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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.¹ More recently chemists have started developing novel catalysts based on metal complexes of non-innocent ligands.² 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.^{1b} More recently, metal complexes of *o*-iminoquinones have been thoroughly investigated.^{1c,3} 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through the R groups being obvious gains of the approach.^{3d} *o*-Diiminoquinones where both the [O] groups have been replaced by [NR] have found rather limited use.⁴ Some such [NR] containing ligands used for synthesizing four-coordinate cobalt complexes have been listed in Fig. 1.^{4,5} 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.⁶ Herein we present the cobalt complex **1** with the ligand Q^{•-}. 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.

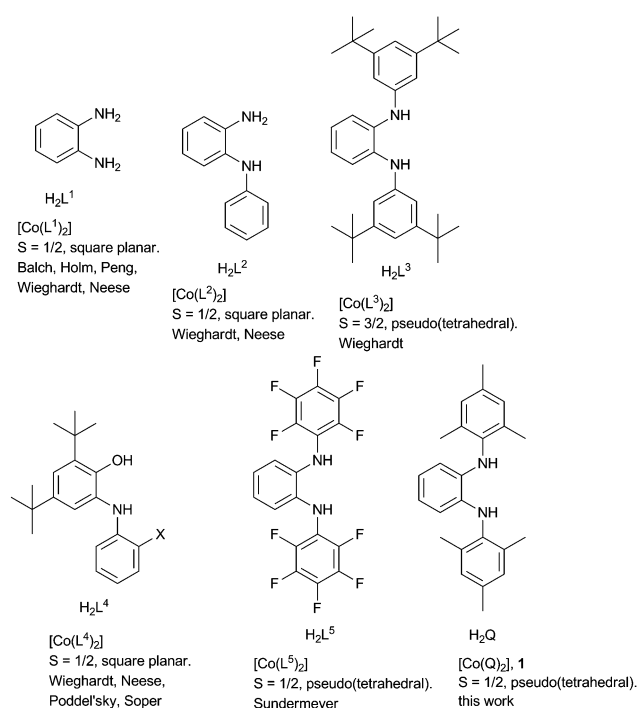


Fig. 1 Selected redox-active ligands with which four-coordinate cobalt complexes have been reported together with the geometry and spin-states of those cobalt complexes.

The complex **1** was synthesized by deprotonation of H₂Q with *n*-BuLi, its reaction with CoCl₂, and the subsequent oxidation of the reaction mixture with pure O₂. Re-crystallization provided **1** in the pure form. The geometric structure of **1**, which crystallizes as a CH₂Cl₂ 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 τ 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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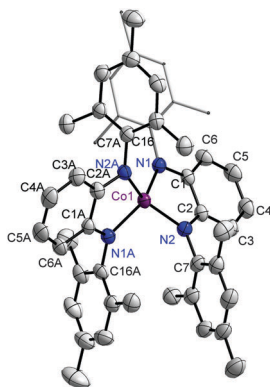


Fig. 2 ORTEP plot of **1**. Ellipsoids are drawn at 50% probability. Hydrogen atoms and solvent molecules have been left out for clarity.

center. The intra-ring C–C bond display a quinoidal distortion with two short and four long bonds (Table S2, ESI[†]). 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.⁷ Additionally, work by the groups of Wieghardt and Neese^{4c–e} 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.*,^{4a} 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[†]). 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 $g_{||} = 4.0 \pm 0.08$, $g_{\perp} = 1.78 \pm 0.01$ for the solid and $g_{||} = 3.75 \pm 0.08$, $g_{\perp} = 1.80 \pm 0.02$ as well as a hyperfine coupling constant of $A_{||} = 850 \pm 30$ MHz for the frozen solution. (Fig. S2, ESI[†]). 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[†]). 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.*^{5a} Subtle substitution

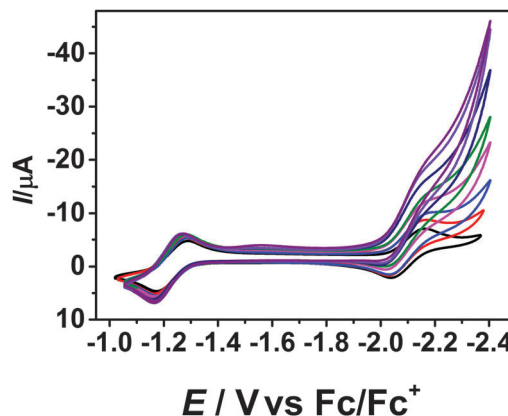


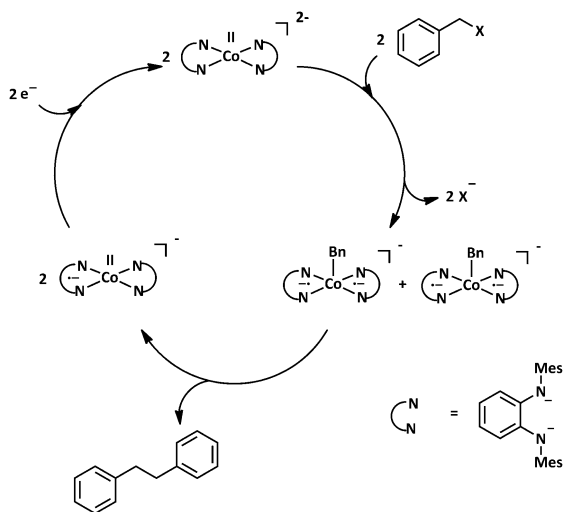
Fig. 3 Cyclic voltammogram of **1** with the addition of benzyl bromide. THF/0.1 M Bu_4NPF_6 , 298 K, 100 $mV s^{-1}$.

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[†]). 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[†]). 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.⁴

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[†]). 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[†]). 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[†]). 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[†]). However, reaction rates with benzyl chloride are slower. For example, at a scan rate of 100 mV s⁻¹, the value of k_{obs} for the reaction with benzyl chloride is about 2.8 s⁻¹. This observation is consistent with the breaking of the C–halide bond as the possible rate determining step. Control reactions were also performed with Bu₄NBr to rule out the involvement of species derived from Br⁻ in catalysis. Such a reaction did not display any catalytic current (Fig. S9 and S13, ESI[†]).

We then turned our attention to the possible mechanism of this (electro)catalytic reaction. A mixture of *in situ* generated [Co(Q²⁻)₂]²⁻ 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^{•-})₂(CH₂Ph)]⁻ (Fig. S15, ESI[†]). Additionally, a chromatographic work-up of the reaction mixture, and ¹H NMR characterization of the organic phase delivered dibenzyl as the exclusive product (Fig. S16, ESI[†]). Control experiments showed that CoCl₂ without the ligand does not deliver any product (Fig. S17, ESI[†]). Taking these observations into consideration, a mechanism shown in Scheme 1 can be postulated. The complex **1**²⁻ activates the C–X bonds of the substrates which lead to a release of X⁻ 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**⁻, the reduction of which regenerates the active catalyst **1**²⁻. This cycle ensures that the **1**/**1**⁻ 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^{•-})Co^{II,HS}(Q^{•-})]. 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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