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(Electro)catalytic C–C bond formation reaction with a redox-active cobalt complex

(Electro)catalytic C–C bond formation reaction is reported for a redox-active cobalt catalyst. Cooperativity between cobalt and the redox-active ligands in electron transfer steps is responsible for this (electro)catalytic process.

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## (Electro)catalytic C–C bond formation reaction with a redox-active cobalt complex†

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**Cooperativity between cobalt and non-innocent ligands in electron transfer processes has been utilized for (electro)catalytic C–C bond formation reactions.**

Redox-active ligands have long fascinated coordination chemists because of the unusual and curious electronic structures of their metal complexes.<sup>1</sup> More recently chemists have started developing novel catalysts based on metal complexes of non-innocent ligands.<sup>2</sup> One feature of redox-active ligands which is often utilized in such catalytic processes is their active participation in various electron transfer steps. Quinones are an important class of redox-active ligands, and historically metal complexes of the all oxygen donating *o*-quinone ligand have been the most studied.<sup>1b</sup> More recently, metal complexes of *o*-iminoquinones have been thoroughly investigated.<sup>1c,3</sup> Such [O] for [NR] isoelectronic substitutions often induce novel properties in the metal complexes; redox-tuning, and steric protection through the R groups being obvious gains of the approach.<sup>3d</sup> *o*-Diiminoquinones where both the [O] groups have been replaced by [NR] have found rather limited use.<sup>4</sup> Some such [NR] containing ligands used for synthesizing four-coordinate cobalt complexes have been listed in Fig. 1.<sup>4,5</sup> We have been pursuing the development of new redox-active ligands where [O] donors are replaced by their isoelectronic [NR] counterpart. Such a substitution often turns out to be immensely helpful while using metal complexes of these ligands for various catalytic transformations.<sup>6</sup> Herein we present the cobalt complex **1** with the ligand Q<sup>•-</sup>. Geometric and electronic structure of this complex has been probed by a battery of methods, and its utility as an (electro)catalyst for C–C bond formation reactions has been investigated.

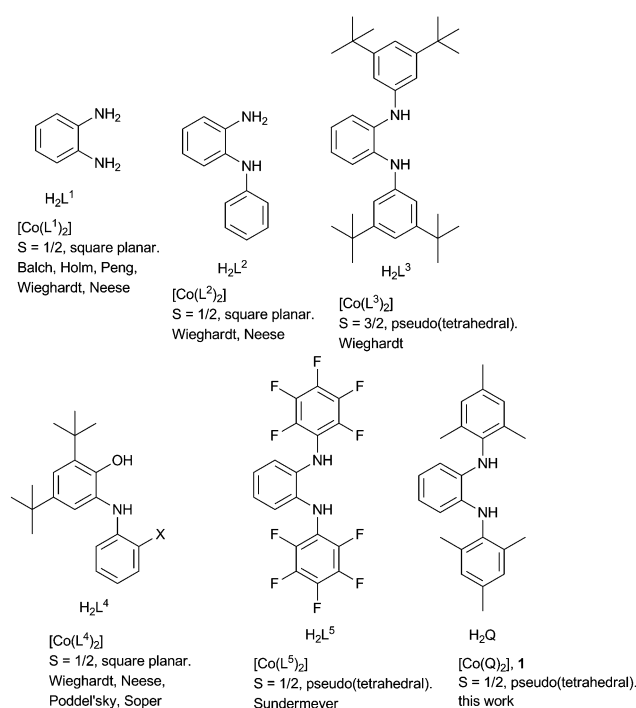


Fig. 1 Selected redox-active ligands with which four-coordinate cobalt complexes have been reported together with the geometry and spin-states of those cobalt complexes.

The complex **1** was synthesized by deprotonation of H<sub>2</sub>Q with *n*-BuLi, its reaction with CoCl<sub>2</sub>, and the subsequent oxidation of the reaction mixture with pure O<sub>2</sub>. Re-crystallization provided **1** in the pure form. The geometric structure of **1**, which crystallizes as a CH<sub>2</sub>Cl<sub>2</sub> solvate, was determined by single crystal X-ray diffraction studies. The cobalt center in **1** is in a (pseudo)tetrahedral environment; being coordinated by the nitrogen donor of two different ligands (Fig. 2).

The  $\tau$  value for this structure is 0.46. The dihedral angle between the two coordinating planes is 50°. The Co–N bond distances of about 1.92 Å points to a high spin (HS) Co(II)

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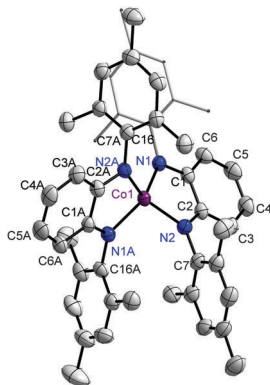


Fig. 2 ORTEP plot of **1**. Ellipsoids are drawn at 50% probability. Hydrogen atoms and solvent molecules have been left out for clarity.

center. The intra-ring C–C bond display a quinoidal distortion with two short and four long bonds (Table S2, ESI<sup>†</sup>). The C–N bond lengths of 1.36 Å also points to the existence of these ligands as  $Q^{\bullet-}$ , and hence neutral **1** can be formulated as  $[(Q^{\bullet-})Co^{II,HS}(Q^{\bullet-})]$ . However, the difference in intra-ring bond lengths for the various redox forms of ligands with all nitrogen donors are known to be less compared to the various redox-forms of their [O,O] and [O,N] counterparts.<sup>7</sup> Additionally, work by the groups of Wieghardt and Neese<sup>4c–e</sup> have shown the existence of valence ambiguity in the corresponding cobalt complex with [O,N] and [N,N] donor ligands (Fig. 1). With this background in mind, the temperature dependence of the magnetic susceptibility of **1** was investigated. The results resemble those of Sundermeyer *et al.*,<sup>4a</sup> indicating an  $S = 1/2$  ground state due to strong antiferromagnetic exchange interactions between the central (HS) Co(II) ion and the surrounding radical ligands (Fig. S1, ESI<sup>†</sup>). The room-temperature effective magnetic moment was determined to be  $2.47 \mu_B$ . Furthermore, the strong  $g$  value anisotropy found in the 5 K EPR spectra of **1** both in the solid state and in frozen solution confirmed a cobalt-centered  $S = 1/2$  spin. Best fits were obtained with  $g_{\parallel} = 4.0 \pm 0.08$ ,  $g_{\perp} = 1.78 \pm 0.01$  for the solid and  $g_{\parallel} = 3.75 \pm 0.08$ ,  $g_{\perp} = 1.80 \pm 0.02$  as well as a hyperfine coupling constant of  $A_{\parallel} = 850 \pm 30$  MHz for the frozen solution. (Fig. S2, ESI<sup>†</sup>). This combined approach delivered results that are best interpreted by considering the resonance form  $[(Q^{\bullet-})Co^{II,HS}(Q^{\bullet-})]$ . Thus, it is seen that there are no simple correlations between ligand type, geometry at the metal center, and spin states for these classes of cobalt complexes (*ca.* Fig. 1).

Cyclic voltammogram of **1** in  $CH_2Cl_2/0.1$  M  $Bu_4NPF_6$  shows two reversible one-electron oxidation waves at  $-0.21$  and  $0.30$  V and a reversible one-electron reduction wave at  $-1.47$  V vs.  $Fc/Fc^+$  (Fig. S3, ESI<sup>†</sup>). A second reduction wave is also observed in  $CH_2Cl_2$ , which shows the onset of a catalytic current. This observation suggests that complex **1** is capable of activating the C–Cl bonds of  $CH_2Cl_2$  catalytically. We note that most complexes listed in Fig. 1 show reversible reduction steps in dichloromethane, indicating that they do not react with  $CH_2Cl_2$ . Only the reduced form of complex  $[Co(L_4)_2]$  has been showed to perform C–Cl activation by Soper *et al.*<sup>5a</sup> Subtle substitution

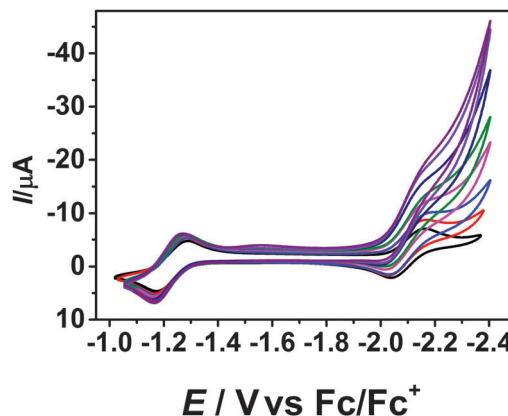


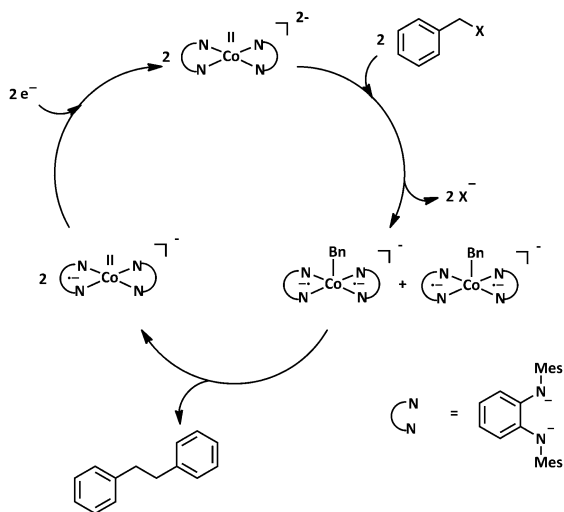
Fig. 3 Cyclic voltammogram of **1** with the addition of benzyl bromide. THF/0.1 M  $Bu_4NPF_6$ , 298 K,  $100$   $mV s^{-1}$ .

changes on the ligand backbone is thus shown to dramatically influence redox-induced chemical reactivity in these complexes. To prove the hypothesis of a catalytic reaction of complex **1** with  $CH_2Cl_2$  following the second reduction step, we recorded the cyclic voltammogram of this complex in THF. Gratifyingly, both reduction waves are electrochemically reversible in THF (Fig. S4, ESI<sup>†</sup>). Reversibility was proven by comparing forward and reverse current heights (which is close to 1), and by plotting the square root of the scan rate *versus* the current peak. The latter plot is linear proving that reduction proceeds reversibly under diffusion control in THF (Fig. S5, ESI<sup>†</sup>). The oxidation waves become irreversible in THF. This is a possible indication of oxidation-induced binding of THF to the cobalt center. Such five-coordinated cobalt complexes have been previously isolated as oxidation products of the neutral four-coordinate cobalt complexes.<sup>4</sup>

Inspired by the catalytic wave observed in  $CH_2Cl_2$  after the second reduction of **1**, we wanted to investigate the utility of **1** as an (electro)catalyst for C–C bond formation reactions. To test this, aliquots of benzyl bromide was added to a solution of **1** in THF. Each additional amount of benzyl bromide resulted in further increase in the catalytic current (Fig. 3), proving a catalytic reaction of **1** with benzyl bromide after the second reduction wave.

It should be noted, that the addition of benzyl bromide does not lead to a change in the intensity or position of the first reduction wave. The catalytic current was determined for each wave after the addition of benzyl bromide. A plot of  $i_{cat}/i_p$  *versus* benzyl bromide concentration delivers a linear fit (Fig. S6, ESI<sup>†</sup>). Additionally, the plot of  $i_{cat}/i_p$  *versus* the square root of the concentration of benzyl bromide is linear as well, proving that the reaction is first order in benzyl bromide concentration (Fig. S7, ESI<sup>†</sup>). Using the  $i_{cat}/i_p$  ratio, we have calculated the observed rate constant ( $k_{obs}$ ) at various scan rates.  $k_{obs}$  is seen to be dependent on scan rate, with a stronger dependence observed at lower scan rates (Fig. S8, ESI<sup>†</sup>). This observation is consistent with the formation of the catalytically active species after the second reduction process. At a scan rate of  $100$   $mV s^{-1}$ , the value of  $k_{obs}$  is approximately  $10$   $s^{-1}$  displaying relatively fast reaction rates. We also tested benzyl chloride as a





Scheme 1 Proposed catalytic cycle for the (electro)catalytic C–C bond formation reaction with **1**.

substrate for this reaction. The trends observed are similar to the reaction with benzyl bromide (Fig. S10–S12, ESI<sup>†</sup>). However, reaction rates with benzyl chloride are slower. For example, at a scan rate of 100 mV s<sup>-1</sup>, the value of  $k_{\text{obs}}$  for the reaction with benzyl chloride is about 2.8 s<sup>-1</sup>. This observation is consistent with the breaking of the C–halide bond as the possible rate determining step. Control reactions were also performed with Bu<sub>4</sub>NBr to rule out the involvement of species derived from Br<sup>-</sup> in catalysis. Such a reaction did not display any catalytic current (Fig. S9 and S13, ESI<sup>†</sup>).

We then turned our attention to the possible mechanism of this (electro)catalytic reaction. A mixture of *in situ* generated [Co(Q<sup>2-</sup>)<sub>2</sub>]<sup>2-</sup> and benzyl chloride were stirred together, and a ESI mass spectrum of the mixture was recorded. The main product observed from this mixture was the five-fold coordinated cobalt complex [Co(Q<sup>•-</sup>)<sub>2</sub>(CH<sub>2</sub>Ph)]<sup>-</sup> (Fig. S15, ESI<sup>†</sup>). Additionally, a chromatographic work-up of the reaction mixture, and <sup>1</sup>H NMR characterization of the organic phase delivered dibenzyl as the exclusive product (Fig. S16, ESI<sup>†</sup>). Control experiments showed that CoCl<sub>2</sub> without the ligand does not deliver any product (Fig. S17, ESI<sup>†</sup>). Taking these observations into consideration, a mechanism shown in Scheme 1 can be postulated. The complex **1**<sup>2-</sup> activates the C–X bonds of the substrates which lead to a release of X<sup>-</sup> and the formation of the aforementioned five-fold coordinated species. The formation of the C–C coupled dibenzyl product leads to a release of **1**<sup>-</sup>, the reduction of which regenerates the active catalyst **1**<sup>2-</sup>. This cycle ensures that the **1**/**1**<sup>-</sup> redox couple of complex **1** remains unchanged during the catalytic cycle, as has been experimentally observed (Fig. 3).

Summarizing, we have presented here a four-coordinate cobalt complex with a redox-active ligand. The geometric and electronic structure of this complex has been probed by a variety of methods, and the complex **1** can be best described

as [(Q<sup>•-</sup>)Co<sup>II,HS</sup>(Q<sup>•-</sup>)]. Despite the apparent similarity of this complex with several reported cobalt complexes, unique catalytic reactivities have been observed with it. Quantification of the catalytic results and a possible mechanistic picture has been presented. It is the subtle cooperative interplay between cobalt and the redox-active ligands that make such catalytic bond formation possible. The results presented here display the catalytic utility of redox-active metal complexes in C–C bond formation reactions, and provide impetus for carrying out studies with a systematic variation of the ligand backbone. Such investigations are likely to shed more light on the catalytic activity of such metal complexes.

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