Journal of Organometallic Chemistry, 332 (1987) C17–C20
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

Electrochemical metal–hydride bond cleavage at the dinitrogen-binding iron centre $\{FeH(Ph_2PCH_2CH_2PPh_2)_2\}^+$, and its electroactivation towards nucleophilic attack

M. Amélia N.D.A. Lemos and Armando J.L. Pombeiro*

Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1096 Lisbon Codex (Portugal)

(Received June 18th, 1987)

Abstract

Complexes *trans*-[FeHL(dppe)$_2$][BF_4] (II: L = CNR; R = Me, Bu^t, C_6H_4OMe-4 or $C_6H_4NO_2$-4. III: L = N_2; dppe = $Ph_2PCH_2CH_2PPh_2$) have been obtained from the reaction of *trans*-[FeHCl(dppe)$_2$] (I) with the appropriate ligand L in the presence of $TlBF_4$. In cyclic voltammetry, at a sufficiently low scan rate, compound II (R = Me) undergoes an anodic ECE process, with metal–hydride bond rupture (proton loss) and metal fluorination, to give *trans*-[FeF(CNMe)(dppe)$_2$][BF_4], which has been electrosynthesized by CPE.

Transition-metal hydride complexes are known to participate in a number of catalytic processes [1] and may be involved in the chemical or biochemical reduction of dinitrogen [2,3] and isocyanides [4].

The study of the dependence of the stability of a metal–hydride bond on the electronic properties of the metal site is important for the understanding of these processes, and electrochemical methods should provide a convenient tool in such a study. Hence, in view of the limited available information, particularly on the redox properties of hydride complexes with N_2-binding metal sites [5] and in continuation of our work on alternative substrates of nitrogenase, such as isocyanides [6,4] and alkynes [7], we have embarked upon the synthesis of isocyanide complexes containing a metal–hydride bond, analogous to dinitrogen compounds, and we have initiated the investigation of their redox properties by electrochemical methods; the preliminary results are reported here.

Complexes *trans*-[FeHL(dppe)$_2$][BF_4] (II: L = CNR; R = Me, Bu^t, C_6H_4OMe-4 or $C_6H_4NO_2$-4. III: L = N_2; dppe = $Ph_2PCH_2CH_2PPh_2$) were prepared by treatment of a THF solution of [FeHCl(dppe)$_2$] (I) with an excess of the appropriate substrate in the presence of $TlBF_4$ as the chloride abstractor (eq. 1), in a route which may be related to the syntheses of comparable depe complexes, *trans*-

0022-328X/87/$03.50

$[FeHL(depe)_2][BPh_4]$ (L = CO, N_2, isocyanide, nitrile or phosphite; depe = $Et_2PCH_2CH_2PEt_2$) [8], and of *trans*-$[FeH(N_2)(dppe)_2][BPh_4]$ [9]. However, it is important that complexes II and III do not contain the BPh_4^- counterion, which would be unsuitable for the present study since it is redox active in the electrochemical anodic potential range under investigation.

$$\underset{\text{(I)}}{\textit{trans}\text{-}[FeHCl(dppe)_2]} + TlBF_4 + L \rightarrow \underset{\substack{\text{(II, L = CNR;}\\ \text{III, L = N}_2\text{)}}}{\textit{trans}\text{-}[FeHL(dppe)_2][BF_4]} + TlCl \qquad (1)$$

Complexes II and III were isolated as yellow solids and characterized by ^1H, ^{31}P NMR and IR spectroscopy, as well as by elemental microanalysis. Thus, e.g. in the IR spectra, $\nu(C{\equiv}N)$ is observed as a strong band in the 2020–2140 cm^{-1} range, and in the ^1H NMR spectra the hydride resonance appears as a high-field quintet (e.g., at δ −11.03 ppm, $^2J(P-H)$ 46.4 Hz, for II, (R = Me) in $(CD_3)_2CO$).

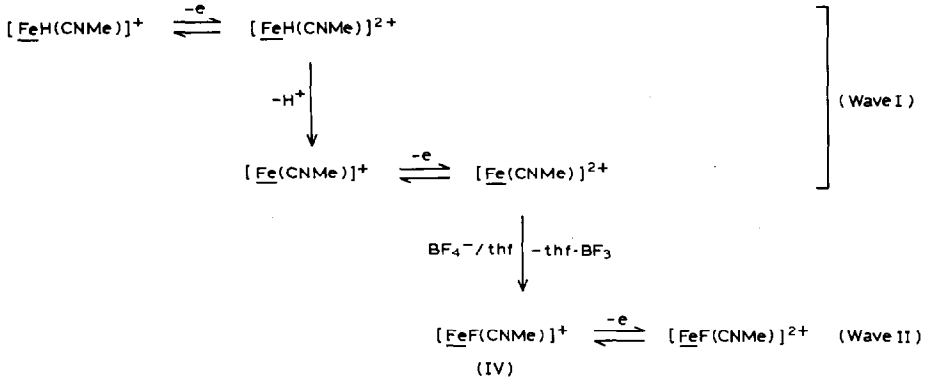
The redox properties of these complexes have been studied by cyclic voltammetry (CV), in the 1000–2 mV s^{-1} scan rate range, at a Pt electrode, in thf/$[NBu_4][BF_4]$ 0.2 *M*. Complexes II exhibit a cathodic wave, which is usually partially reversible, with $E^{red}_{1/2}$ in the range −1.8 to −1.0 V vs. SCE, possibly following a type of process already noted [10] for related species, involving retention of the metal–hydride bond. However, we have observed that this bond in complexes II is rather sensitive to oxidation, and now we report only their anodic behaviour.

Although the dinitrogen complex III appears to undergo an irreversible anodic process (at $E^{ox}_{1/2}$ 0.94 V vs. SCE), with the expected evolution of N_2, as a result of metal oxidation, in the case of the isocyanide complexes II without such a labile ligand, two anodic waves are observed by CV (typically at 100 mV s^{-1}); the first one (wave I at $^IE^{ox}_{1/2}$ 0.82–0.99 V vs. SCE) has partial reversible character for complexes with the alkyl isocyanide ligands but is irreversible for the aryl species, whereas the second one appears to be reversible for both types of complexes (wave II at $^{II}E^{ox}_{1/2}$ 0.95–1.24 V vs. SCE).

The overall cyclic voltammetric behaviour of all the isocyanide complexes appears to show a common pattern, and that of II, (L = CNMe), chosen as a typical example, was studied in more detail. The obtained data are consistent with the mechanism shown in Scheme 1 in which the first anodic wave ($^IE^{ox}_{1/2}$ 0.83 V vs. SCE) corresponds to an ECE mechanism [11] involving the metal–hydride bond cleavage, with proton loss, as a result of a single-electron oxidation; subsequent oxidation at the same potential gives $[Fe(CNMe)(dppe)_2]^{2+}$ which, upon nucleophilic attack by BF_4^- gives the fluoro complex *trans*-$[FeF(CNMe)(dppe)_2]^+$ (IV), which was electrosynthesized by CPE at the anodic wave I and isolated as the red BF_4^- salt; it was characterized by elemental microanalysis, IR, ^1H, ^{31}P and ^{19}F NMR spectroscopy (e.g., the ^{19}F resonance of the fluoride ligand is observed as a quintet, $^2J(P-F)$ 22 Hz at δ −554.4 ppm rel. $CFCl_3$, in CD_2Cl_2).

Complex IV undergoes a single-electron reversible oxidation (at $E^{ox}_{1/2}$ 1.01 V vs. SCE) which corresponds to the above-mentioned anodic wave II. The number of electrons involved in the electrosynthesis of IV and in its reversible anodic process were measured by coulommetry.

Monitoring the current functions $i_p\nu^{-1/2}C^{-1}$ at various scan rates (ν in the above-mentioned range) reveals that upon increase of ν, there is a tendency for the occurrence of a single electron reversible anodic process at wave I with a concom-



Scheme 1. Anodic processes for complex II (L = CNMe), at a Pt electrode, in thf-$[Bu_4N][BF_4]$ 0.2 *M*. [Fe stands for *trans*-{Fe(dppe)$_2$}]

itant disappearance of wave II; this CV limiting behaviour at high scan rates corresponds to the suppression of the chemical step at wave I. However, upon lowering of ν, there is a pronounced decrease of the reversible character of wave I, with an increase of the peak current of the reversible wave II, the former tending to a two-electron process, which is consistent with significant rupture of the Fe–H bond and the subsequent steps of Scheme 1.

Addition of a base (pyridine), with a promoting effect on proton loss, results in the expected enhancement of the current function for wave I.

Proton loss from a metal as a result of its oxidation is known to occur for other transition-metal hydride complexes, such as $[W(\eta^5\text{-}C_5H_5)_2H_2]$ or $[Mo(\eta^5\text{-}C_5H_5)(CO)_3H]$, but the resultant neutral paramagnetic species undergo metal–metal bond formation (dimerization) or reductive elimination [12].

In our system a metal–hydride bond is anodically cleaved with proton loss, concomitant reduction of the metal, and increase of its reducing power, thus promoting further oxidation of the metal, which is then activated towards attack by a nucleophile; the coordination of the latter also enhances the reducing ability of the metal. These observations may be of some significance for the understanding of the chemical or biochemical reduction of substrates, such as isocyanides or dinitrogen, bound to a metal–hydride site.

Acknowledgements. This work was supported by the National Institute for Scientific Research (I.N.I.C.). The authors are also indebted to Dr. C.J. Pickett (Unit of Nitrogen Fixation, University of Sussex, U.K.) for helpful discussions.

References

1 See, e.g., C. Masters, Homogeneous Transition-Metal Catalysis, Chapman and Hall, London, 1981; G.W. Parshall, Homogeneous Catalysis, John Wiley & Sons, New York, 1980.
2 J. Chatt and R.L. Richards, J. Organomet. Chem., 239 (1982) 65; R.A. Henderson, G.J. Leigh and C.J. Pickett, Adv. Inorg. Chem. Radiochem., 27 (1983) 197.
3 B.K. Burgess in T.G. Spiro (Ed.), Molybdenum Enzymes, Ch. 4, John Wiley & Sons, New York, 1985.
4 E. Singleton and H.E. Oosthuizen, Adv. Organometal. Chem., 22 (1983) 209; A.J.L. Pombeiro, Memórias da Academia das Ciências de Lisboa, Classe de Ciências, 23 (1980) 393.

5 T.I. Al-Salih and C.J. Pickett, J. Chem. Soc. Dalton, (1985) 1255.
6 A.J.L. Pombeiro in J. Chatt, L.M.C. Pina and R.L. Richards (Eds.), New Trends in the Chemistry of Nitrogen Fixation, Ch. 10, Academic Press, London, 1980; A.J.L. Pombeiro and R.L. Richards, Transition Metal Chem., 5 (1980) 55; A.J.L. Pombeiro, M.F.N.N. Carvalho, P.B. Hitchcock and R.L. Richards, J. Chem. Soc. Dalton, (1981) 1629.
7 A.J.L. Pombeiro, J.C. Jeffery, C.J. Pickett and R.L. Richards, J. Organomet. Chem., 277 (1984) C7; D.L. Hughes, A.J.L. Pombeiro, C.J. Pickett and R.L. Richards, J. Chem. Soc. Chem. Commun., (1984) 992.
8 G.M. Bancroft, M.J. Mays, B.E. Prater and F.P. Stefanini, J. Chem. Soc. A, (1970) 2146.
9 P. Giannoccaro, M. Rossi and A. Sacco, Coord. Chem. Rev., 8 (1972) 77.
10 G. Pilloni, G. Zotti, Q.G. Mulazzani and P.G. Fuochi, J. Electroanal. Chem. Interf. Electrochem., 137 (1982) 89.
11 R.S. Nicholson and I. Shain, Anal. Chem., 37 (1965) 178.
12 R.J. Klingler, J.C. Huffman and J.K. Kochi, J. Am. Chem. Soc., 102 (1980) 208.