



NEW CATALYSTS FOR THE ELECTROCHEMICAL REDUCTION OF PROTON

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Abstract

Iron acetylide $\text{Cp}(\text{CO})(\text{Ph}_3\text{P})\text{Fe}-\text{C}\equiv\text{CPh}$ (**Fe1**), rhenium vinylidene $\text{Cp}^*(\text{CO})_2\text{Re}=\text{C}=\text{C}(\text{H})\text{Ph}$ (**Re1**), and manganese isonitrile complexes $\text{Cp}(\text{CO})_2\text{Mn}=\text{C}=\text{NR}$ (**Mn3**, $\text{R}=\text{Me}$; **Mn4** $\text{R}=\text{'Bu}$) were tested for activity in the electrochemical reduction of proton (ERP). Complexes **Fe1** and **Re1** were found to be catalytically active in the ERP. Their protonated forms $[\text{Cp}(\text{CO})(\text{Ph}_3\text{P})\text{Fe}=\text{C}=\text{C}(\text{H})\text{Ph}]\text{BF}_4$ (**Fe1H⁺**) and $[\text{Cp}^*(\text{CO})_2\text{Re}=\text{C}-\text{CH}_2\text{Ph}]\text{BF}_4$ (**Re1H⁺**) were reduced to corresponding 19e radicals (**Fe1H[•]**) and (**Re1H[•]**) followed by homolysis of $\text{C}_\beta-\text{H}$ bonds to regenerate starting complexes **Fe1** and **Re1**.

Key words: electrochemical reduction, cyclic voltammogram, vinylidene complexes, alkynyl complexes, carbyne complexes.

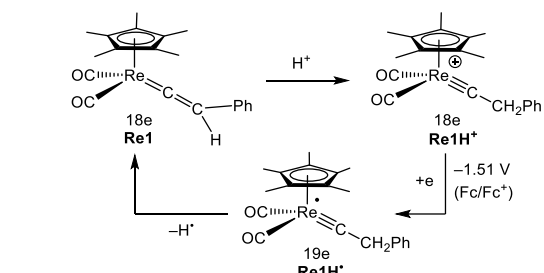
Introduction

Earlier we have shown [1] that manganese vinylidene $\text{Cp}(\text{CO})(\text{Ph}_3\text{P})\text{Mn}=\text{C}=\text{C}(\text{H})\text{Ph}$ (**Mn1**) and allenylidene $\text{Cp}(\text{CO})_2\text{Mn}=\text{C}=\text{C}=\text{CPh}_2$ (**Mn2**) complexes catalyze the electrochemical reduction of proton in dichloromethane in the presence of $\text{HBF}_4\cdot\text{OEt}_2$. The proposed scheme included the protonation of the complexes and the reduction of their protonated forms to a 19e state undergoing ready homolysis of the $\text{C}_\beta-\text{H}$ bond. These results suggest that other transition metal $\eta^1-\sigma,\pi$ -complexes with protonated forms containing a $\text{C}-\text{H}$ or $\text{N}-\text{H}$ bond conjugated with a multiple metal–carbon bond can also exhibit catalytic activity in the ERP.

In this work, the electrochemical behavior of iron acetylide $\text{Cp}(\text{CO})(\text{Ph}_3\text{P})\text{Fe}-\text{C}\equiv\text{CPh}$ (**Fe1**), rhenium vinylidene $\text{Cp}^*(\text{CO})_2\text{Re}=\text{C}=\text{C}(\text{H})\text{Ph}$ (**Re1**), and manganese isonitrile complexes $\text{Cp}(\text{CO})_2\text{Mn}=\text{C}=\text{NR}$ (**Mn3**, $\text{R}=\text{Me}$; **Mn4** $\text{R}=\text{'Bu}$) in the presence of HBF_4 was studied by cyclic voltammetry.

Results and discussion

The cyclic voltammogram (CV) of complex **Re1** in CH_2Cl_2 displays one irreversible oxidation peak **A** at +0.24 V (see Fig. S1 in the Electronic supplementary information (ESI)). The CV of its protonated form $[\text{Cp}^*(\text{CO})_2\text{Re}=\text{C}-\text{CH}_2\text{Ph}]\text{BF}_4$ (**Re1H⁺**) displays a single-electron reduction peak **B** at –1.51 V (Fig. S1 in the ESI), which is irreversible even at the scan rate of $100 \text{ V}\cdot\text{s}^{-1}$, and a hardly visible oxidation peak **A** at +0.24 V, identical to that of vinylidene complex **Re1**. The addition of HBF_4 (Fig. 1) afforded a significant increase in the intensity of the cathode peak **B** at –1.51 V (changes in the region of almost unobservable peak **A** occurs at a noise level). A significant



increase in the cathode peak **B** current can be explained by the catalytic reduction of proton (catalytic current) similarly to the earlier observations for **Mn1** and **Mn2** [1].

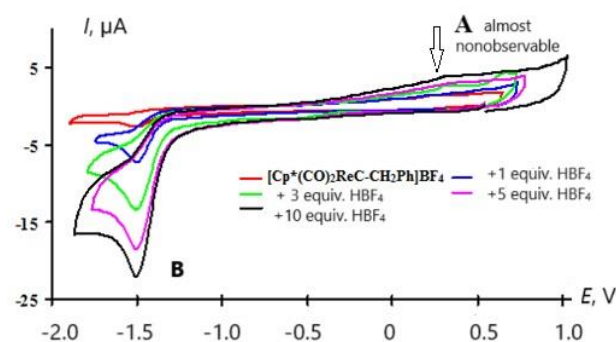
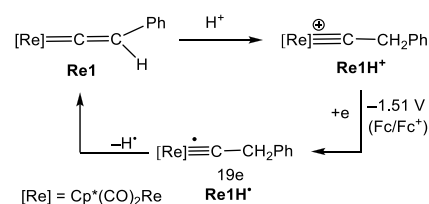


Figure 1. CV for complex **Re1H⁺** in the presence of different amounts of HBF_4 (GC electrode, CH_2Cl_2 , 0.1 M Bu_4NPF_6 , $1\cdot 10^{-3}$ M, $200 \text{ mV}\cdot\text{s}^{-1}$, potentials are given relative to Fc/Fc^+).

We believe that the catalytic reduction of proton occurs according to Scheme 1.



Scheme 1. Catalytic cycle for the reduction of proton by complex **Re1**.

The cyclic voltammogram of **Fe1** displays two irreversible oxidation peaks at +0.19 V (**C**) and +1.06 V (**D**) (Fig. S2 in the

ESI). Upon reverse scan, there appeared a reduction peak at -1.07 V (**E**). The CV of protonated form **Fe1H⁺** displayed a single-electron reduction peak **F** at -1.32 V (Fig. 2) totally irreversible even at the scan rate of $100 \text{ V} \cdot \text{s}^{-1}$. With an increase in the acid amount, the reduction peaks of **Fe1H⁺** appear to be catalytic and significantly increase and no oxidation peak of starting iron acetylide **Fe1** is observed due to the fast protonation of **Fe1** to **Fe1H⁺**.

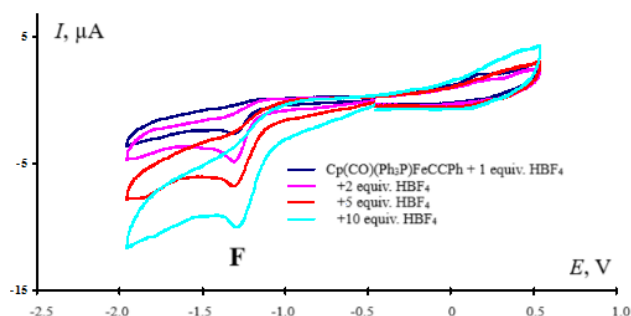
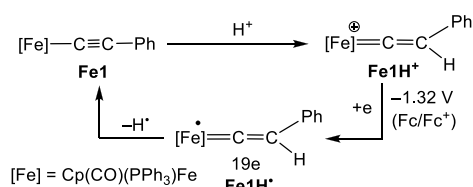


Figure 2. CV for complex **Fe1** in the presence of different amounts of HBF_4 (GC electrode, CH_2Cl_2 , $0.1 \text{ M Bu}_4\text{NPF}_6$, $1 \cdot 10^{-3} \text{ M}$, $200 \text{ mV} \cdot \text{s}^{-1}$, potentials are given relative to Fc/Fc^+).

These observations fit into the catalytic cycle presented in Scheme 2.



Scheme 2. Catalytic cycle for the reduction of proton by complex **Fe1**.

We also studied the electrochemical behavior of manganese isonitrile complexes **Mn3**, **Mn4**. However, both these compounds were found to be inactive in the ERP, since the equilibrium in their protonation reactions is shifted towards the starting compounds and, therefore, no reduction peaks of their protonated forms are observed in the CVs.

The CV data obtained in this work and earlier allow us to compare complexes **Mn1**, **Mn2** and **Re1**, **Fe1** by the following parameters: 1) the reduction potential of the catalyst protonated form; 2) the irreversibility of reduction of the catalyst protonated form; and 3) the magnitude of catalytic current.

The solvated proton in dichloromethane is reduced at about -2.24 V relative to Fc/Fc^+ . The catalyst protonated form, rather than proton, is reduced during the ERP. The less negative is the reduction potential of the protonated form, the more favorable is the ERP process in terms of energy. In this regard, the above-mentioned complexes range as follows: **Mn2** (-0.93 V) > **Fe1** (-1.32 V) > **Re1** (-1.51 V) > **Mn1** (-1.78 V).

Regarding the irreversibility of reduction of protonated forms, the complexes arrange in the following order: **Mn1** \approx **Fe1** > **Re1** >> **Mn2**.

The data on the relative change in catalytic currents are given in Table 1.

In this respect, the discussed complexes arrange as follows: **Re1** > **Mn1** > **Fe1** > **Mn2**. The catalytic currents are higher for

Table 1. Relative change in the catalytic current vs. the amount of added acid

HBF_4 , equiv.	Catalytic current change as a function of the added acid amount, in % relative to that for the protonated form			
	Mn2	Fe1	Mn1	Re1
1	145	–	182	440
2	–	210	–	–
3	162	–	273	790
5	182	265	315	1085
10	–	370	465	1345

the vinylidene complexes, since their protonated (carbyne) forms have two $\text{C}_\beta\text{--H}$ bonds instead of one as in the case of protonated allenylidene **Mn2** and acetylide **Fe1**.

Considering all these parameters together, rhenium vinylidene complex $\text{Cp}^*(\text{CO})_2\text{Re}=\text{C}=\text{CHPh}$ (**Re1**) seems to be the best compound among the above-mentioned complexes in terms of catalytic activity. This is not surprising, because the HOMO–LUMO gap increases on going downward the group.

Conclusions

Thus, a concept of catalytic reduction of proton to hydrogen through the activation of the C--H (rather than M--H [2]) bond is demonstrated by the example of rhenium complex **Re1** and iron acetylide **Fe1**. The results obtained in this work and earlier for complexes **Mn1**, **Mn2** indicate that, varying the ligand environment and the nature of a metal in the above-mentioned $\eta^1\text{-}\sigma,\pi$ -complexes, one can change the catalyst efficiency and synthesize more active catalysts in a tailor-made manner.

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Electronic supplementary information

Electronic supplementary information (ESI) available online: the CV data, synthetic procedures, and a brief state-of-the-art review. For ESI, see DOI: 10.32931/ioXXXXx.

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