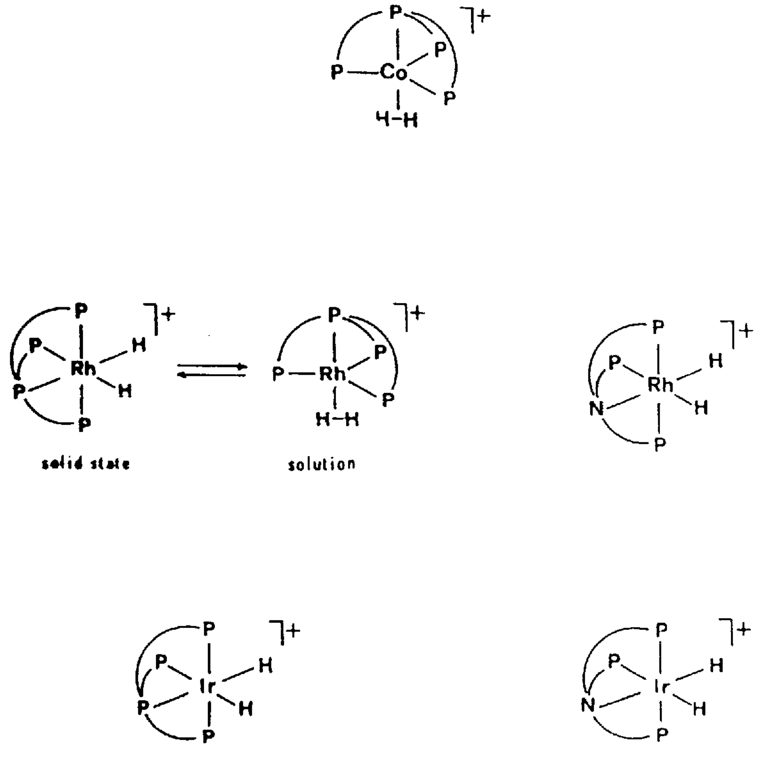
FIGURE 8 Perspective view of $[Re(H)_4\{PhP(CH_2CH_2CH_2PCy_2)_2\}(H_2)]^+$. H–H, 1.08 Å (from Ref. 20).

Walton's idea has been applied by us to a family of dihydride complexes displaying both classical and nonclassical structures.[4]

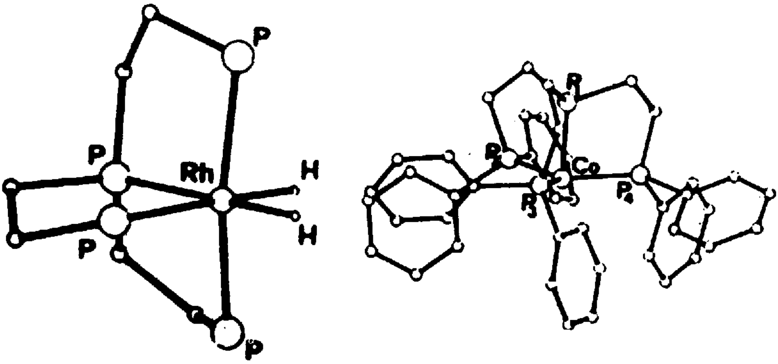
A first series of such compounds,[22-25] with the tetradentate phosphine ligands $PP_3 = P(CH_2CH_2PPh_2)_3$ and $NP_3 = N(CH_2CH_2PPh_2)_3$, is illustrated in Scheme 3.

In particular, the solid-state X-ray structure of $[(PP3)Co(H2)]^{+}$ [23] and $[(PP3)Rh(H)2]^{+}$ [22] is shown in Fig. 9.

It is well known that, on going from cobalt to iridium, the electron density at the metal increases, thus increasing metal-to-ligand



SCHEME 3



(a) (b)

FIGURE 9 Perspective view of: (a) $[(PP_3)Co(H_2)]^+$. The H_2 fragment has not been directly located (from Ref. 23); (b) $[(PP_3)Rh(H)_2]^+$ (from Ref. 22).

backdonation. This causes oxidative addition of dihydrogen to iridium and coordination of intact dihydrogen to cobalt (arrested oxidative addition). At the level of rhodium an isomerization between the two limiting forms has been noted.[22,24]

As dihydrogen complexes in solution, $[(PP_3)Co(H_2)]^+$ and $[(PP_3)Rh(H_2)]^+$ would have the metal in the oxidation state +1. Accordingly, they were expected to undergo well-detectable oxidation processes.[26] As illustrated in Fig. 10, this is just what happens in tetrahydrofuran solution. In fact, irreversible one-electron oxidations take place at $E_p = +0.45$ V and $E_p = +0.73$ V, vs. SCE, for the cobalt and rhodium complexes, respectively.[27]

In addition, the redox pattern in the reverse scan, after traversing the oxidation step, shows formation of the corresponding d^7 monohydride species. This was confirmed by comparison with the redox pattern of the authentic monohydride $(PP_3)MH$ species (M = Co,[28] Rh),[24] as well as by the ESR fingerprint of their monocations.[4] In summary, electrochemistry proves that the one-electron oxidation of the nonclassical dihydrides induces deprotonation according to

$$[(PP_3)M(H_2)]^+ \xrightarrow[-H^+]{-e} [(PP_3)MH]^+ \quad (M = Co, Rh).$$

In contrast, the classical dihydride M(III) congeners (namely, $[(NP_3)Rh(H)_2]^+$, $[(PP_3)Ir(H)_2]^+$, $[(NP_3)Ir(H)_2]^+$) do not exhibit

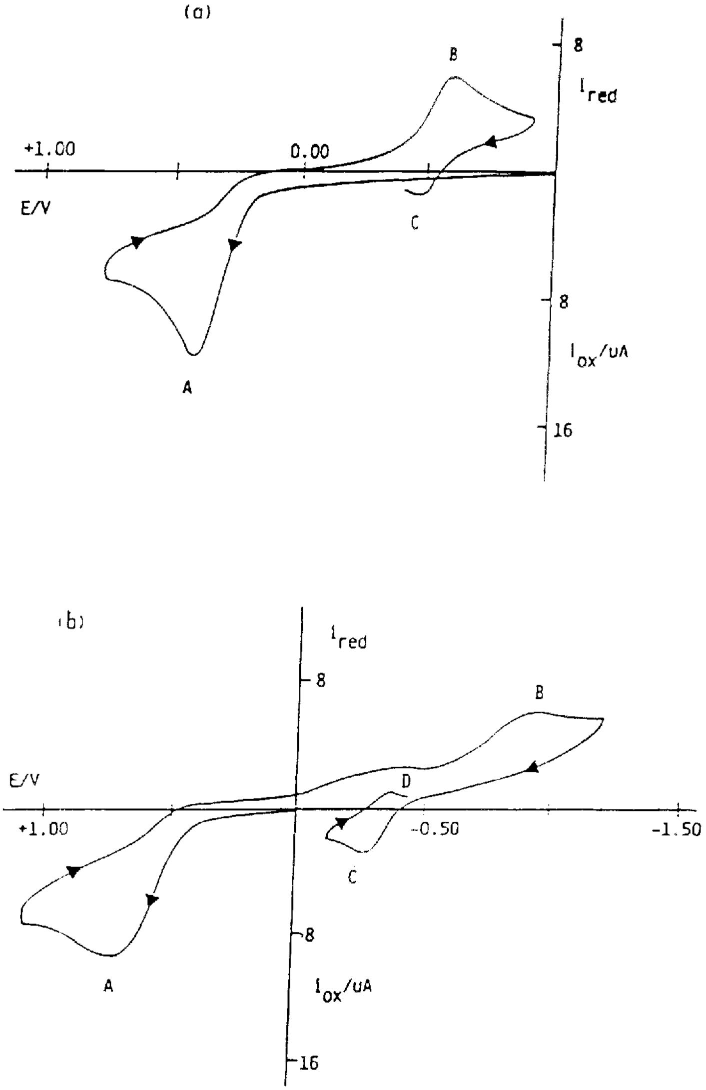


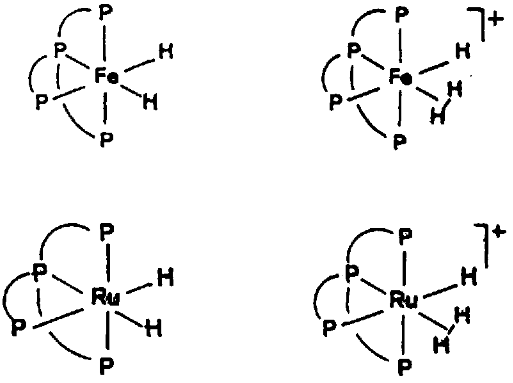
FIGURE 10 Cyclic voltammograms recorded at a platinum electrode on argon-deaerated THF solutions of: (a) $[(PP_3)Co(H_2)]^+$; (b) $[(PP_3)Rh(H_2)]^+$. Scan rate 0.2 Vs^{-1}

oxidation processes in the solvent range (also, they unexpectedly do not exhibit reduction steps).

Let us now examine the redox behavior of another series of classical and nonclassical hydride derivatives[4,29,30] (Scheme 4). The metals are in the d^6 configuration, and the nonclassical compounds have a hydride ligand *cis* to the dihydrogen molecule.

It must be noted that the present complexes are stable in solution, under argon atmosphere, only for a few minutes, so that a deep investigation is precluded. Indeed, like many other dihydrogen complexes,[1] these compounds are stable under dihydrogen atmosphere, which, however, cannot be employed in electrochemical tests, because of its non-innocent behavior towards oxidation. This, really, constitutes a severe limitation to the electrochemical approach presented here.

The redox pattern of the iron derivatives is congruent with the formal +2 oxidation state of the metal, both in the neutral dihydride and in the cationic *cis*–hydride–dihydrogen complex. In fact, as shown in Fig. 11, $(PP_3)Fe(H)_2$ undergoes an oxidation step at $E_p = -0.51$ V, while $[(PP_3)Fe(H)(H_2)]^+$ is oxidized at $E_p = +0.80$ V. Such an oxidation is attributable, in both cases, to a Fe(II)/Fe(III) redox change. The significant difference between the two oxidation potentials is simply due to the electrostatic effects which favor electron removal from the neutral species.[31] An in-



SCHEME 4

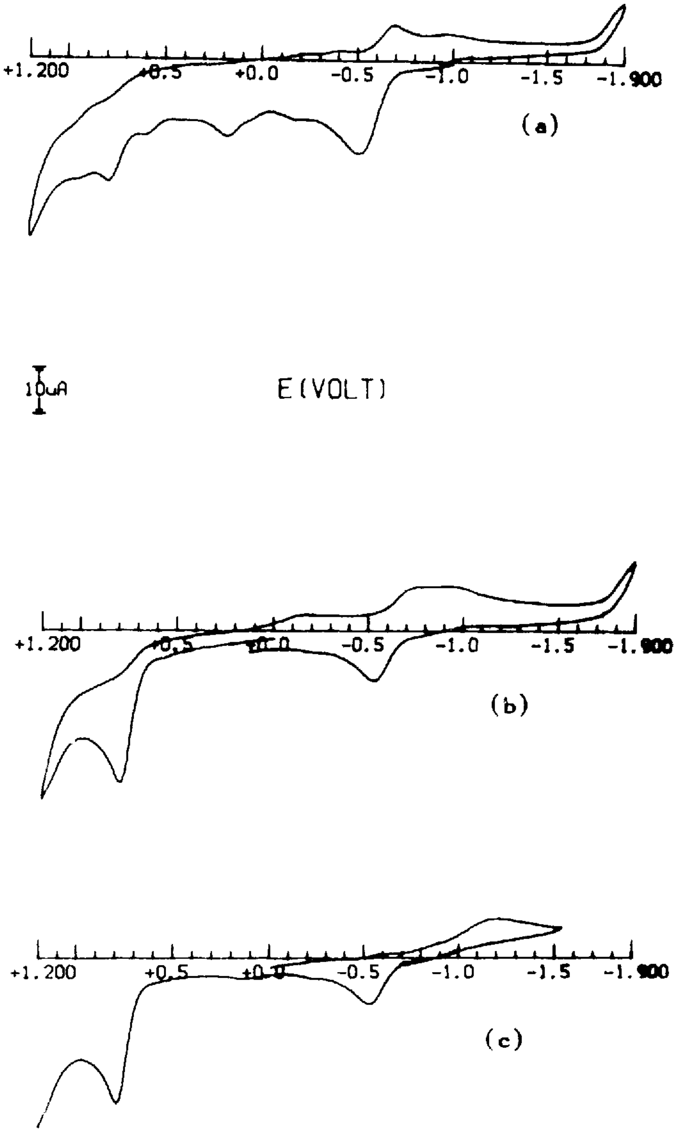


FIGURE 11 Cyclic voltammograms recorded at a platinum electrode on argon-deaerated THF solutions of: (a) $(PP_3)Fe(H)_2$; (b, c) $[(PP_3)Fe(H)(H_2)]^+$. Scan rate 0.2 Vs^{-1}.

teresting feature, deducible from Fig. 11c, concerns the cathodic reduction of $[(PP_3)Fe(H)(H_2)]^+$, at $E_p = -1.2$ V, which generates the neutral dihydride complex.

An apparently similar trend might be attributed to the dihydride and hydride–dihydrogen ruthenium(II) homologues. As illustrated in Fig. 12, $(PP_3)Ru(H)_2$ undergoes a first oxidation step ($E_p = +0.08$ V), easier than the corresponding one exhibited by $[(PP_3)Ru(H)(H_2)]^+$ ($E_p = +0.41$ V), because of Coulombic effects. The presence of successive oxidation processes is consistent with the ability of ruthenium to exhibit oxidation states higher than +3. Unfortunately, the remarkable instability in solution of these complexes under non-hydrogen atmosphere, preventing deeper investigations, makes uncertain any precise attribution.[33]

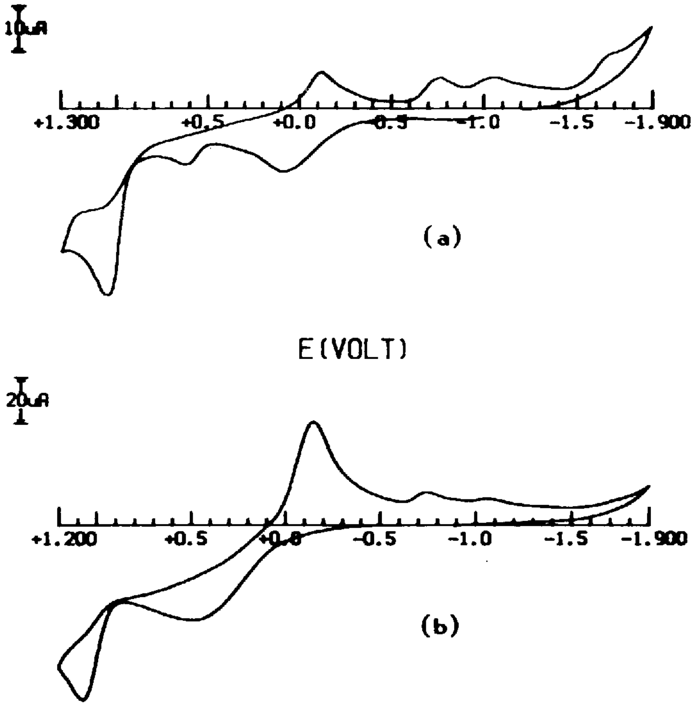


FIGURE 12 Cyclic voltammograms exhibited at a platinum electrode by argon-deaerated THF solutions of: (a) $(PP_3)Ru(H)_2$; (b) $[(PP_3)Ru(H)(H_2)]^+$. Recorded within one minute from dissolution, at scan rate of 0.2 Vs^{-1}.

To strengthen our persuasion on the reliability of electrochemical measurements to contribute to the discrimination between classical and nonclassical polyhydride structures, we wish to survey two recent papers dealing with electrochemistry of hydride complexes.

Cotton has briefly reported on the electrochemical response of $ReCl(PMePh_2)_4(H_2)$ and $ReH_3(PMePh_2)_4$.[34] In accordance with its dihydrogen coordination (Fig. 13),[35] the Re(I) complex $ReCl(PMePh_2)_4(H_2)$ undergoes an easy oxidation process ($E^{0\prime} = -0.07$ V, vs. Ag/AgCl, in CH_2Cl_2 solution) quite close to that exhibited by the Re(I) species $ReCl(CO)_3(PMePh_2)_2$ ($E^{0\prime} = -0.17$ V). Contrasting results are obtained as far as the ReH_3 complex is concerned. In fact, the X-ray structure suggests a classical trihydride coordination, whereas the NMR parameters are more consistent with a nonclassical coordination. In favor of a Re(I) nature, and hence a $Re(H)(H_2)$ assembly, $ReH_3(PMePh_2)_4$ undergoes an oxidation step ($E^{0\prime} = -0.17$ V) much easier than that exhibited by the authentic Re(III) complex $ReCl_3(PMePh_2)_3$ ($E^{0\prime} = +0.9$

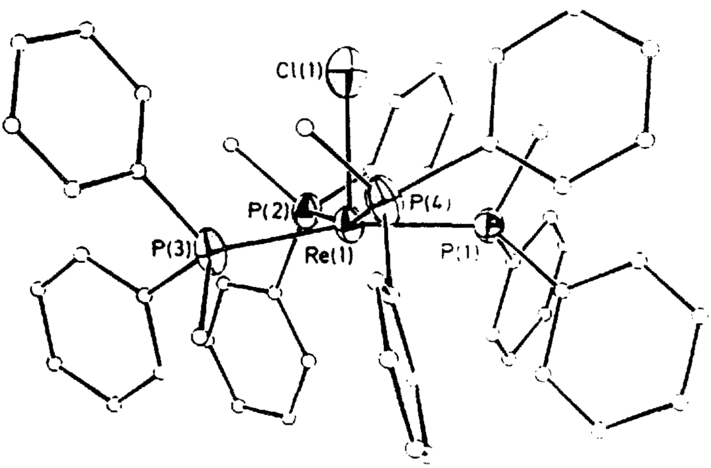


FIGURE 13 Molecular structure of $ReCl(PMePh_2)_4(H_2)$. The H_2 fragment has not been directly located (from Ref. 35).

V), and in the same potential region exhibited by the preceding Re(I) complexes.[36]

We naively note that such a discrepancy (and those previously discussed in connection with Walton's contribution) could be accounted for by considering, in addition to the possibility that the structure accidentally refers to the classical isomer[34] from the homogeneous equilibrium Dihydride = Dihydrogen, the occurrence of the tautomeric heterogeneous equilibrium $\text{Dihydride}_{(\text{solid state})} = \text{Dihydrogen}_{(\text{solution})}$.[24] Really, among the different isomerisms usually taken into consideration,[37] this one is the least invoked.

Finally, Taube has recently reported that the complex $[Os(NH_3)_5(H_2)]^{2+}$ undergoes a relatively easy one-electron oxidation ($E^{0'} = +0.58$ V, vs. NHE, in MeCN solution) to the stable congener $[Os(NH_3)_5(H_2)]^{3+}$. In addition to spectroscopic evidence, the true nature of Os(II)–Os(III) dihydrogen complexes for this redox couple is proved by the fact that subsequent oxidation at $E_p = +1.3$ V leads to the Os(III) species $[Os(NH_3)_5(MeCN)]^{3+}$ with concomitant deprotonation.[15] A similar redox pattern would be inconsistent with a classical dihydride–Os(IV) formulation of the starting dicationic species.

CONCLUSIONS

Under the idea of collecting and contrasting as many results as possible on subjects which have hidden their intimate nature for a long time, the aim of this report (which intends to promote further investigations, rather than to be an account of established procedures) is to draw attention to electrochemistry as a simple technique to gain insight into the problem of classical or nonclassical coordination of hydrogen in metal complexes. Taken preliminarily into account the cited limitation of having complexes stable in solution under a non-hydrogen atmosphere, it seems evident that electrochemistry shows good reliability in those cases where a metal center, formally in the highest oxidation state under a classical hydride formulation, undergoes oxidation steps only consistent with a nonclassical coordination of dihydrogen. In ambiguous cases of redox changes compatible with intermediate oxidation states of the metal, only speculations can be advanced by comparison with the response of congeners of ascertained oxidation states. The best target for the electrochemical approach would have to be paramagnetic complexes or diamagnetic species exhibiting T_1(min) values at the borderline of classical and nonclassical formulations. Obviously, further confirmation on the reliability of the method we propose requires a systematic study by the dihydrogen community.

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