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Molecular cobalt electrocatalyst for proton reduction at low overpotential[†]

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Linear trimetallic Co^{III}/Co^{III} cobalt complexes with bridging acyl-alkoxy ligands are electrocatalysts for the reduction of tosic acid in acetonitrile. The $-OCMe_2CH_2COMe$ complex appears to operate homogeneously, and at a modest onset overpotential of 175 mV. A turnover frequency of *ca.* 80 s⁻¹ was observed at an overpotential of 300 mV.

Solar driven water splitting for chemical energy storage is an area of active research, given the potential application of such technology for solving current energy problems.^{1,2} Water splitting couples the oxidation of water with the reduction of protons to form hydrogen fuel. Platinum is an excellent catalyst for the hydrogen evolution reaction (HER); however, due to its scarcity, great effort is being directed toward finding cheaper and more earth abundant alternatives. Many first-row metal catalysts have been developed, including hydrogenase mimics³⁻⁵ and other types of complexes.⁶⁻¹⁰ One of the challenges for HER catalyst design is achieving a good catalytic rate at a modest overpotential. Thus, many of the synthetic catalysts exhibit rapid rates, but only at potentials much higher than the thermodynamic potential for acid reduction.^{3-7,9} Herein we report two trimetallic cobalt complexes, one of which exhibits an onset for HER at overpotentials as low as 175 mV. Appreciable catalytic rates are achieved at $\eta > 225$ mV, and experimental evidence suggests that the catalysis occurs homogeneously.

The tricobalt complex $[Co_3(C_5H_9O_2)_6][BF_4]_2$ (1) was synthesized by reaction of $Co[N(SiMe_3)_2]_2$ with 3 equivalents of 3-hydroxy-3methyl-2-butanone (HOCMe₂COMe), accompanied by an *in situ* oxidation of cobalt with an equivalent of AgBF₄ as shown in Scheme 1. Red crystals of 1 were isolated in 85% yield by cooling the reaction solution to -80 °C.



Scheme 1 Synthesis of compounds 1 and 2.



Fig. 1 Structure of **1** determined by single-crystal X-ray diffraction. The thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms, THF molecules, and counter anions are omitted for clarity.

The structure of **1** (Fig. 1) may be described as containing two pseudo-octahedral, tris(chelate) Co^{III} complexes that serve as tridentate ligands for a central Co^{III} ion. Both Co^{III} [OCMe₂COMe]₃ moieties are complexed to Co^{II} by sharing of an octahedral face comprised of three alkoxy oxygen atoms. Note that several related trinuclear 2Co^{III}/Co^{II} complexes have been reported.^{11,12}

The analogous complex $[Co_3(C_6H_{11}O_2)_6][BF_4]_2$ (2) was synthesized similarly, using 4-hydroxy-4-methyl-2-pentanone (HOCMe₂CH₂COMe) as the ligand precursor. X-ray quality crystals of this complex were not obtained, but it is believed to have a structure analogous to

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that of 1, on the basis of combustion analysis and spectroscopic evidence (NMR, IR, and UV-vis). For example, paramagnetically shifted resonances for the methyl groups of 2, at 66.73 and -95.41 ppm, are similar to the corresponding resonances of 1 at 70.70 and -97.14 ppm. A peak unique to 2 at -7.04 ppm is assigned to the methylene protons (see Fig. S1, ESI†). Infrared spectra of 1 and 2 also exhibit similar features, most notably symmetric and asymmetric C–O stretches for the bridging alkoxy groups (1054, 875 cm⁻¹ for 2 and 1042, 885 cm⁻¹ for 1), consistent with literature values for such bridging alkoxides in transition metal complexes.^{13,14} The ν (C=O) stretches for 1 and 2 both appear at 1658 cm⁻¹. Also, the UV-vis spectra of 1 and 2 exhibit similar broad charge transfer bands (340 nm for 1 and 380 nm for 2; Fig. S11, ESI†) which give them a red color.

The redox behavior of **1** and **2** is unexceptional in the absence of acid. Compound **2** displays only one, quasireversible redox event at *ca.* 0.37 V vs. $Fc^{+/0}$ in acetonitrile (Fig. S2, ESI[†] inset; all potentials are referenced to $Fc^{+/0}$), which is assigned to the Co^{III/II} couple for the central cobalt ion. The Co^{III/II} couple of **2** is similar to the oxidation potential of Ag⁺ measured in a less polar solvent (0.41 V in THF),¹⁵ which explains why the central Co^{II} is not oxidized by AgBF₄. Compound **1** displayed no noticeable redox events (in scan rate ranges of 1 mV s⁻¹ to 100 mV s⁻¹) before reaching potentials too oxidizing or reducing to induce decomposition. Presumably, the corresponding Co^{III/II} couple for **1** is not readily discernible because it coincides with the oxidative decomposition occurring at *ca.* 0.65 V.

In the presence of tosic acid, cathodic current enhancements are observed in the cyclic voltammograms (CVs) of **2** in acetonitrile (0.4 mM) with 0.1 M [N^{*n*}Bu₄]PF₆ as a supporting electrolyte (Fig. 2). A linear growth in the catalytic current is observed with incremental increases in the acid concentration (Fig. S12, ESI[†]).

Notably, the CV of 2 displays an onset for the catalytic current near the reported thermodynamic potential (E°) of tosic acid reduction at -0.50 V in acetonitrile.¹⁶ The onset overpotential for 2 was defined by the lowest potential at which >80% Faradaic efficiency was observed during electrolysis (see below). Faradaic efficiency measurements were conducted by comparing the headspace H₂ concentration measured by GC to the charge



Fig. 2 Cyclic voltammogram of 2 in the presence of tosic acid (scan rate 100 mV s^{-1}). A linear growth in the current with added amounts of acid was observed, and the onset overpotential for the reduction of tosic acid is close to the thermodynamic value.

passed in constant potential electrolysis experiments (see ESI,[†] Fig. S3 and S4 for details). Faradaic efficiencies of 84%, 83%, and 86% were recorded for electrolyses performed at overpotentials (η ; $\eta = |E - E^{\circ}|$) of 175 mV, 225 mV, and 275 mV, respectively. Faradaic efficiencies of greater than 93% were recorded for electrolyses at $\eta \geq 300$ mV. Electrolyses were performed such that more than 10 Coulombs passed before the GC analyses.

Turnover frequencies (TOFs) for the catalyst were estimated by using eqn (1) derived by Kubiak and coworkers for homogeneous electrocatalytic systems assuming an EC' mechanism (see ESI† for detailed calculations).¹⁷

$$\text{TOF} = \frac{1}{D_{\rm c}} \left(\frac{j_{\rm lim}}{nF[\rm C]} \right)^2 \tag{1}$$

The diffusion coefficient for compound 2 was measured electrochemically to be 6.0×10^{-6} cm² s⁻¹ (see ESI⁺). From eqn (1), the calculated TOF of 2 at $\eta = 300$ mV was *ca.* 80 s⁻¹. This estimated TOF is comparable to other cobalt catalysts found in the literature;^{8,9} however, the catalytic onset of *ca*. $\eta = 175$ mV is low for a cobalt catalyst.¹⁰ Notably, Gray and Winkler have recently reported Co(triphos) compounds (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane) that reduce protons at overpotentials as low as 15 mV.¹⁰ Various control experiments indicated that complex 2 is required for the electrocatalysis. Thus, no detectable amounts of H₂ were produced at η = 300 mV in 8 h of electrolysis from 25 mM tosic acid acetonitrile solutions containing HOCMe2- CH_2COMe , $Co(NO_3)_2$, or $Co(OTs)_2$. Compound 1 was subjected to identical reaction conditions and was shown to be active for proton reduction catalysis, but at high overpotentials ($\eta > 350$ mV; see ESI,† Fig. S6).

Recently, Savéant and coworkers reported that the active species for a family of molecular chlathrochelate cobalt catalysts for proton reduction were in fact cobalt-containing nanoparticles generated on the electrode surface.¹⁸ Thus, several experiments were conducted to investigate the possible conversion of 2 to nanostructured or insoluble materials, and to determine the homogeneity of the catalysis. A rinse test was performed, whereby the glassy carbon electrode used for catalysis was removed from the reaction solution, rinsed gently with acetonitrile, and then placed in a fresh solution with supporting electrolyte and tosic acid. A voltammogram obtained after this procedure was identical to that obtained with a new glassy carbon electrode in the same solution. Additional experiments designed to identify any nanoparticles that form during catalysis utilized transmission electron microscopy (TEM). Catalysis was performed using a TEM grid as an electrode, which was subsequently analyzed by TEM. No visible particle formation occurred after application of potentials less reducing than -0.99 V. Catalyst decomposition was forced by driving the potential beyond the stability limit of the catalyst (<-1.0 V), in which case a large current was observed along with deposition of particles on the TEM grid (Fig. 3).

Nanoparticles of cobalt on glassy carbon electrodes were deliberately prepared by applying -1.4 V to a clean glassy carbon electrode in a solution of 2 with 20 mM tosic acid.

Fig. 3 Cyclic voltammogram of **2** in the presence of tosic acid at potentials more negative than its stability limit (left; scan rate 100 mV s⁻¹). Large current enhancement was observed due to electroplating of cobalt nanoparticles (shown in inset; scale bar 100 nm). The acid concentrations are 0 mM, 5 mM, and 9 mM for black, red, and green traces, respectively. CV of compound **2** in catalysis conditions and that of a glassy carbon electrode with pre-deposited NPs (right; scan rate 100 mV s⁻¹).

The electrode was then rinsed with acetonitrile and placed into a 20 mM tosic acid solution in the absence of **2**, and the nanoparticles on the electrode yielded the voltammogram displayed in Fig. 3. The deposited particles were not responsible for proton reduction catalysis at low overpotentials, suggested by the absence of a current response at potentials less than -1.0 V, and well within the range in which compound **2** exhibited catalysis.

A further test of the homogeneity of electrocatalysis involved a Koutecky–Levich analysis using a rotating disk electrode. A Koutecky–Levich plot of **2** at $\eta = 275$ mV is displayed in Fig. S8 (ESI[†]) and the voltammograms at various rotating rates are plotted in Fig. S7 (ESI[†]). The observed deviation from linearity in the Levich plot for **2** is suggestive of homogeneous catalysis, because the diffusion limited current is reached at low rotation rates (600 rpm).¹⁹ Electrode-bound catalysts typically exhibit linear behavior to rotation rates higher than 1000 rpm.¹⁹ Thus, the tests described above strongly suggest that the proton reduction catalysis by **2** occurs homogeneously.

In the presence of one equivalent of tosic acid, compound 2 displays a reduction event at ca. -0.7 V, observed electrochemically by differential pulse voltammetry (DPV; Fig. S9, ESI⁺). Since this reduction is not observed in the absence of acid, it is attributed to a protonated form of 2. In the presence of additional acid, a catalytic reduction wave grows at -0.7 V, indicating that this catalysis is initiated by the protonation of 2. Thus, a possible catalytic cycle consistent with this observation is displayed in Fig. 4. In this scenario, protonation of 2 precedes reduction of the central cobalt to Co^I. This reduced cobalt center is then protonated to produce a Co^{III} hydride, which would then undergo a one-electron reduction to a Co^{II} hydride that couples with a nearby, oxygen-bound proton to form H₂. The formation of a Co^{III} hydride from Co^I has frequently been proposed in the literature, and a Co^{III} hydride has been spectroscopically observed in proton reduction.¹⁰

The results described above provide an intriguing structural type for consideration in the design and synthesis of new electrocatalysts for proton reduction. Importantly, the structures of 1 and 2 are relatively simple, and involve a central Co^{II} cation sandwiched by neutral, tridentate ligands. Notably, a wide



Fig. 4 Proposed mechanism for proton reduction catalysis by 2.

variety of analogous structures should be readily generated by addition of neutral, tridentate donors to a source of the Co^{II} cation. In an initial effort to pursue this theme, the known, dicationic bis[tri(pyrazolyl)methane] complex of cobalt was synthesized as reported in the literature.²⁰ This complex, $[Co(tpm)_2]$ [BF₄]₂ (tpm = tri(pyrazolyl)methane), is a catalyst for tosic acid reduction in acetonitrile (1-4 mM) and exhibits electrochemical behavior similar to that of 1, while displaying catalysis at $\eta > 300$ mV (Fig. S10, ESI[†]). Note, however, that this complex is fundamentally different from 1 and 2, in that the nitrogen donors of the tpm ligands lack available lone pairs for binding protons, and this may explain the higher onset potential for catalysis. The [Co(tpm)₂][BF₄]₂ complex also exhibits limited stability with tosic acid concentrations higher than 10 mM. It is presumed that the Co^{III} in compound 2 increases the basicity of the bridging alkoxy oxygen, enabling the facile binding of protons and the subsequent coupling to the neighboring hydride.

In summary, the trimetallic cobalt complex 2 functions as an efficient catalyst for the proton reduction reaction, operating at a low onset overpotential of 175 mV. Related trimetallic complexes should be of interest as electrocatalysts. For example, Chaudhuri and coworkers have reported the synthesis of valence-trapped compounds similar in structure to 1 and 2, using bicyclic octahedral Cr^{III} metalloligands that incorporate various central metal cations, including Mn^{II}, Co^{II} and Ni^{II}.²¹

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