Supporting Information

General Information

The reagents used, $CoCl_2 \cdot 4H_2O$, phenylboronic and *n*-butylboronic acids as well as the sorbents and organic solvents were obtained commercially (Fluka and Chemapol). The dichloroglyoxime (denoted as Cl_2GmH_2) was prepared by chlorination of glyoxime as described in Ref. SI1 The complexes $Co(Cl_2Gm)_3(BC_6H_5)$ and $Co(Cl_2Gm)_3(Bn\text{-}C_4H_9)$ were prepared as described in Ref. 9f.

Cyclic voltammetry. Cyclic voltammetry (CV) experiments were carried out in acetonitrile solutions with 0.1 M $((n\text{-}C_4H_9)_4N)BF_4$ as a supporting electrolyte using a model Parstat 2273 (Prinston Applied Research, USA) potentiostat with a conventional one-compartment three-electrode cell (10 ml of solution). Glass carbon (GC) electrode with an active surface area of 0.125 cm^2 was used as a working electrode. The electrode was thoroughly polished and rinsed before measurements. A platinum counter electrode and a standard $Ag/AgCl/KCl_{aq}$. reference electrode were applied. All the solutions were thoroughly deaerated by passing argon through them before the CV experiments and above them during the measurements.

Controlled-potential electrolysis. 50 mM $HClO_4$ acetonitrile solution with 0.1 M $((n\text{-}C_4H_9)_4N)BF_4$ was electrolyzed in the presence of the complexes $Co(Cl_2Gm)_3(BC_6H_5)_2$ and $Co(Cl_2Gm)_3(Bn\text{-}C_4H_9)_2$ for 60 min at – 500 mV *vs* $Ag/AgCl/KCl_{aq}$. The production of the molecular hydrogen with a Faraday yield of 99% was confirmed by gas chromatography analysis.

Hydrogen Detection. Gas chromatography analysis of gases evolved during the electrolysis was performed with a Varian 450 GC equipped with a pulsed discharge helium ionization detector D-4-I-VA38-R. Hydrogen production was quantitatively detected using a 30 m-in-length stainless steel column with inside diameter 250 μm at 120°C for the detector and at 80°C for the oven. The carrier gas was helium flowing at a rate of 40 ml min^{-1}. The injections (250 μL) were performed *via* a sampling loop. The retention time of gaseous H_2 was 2.48 min.

Spectroelectrochemical studies. The UV-vis spectra (Fig. SI1) were recorded using a Cary 50 UV/Vis spectrophotometer under argon. The spectra of the *in situ* electrogenerated species were measured using a one-compartment three-electrode quartz cell with the optical lenght of 10 mm mounted in this. The working electrode was a platinum grid (3 cm × 0.7 cm × 0.3 mm) with a teflon-covered wire (used to avoid the electrolysis elsewhere than in the quartz window). The reference and counter electrodes were positioned on the top of the cell.

Kinetic studies. CV was used to study the kinetics of the electrocatalysis. All these studies were performed in an electrochemical cell (10 ml of 0.1 M $((n\text{-}C_4H_9)_4N)BF_4$ acetonitrile solution). The working electrode was a glassy carbon disk ($s = 0.125\ cm^2$), and the counter electrode was a platinum wire in a glass tube with a porous Vycor tip filled with 0.1 M $((n\text{-}C_4H_9)_4N)PF_6$ acetonitrile solution.

Supporting Information References

SI1. Ponzio, G.; Baldrocco, F. *Gazz. Chim. Ital.* **1930**, *60*, 415.

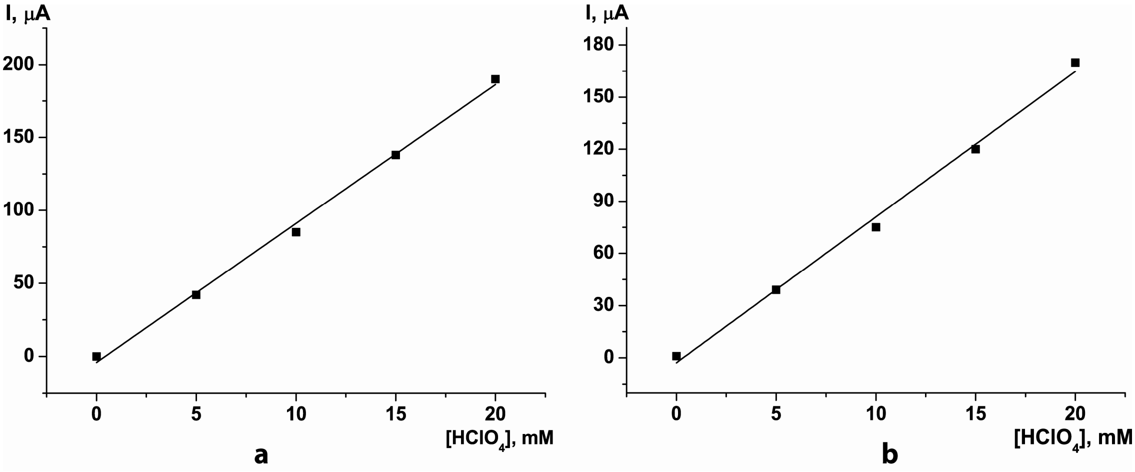

Fig. SI1. Plots of the electrocatalytic current for 1.0 mM acetonitrile solutions of the complexes $Co(Cl_2Gm)_2(BC_6H_5)_2$ (**a**) and $Co(Cl_2Gm)_2(Bn\text{-}C_4H_9)_2$ (**b**) *versus* $HClO_4$ concentration in 0.1 M $((n\text{-}C_4H_9)_4N)BF_4$ at scan rate 100 mV s^{-1}; GC electrode relative to Ag/AgCl/KCl$_{aq}$

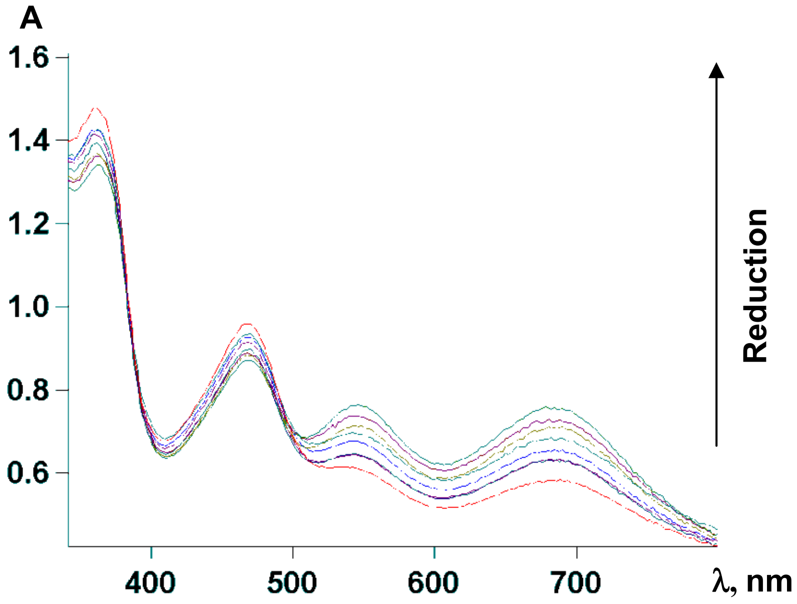

Fig. SI2. UV-vis spectra of 1 mM acetonitrile solution of the complex $Co(Cl_2Gm)_3(BC_6H_5)_2$ in 0.1 M $((n\text{-}C_4H_9)_4N)BF_4$ upon the gradual electrochemical reduction at *E*= – 300 mV on platinum grid electrode.