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# Redox-active ligand-mediated Co–Cl bond-forming reactions at reducing square planar cobalt(III) centers

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#### ABSTRACT

Synthetic routes to new square planar cobalt complexes with redox-active amidophenolate chelates are presented. Contrary to previous reports, steric bulk on the ligands is not a prerequisite to formation of the low-coordinate materials. X-ray crystal structure metrical data of the neutral  $S = \frac{1}{2}$  complexes are most consistent with cobalt(III) bound to one iminobenzoseminonate(1–) radical and one amidophenolate(2–) ligand. Addition of 1e<sup>-</sup> affords reduced congeners that are also square planar cobalt(III) because the redox-active ligand accepts an electron to generate bis(amidophenolate) species. The redox-activity of the ligands facilitates reactions with chlorine electrophiles to generate square pyramidal products containing new Co–Cl bonds. The bond-forming reactions all formally require oxidation of the metal fragment but there is no change in formal cobalt oxidation state. Instead, the reaction proceeds with oxidation of the amidophenolate ligands. Control of ligand oxidation state provides a mechanism for 1e<sup>-</sup> versus 2e<sup>-</sup> selectivity in the bond-forming reactions.

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#### 1. Introduction

The ability to make and break bonds with a high degree of selectivity has applications ranging from small-scale organic synthesis to energy conversion and the production of clean chemical fuels [1-5]. Selectivity in many synthetically useful methods for redox transformations of small-molecule substrates is predicated on the ability of platinum group inorganic and organometallic catalysts to mediate the transfer of multiple electrons in a single step [5–11]. The utility of these precious metal catalysts derives, in part, from their thermodynamic propensity to deliver multiple electron equivalents while avoiding odd-electron intermediates [12]. Accordingly, modification of supporting ligands is often employed as a strategy to modulate reactivity by fine tuning steric and electronic properties, but the ligands are typically redox inert [13]. Although these catalysts are powerful and sophisticated, cost and toxicity issues inherent to the precious metals can limit their utility.

Catalysts featuring naturally abundant transition metal centers offer the potential to address these issues. We are therefore pursuing the development of later first-row transition metal complexes as surrogates for platinum group catalysts, particularly those that rely on multielectron oxidative addition and reductive elimination steps in catalytic cycles for small-molecule activation and functionalization. The main challenge in translating these organometallic-type transformations to mononuclear 3d metal catalysts is in developing a multielectron capacity at metals that typically prefer only single electron redox changes. One successful approach to this problem is to stabilize metal ions in atypical, high-energy oxidation states, often through novel ligand design strategies [14–21]. An alternative strategy is to utilize cooperative redox changes between a metal center in common oxidation states and a redox-active ligand that can support charge localized structures [22–25]. This approach has been widely employed in reactions at metalloporphyrin complexes [26]. Recently, a number of other redox-active ligands have been shown to facilitate metal-centered redox reactions with small-molecules [27–39]. These ligands are more modular and afford the benefits of a high degree of electronic tunability and flexibility in coordination environment.

Reported herein are our initial efforts to utilize the close match in frontier orbital energies between redox-active ligands and cobalt(III) for bond-forming reactions at the metal center. Towards this goal, we have prepared and characterized new square planar cobalt complexes with amidophenolate ligands that were previously reported to be inaccessible [40]. X-ray crystallographic data is used to rationalize the electronic structures of these species, prompting a reevaluation of a previously reported assignment for a related complex [41]. Finally, control of ligand oxidation state is shown to facilitate redox 1e<sup>-</sup> versus 2e<sup>-</sup> selectivity in Co-Cl bond-forming reactions, establishing the ability of redox-active ligands to engender multielectron reactivity at square planar cobalt(III).





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#### 2. Experimental

#### 2.1. General considerations

Unless otherwise noted, all manipulations were performed under anaerobic conditions using standard vacuum line techniques, or in an inert atmosphere glove box under purified nitrogen. All NMR spectra were acquired on a Varian Mercury 300 spectrometer (300.323 MHz for <sup>1</sup>H) at ambient temperature. Chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak serving as an internal reference. Solution state magnetic moments were determined by Evans' NMR method [42,43]. UV-visible absorption spectra were acquired using a Varian Cary 50 spectrophotometer. Unless otherwise specified, all electronic absorption spectra were recorded at ambient temperatures in 1 cm quartz cells. IR spectra were obtained using attenuated total reflection (ATR) with a diamond plate on a Thermo Scientific Nicolet 4700 Fourier-transform infrared spectrophotometer. All mass spectra were recorded in the Georgia Institute of Technology Bioanalytical Mass Spectrometry Facility. Fast-atom bombardment mass spectrometry (FAB-MS) was performed using a VG Instruments 70-SE spectrometer. Cyclic voltammetric measurements were made using a CH Instruments CHI620C potentiostat in a three component cell consisting of a platinum disk working electrode, a platinum wire auxiliary electrode, and a non-aqueous AgNO<sub>3</sub>/Ag reference electrode. All electrochemical experiments were performed in CH<sub>3</sub>CN with 0.1 M [<sup>n</sup>Bu<sub>4</sub>N][PF<sub>6</sub>] as the supporting electrolyte. Electrochemical data are referenced and reported to Fc<sup>+</sup>/Fc as an internal standard. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA. All analyses were performed in duplicate, and the reported compositions are the average of the two runs.

#### 2.2. Methods and materials

Anhydrous acetonitrile (CH<sub>3</sub>CN), tetrahydrofuran (THF), toluene, dichloromethane, and pentane solvents for air- and moisture-sensitive manipulations were purchased from Sigma-Aldrich, further dried by passage through columns of activated alumina, degassed by at least three freeze-pump-thaw cycles, and stored under N<sub>2</sub> prior to use. Methanol (anhydrous, 99.0%) was purchased from Honeywell Burdick & Jackson, and used as received. Deuterated acetonitrile (CD<sub>3</sub>CN) was purchased from Cambridge Isotope Laboratories, degassed by three freeze-pump-thaw cycles, vacuum distilled from CaH<sub>2</sub>, and stored under a dry N<sub>2</sub> atmosphere prior to use. The ligands 2.4-di-tert-butyl-6-(2.6-diisopropylphenylimino)benzoquinone (**ibq**<sup>iPr</sup>) and 2,4-di-tert-butyl-6-(phenylamino)phenol (H<sub>2</sub>ap<sup>Ph</sup>) were prepared by literature methods [44,45]. All characterization data matched those referenced. Co(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and Co<sub>2</sub>(CO)<sub>8</sub> were purchased from Strem Chemical, Inc. All other chemicals were purchased from Sigma-Aldrich and used as received.

### 2.3. Preparation of $Co^{III}(isq^{Ph})(ap^{Ph})$

In modification of a literature procedure [46],  $Co(ClO_4)_2 \cdot 6H_2O$ (0.365 g, 1.00 mmol) and  $H_2ap^{Ph}$  (0.596 g, 2.00 mmol) were combined in a 50 mL round bottom flask with a stirbar and dissolved in 20 mL anhydrous methanol. Dropwise addition of Et<sub>3</sub>N (560 µL, 4.02 mmol) with vigorous stirring immediately afforded a clear dark blue solution. The flask was fitted to a condenser and the reaction mixture was heated to reflux in air for 1 h, then cooled to ambient temperature for 2 h to deposit a dark blue precipitate. The solids were recovered by vacuum filtration, washed with cold anhydrous methanol (3 × 2.0 mL, ice cold), and dried *in vacuo* to yield Co<sup>III</sup>(isq<sup>Ph</sup>)(ap<sup>Ph</sup>) (0.368 g, 0.566 mmol, 57%). Crystalline solids suitable for single crystal X-ray diffraction were recovered by slow diffusion of pentane into saturated  $CH_2Cl_2$  solution in the absence of light. UV–vis (THF) nm ( $\varepsilon$ ,  $M^{-1}$  cm<sup>-1</sup>): 280 (15 700), 675 (11 500), 900 (16 200). FAB-MS (m/z): 649 [M]<sup>+</sup>. FTIR (ATR): 3062 (w), 3041 (w), 3026 (w), 2956 (m), 2900 (m), 2863 (m), 1579 (w), 1536 (w), 1481 (m), 1432 (m), 1356 (m), 1302 (m), 1260 (m), 1215 (w), 1183 (w), 1138 (s), 1104 (s), 1025 (m), 1002 (w), 922 (m), 910 (m), 881(w), 859 (m), 824 (w), 766 (w), 738 (s), 692 (s), 659 (s), 609 (w), 571 (m), 540 (m), 510 (s), 467 (m), 424 (m) cm<sup>-1</sup>. The sample for elemental analysis was washed in methanol, as described above. The reported analysis is for Co<sup>III</sup>(isq<sup>Ph</sup>)(ap<sup>Ph</sup>)·1.3MeOH, and the presence of the methanol in the sample was confirmed by <sup>1</sup>H NMR spectroscopy. *Anal.* Calc. for C<sub>41.3</sub>H<sub>53.9</sub>N<sub>2</sub>CoO<sub>3.3</sub>: C, 71.74; H, 8.05; N, 4.05. Found C, 71.36; H, 7.62; N, 4.16%.

#### 2.4. Preparation of Co<sup>III</sup>(isq<sup>iPr</sup>)(ap<sup>iPr</sup>)

In modification of a literature procedure [41], a five dram scintillation vial was charged with a solution of  $Co_2(CO)_8$  (0.069 g, 0.203 mmol) in 10 mL toluene and a stir bar. Slow addition of a solution of ibq<sup>iPr</sup> (0.308 g, 0.811 mmol) in 5 mL toluene with vigorous stirring immediately afforded a blue solution. The solution was stirred for 1 h at ambient temperature and the volume was reduced to 4 mL to precipitate dark blue solids. The solids were collected by vacuum filtration in air, washed with toluene  $(2 \times 2.0 \text{ mL}, \text{ ice cold})$  and dried *in vacuo* to give Co<sup>III</sup>(isq<sup>iPr</sup>)(ap<sup>iPr</sup>) (0.255 g, 0.312 mmol, 77%). Slow diffusion of toluene into a saturated THF solution afforded single crystals of Co<sup>III</sup>(isq<sup>iPr</sup>)(ap<sup>iPr</sup>) suitable for assignment of connectivity by X-ray diffraction. UV-vis (THF) nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 280 (15 500), 680 (10 400), 905 (15 400). FAB-MS (m/z): 817 [M]<sup>+</sup>. FTIR (ATR): 3061 (w), 2959 (m), 2925 (m), 2902 (m), 2864 (m), 1535 (w), 1462 (w), 1357 (m), 1327 (w), 1298 (m), 1257 (w), 1230 (w), 1215 (w), 1181 (w), 1133 (s), 1097 (s), 1019 (m), 911 (w), 897 (m), 859 (m), 825 (w), 737 (m), 680 (w), 657 (s), 586 (w), 565 (w), 514 (s), 506 (s), 471 (m). 433 (m)  $cm^{-1}$ .

#### 2.5. Preparation of Na[Co<sup>III</sup>(ap<sup>Ph</sup>)<sub>2</sub>]

A five dram scintillation vial was charged with sodium-mercury amalgam beads (5% Na, 0.250 g, 0.544 mmol) and Co<sup>III</sup>(isq<sup>Ph</sup>)(ap<sup>Ph</sup>) (0.350 g, 0.539 mmol) and 10 mL CH<sub>3</sub>CN. The reaction mixture was fitted with a Teflon-lined cap and stirred for 12 h under N<sub>2</sub>. During this time a color change was observed from dark blue to purple. The solution was collected by vacuum filtration and the solvent was removed in vacuo to afford  $Na[Co^{III}(ap^{Ph})_2]$  (0.341 g, 0.504 mmol, 94%) as purple power. UV-vis (CH<sub>3</sub>CN) nm (*ε*, M<sup>-1</sup> cm<sup>-1</sup>): 295 (20000), 540 (4910), 850 (10600). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN, δ): 58.89 (2H), 35.62 (2H), 26.82 (4H), 8.29 (18H), -0.17 (18H), -7.43 (2H), -24.62 (4H) (all br s). The sample for elemental analysis was collected from a CH<sub>3</sub>CN solution. The reported analysis is for Na[Co<sup>III</sup>(ap<sup>Ph</sup>)<sub>2</sub>]·2CH<sub>3</sub>CN, and the presence of CH<sub>3</sub>CN in the sample was confirmed by <sup>1</sup>H NMR spectroscopy. Anal. Calc. for C44H56N4C0O2Na: C, 70.01; H, 7.48; N, 7.42. Found: C, 70.31; H, 7.53; N, 7.00%.

#### 2.6. Preparation of Na[Co<sup>III</sup>(ap<sup>iPr</sup>)<sub>2</sub>]

This complex was prepared using sodium-mercury amalgam beads (5% Na, 0.211 g, 0 459 mmol) and Co<sup>III</sup>(isq<sup>iPr</sup>)(ap<sup>iPr</sup>) (0.368 g, 0.449 mmol) in a procedure directly analogous to that described above for Na[Co<sup>III</sup>(ap<sup>Ph</sup>)<sub>2</sub>], to give Na[Co<sup>III</sup>(ap<sup>iPr</sup>)<sub>2</sub>] (0.351 g, 0.417 mmol, 93%). UV-vis (CH<sub>3</sub>CN) nm ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 290 (15 200), 535 (4430), 835 (9810). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN,  $\delta$ ): 52.45 (br s, 2H), 34.18 (br s 2H), 24.71 (br d, *J* = 8 Hz, 4H), 10.11

(br t, *J* = 8 Hz, 2H), 7.94 (br s, 18H), 1.43 (br s, 12H), -0.32 (br s, 18H), -10.42 (br s, 4H), -13.91 (br s, 12H).

#### 2.7. Preparation of $(Cp_2^*Co)[Co^{III}(ap^{iPr})_2]$

In an adaption of a literature procedure [46], Cp<sub>2</sub><sup>\*</sup>Co (0.040 g, 0.121 mmol) and Co<sup>III</sup>(isq<sup>iPr</sup>)(ap<sup>iPr</sup>) (0.098 g, 0.119 mmol) were combined in a five dram scintillation vial and dissolved in 10 mL CH<sub>3</sub>CN with vigorous stirring. The reaction mixture was fitted with a Teflon-lined cap and stirred for 3 h under N<sub>2</sub> to generate a dark-purple solution. The volume of the solution was reduced to 3 mL *in vacuo* and stored at  $-20 \,^{\circ}$ C for 48 h to yield (Cp<sub>2</sub><sup>\*</sup>Co)[Co<sup>III</sup>(ap<sup>iPr</sup>)<sub>2</sub>] (0.111 g, 0.0965 mmol, 80%) as violet microcrystals. Purity was determined by comparison of the UV-vis spectrum of the isolated product to that reported above for the sodium salt. Slow cooling of a saturated CH<sub>3</sub>CN solution afforded single crystals of (Cp<sub>2</sub><sup>\*</sup>Co)[Co<sup>III</sup>(ap<sup>iPr</sup>)<sub>2</sub>] suitable for study by X-ray diffraction.

#### 2.8. X-ray crystallography

Single crystals of Co<sup>III</sup>(ap<sup>Ph</sup>)(isq<sup>Ph</sup>) and (Cp<sub>2</sub><sup>\*</sup>Co)[Co<sup>III</sup>(ap<sup>iPr</sup>)<sub>2</sub>]·2CH<sub>3</sub>CN suitable for X-ray diffraction analysis were coated with Paratone N, suspended in a small fiber loop and placed in a cooled nitrogen gas stream at 173 K on a Bruker D8 APEX II CCD sealed tube diffractometer. Diffraction data for Co<sup>III</sup>(ap<sup>Ph</sup>)(isq<sup>Ph</sup>) was collected using graphite monochromated Cu K $\alpha$  ( $\lambda$  = 1.54178 Å) radiation. Data for (Cp<sup>\*</sup><sub>2</sub>Co)[Co<sup>III</sup>(ap<sup>iPr</sup>)<sub>2</sub>] 2CH<sub>3</sub>CN was obtained with graphite monochromated Mo K $\alpha$  ( $\lambda$  = 0.71073 Å) radiation. All other data collection procedures, data processing and programs were the same for both samples. Data were measured using a series of combinations of phi and omega scans with 10 s frame exposures and 0.5° frame widths. Data collection, indexing and initial cell refinements were all carried out using APEX II software [47].Frame integration and final cell refinements were done using SAINT software [48]. The final cell parameters were determined from least-squares refinement on 2789 reflections for Co<sup>III</sup>(ap<sup>Ph</sup>)(isq<sup>Ph</sup>) and 2968 reflections for (Cp<sup>\*</sup><sub>2</sub>Co)[Co<sup>III</sup>(ap<sup>iPr</sup>)<sub>2</sub>]·2CH<sub>3</sub>CN. The structures were solved using direct methods and difference Fourier techniques using the SHELXTL program package [49]. Hydrogen atoms were placed in their expected chemical positions using the HFIX command and were included in the final cycles of least-squares with isotropic Uii's related to the atoms ridden upon. All non-hydrogen atoms were refined anisotropically. Details of data collection and structure refinement are provided in Table 1.

#### 3. Results

#### 3.1. Preparation and characterization of Co<sup>III</sup>(*ap*<sup>Ar</sup>)(*isq*<sup>Ar</sup>) complexes

Charge neutral, four-coordinate cobalt complexes were obtained by modifications of literature procedures: via stoichiometric reaction of  $Co_2(CO)_8$  with  $ibq^{iPr}$  in toluene [41], or by addition of  $Co(ClO_4)_2 \cdot 6H_2O$  to  $H_2ap^{Ph}$  in basic MeOH (ibq<sup>iPr</sup> = 2,4-di-tert-butyl-6-(2,6-diisopropylphenylimino)benzoquinone;  $H_2ap^{Ph} = 2,4$ di-tert-butyl-6-(phenylamino)phenol; Scheme 1) [46]. A single crystal X-ray structure of the Ph derivative is provided in Fig. 1a. It contains cobalt bound to two coplanar ligands. The N-phenyl substituents are rotated out of the plane defined by the square planar cobalt core, with Co-N-C-C torsion angles of -107.63(19)° and 68.5(2)°. The cobalt lies on an inversion center making the two aminophenol-derived ligands crystallographically identical. The C–O, C–N and C–C bond distances shown in Fig. 1b exhibit a small but significant quinoid distortion that is in good agreement with the mean of those typical for  $[ap^{Ph}]^{2-}$  and  $[isq^{Ph}]^{\bullet-}$  [25,46], suggesting that the complex is best formulated as Co<sup>III</sup>(ap<sup>Ph</sup>)(isq<sup>Ph</sup>) (isq<sup>Ph</sup> = 2,4-di-tert-butyl-6-(phenylimino)semiquinonate). All of

#### Table 1

Crystallographic data and structure parameters for  $Co^{III}(ap^{Ph})(isq^{Ph})$  and  $(Cp_2^*Co)[Co^{III}(ap^{iPr})_2]$ -2CH<sub>3</sub>CN.

Complex	Co <sup>III</sup> (ap <sup>Ph</sup> )(isq <sup>Ph</sup> )	$(Cp_2^*Co)[Co^{III}(ap^{iPr})_2] \cdot 2CH_3CN$
Empirical formula	C40H50CoN2O2	C <sub>76</sub> H <sub>110</sub> Co <sub>2</sub> N <sub>4</sub> O <sub>2</sub>
Formula weight	649.75	1229.54
T (K)	173(2)	173(2)
Crystal system	triclinic	monoclinic
Space group	p <u>1</u>	P2 <sub>1</sub> /c
Unit cell dimensions		
a (Å)	5.8590(2)	9.3811(1)
b (Å)	11.7285(4)	17.0552(4)
<i>c</i> (Å)	13.6999(6)	21.9136(5)
α (°)	110.421(2)	90
β(°)	93.205(2)	92.785(2)
γ (°)	93.739(2)	90
V (Å <sup>3</sup> )	877.26(6)	3501.96(14)
Ζ	1	2
$D_{\text{calc}}$ (g cm <sup>-1</sup> )	1.230	1.166
Absorption coefficient (mm <sup>-1</sup> )	4.102	0.520
Crystal size (mm)	$0.37 \times 0.12 \times 0.10$	$0.36 \times 0.11 \times 0.10$
$\theta$ range for data collection (°)	4.29-66.89	1.51-27.15
Index ranges	$-6 \leqslant h \leqslant 6$	$-10 \leqslant h \leqslant 12$
	$-13 \leqslant k \leqslant 13$	$-18 \leqslant k \leqslant 21$
	$-15 \leqslant l \leqslant 12$	$-27 \leqslant l \leqslant 28$
Reflections collected/unique	5817/2624	23 193/7686
Goodness of fit on $F^2$	1.056	1.015
$R\left[I > 2\sigma(I)\right]$	0.0338	0.0542
$wR_2$ (all data)	0.0873	0.1579



Ar = phenyl (**Ph**) or 2,6-diisopropylphenyl (<sup>i</sup>**Pr**)

#### Scheme 1.

the bond distances are crystallographically indistinguishable from the previously reported structures of the <sup>i</sup>Pr analog [41], and a congener containing one *ortho*-triflouromethyl substituent on the *N*-aryl ring [46]. The solution magnetic moment of 2.18  $\mu_B$  for Co<sup>III</sup>(ap<sup>Ph</sup>)(isq<sup>Ph</sup>) at 25 °C in THF is in agreement with a previously reported value for the trifluoromethyl analog [46]. This was proposed to result from intramolecular antiferromagnetic coupling between the intermediate spin *S* = 1 cobalt(III) ion and one iminobenzoseminonate(1–) radical ligand to yield an *S* = ½ ground state.

#### 3.2. Preparation and characterization of $[Co^{III}(ap^{Ar})_2]^-$ complexes

Addition of 1 equiv Cp<sup>\*</sup><sub>2</sub>Co or Na (as 5% Na-Hg amalgam) to the blue Co<sup>III</sup>(ap<sup>Ar</sup>)(isq<sup>Ar</sup>) complexes in CH<sub>3</sub>CN under N<sub>2</sub> affords darkpurple products over hours at ambient temperature. Recrystallization of the <sup>i</sup>Pr derivative from CH<sub>3</sub>CN yielded single crystals of the cobaltocenium salt suitable for analysis by X-ray diffraction. As shown in Fig. 2a, the cobalt anion retains its square planar geometry. Two CH<sub>3</sub>CN solvent molecules per anion are located in the crystal structure but are not bound to cobalt. As in the neutral species. the ligands in the anion are crystallographically indistinguishable, and the *N*-aryl rings are nearly orthogonal to the plane defined by the square planar cobalt center, with Co-N-C-C torsion angles of -91.0(3)° and 82.8(3)°. However, the aromatic C-C bond distances (Fig. 2b) are identical within  $3\sigma$  (1.40 ± 0.01 Å), and the ligand C–O and C-N bond distances are elongated as compared to Co<sup>III</sup>(ap<sup>iPr</sup>)(isq<sup>iPr</sup>). The reduced complexes are therefore best formulated as  $[Co^{III}(ap^{Ar})_2]^-$  [25,41].

The  $[Co^{III}(ap^{Ar})_2]^-$  complexes exhibit diagnostic broad, paramagnetically shifted <sup>1</sup>H NMR spectra ( $\delta$  +59 to -24 ppm) at ambi-



**Fig. 1.** (a) Solid-state structure of  $Co^{III}(ap^{Ph})(isq^{Ph})$  drawn with 50% probability ellipsoids. Hydrogen atoms omitted for clarity. Selected bond angles (deg): O1-Co1-N1 85.58(6), O1-Co1-N1A 94.42(6). (b) Schematic of selected bond lengths (Å) in  $Co^{III}(ap^{Ph})(isq^{Ph})$ .



**Fig. 2.** (a) Solid-state structure of the anion in  $(Cp^*_2C0)[Co^{III}(ap^{iPr})_2]$ -2CH<sub>3</sub>CN shown with 50% probability ellipsoids. Hydrogen atoms, CH<sub>3</sub>CN solvate molecules and countercation omitted for clarity. Selected bond angles (deg): 01–Co1–N1 85.75(8), 01–Co1–N1A 94.25(8). (b) Schematic of selected bond lengths (Å) in  $[Co^{III}(ap^{iPr})_2]^-$ .

ent temperatures. The solution magnetic moment of 2.77  $\mu_B$  for  $[Co^{III}(ap^{Ph})_2]^-$  at 25 °C in CH<sub>3</sub>CN is consistent with two unpaired electrons as intermediate spin *S* = 1 cobalt(III) in a square planar ligand field. Cyclic voltammograms of both  $[Co^{III}(ap^{Ar})_2]^-$  complexes display two quasi-reversible 1e<sup>-</sup> redox couples, centered at -0.350 and -0.770 V versus Fc<sup>+</sup>/Fc for the Ph derivative and -0.339 and -0.809 V versus Fc<sup>+</sup>/Fc for the iPr congener (Fig. 3). Because the Co<sup>III</sup>(ap<sup>Ar</sup>)(isq<sup>Ar</sup>) complexes are not reduced by Cp<sub>2</sub>\*Fe (with a reduction potential of -0.48 V versus Fc<sup>+</sup>/Fc in CH<sub>3</sub>CN) [50], the redox event at more negative potential is assigned to interconversion of Co<sup>III</sup>(ap<sup>Ar</sup>)(isq<sup>Ar</sup>) and  $[Co^{III}(ap^{Ar})_2]^-$ .

# 3.3. Redox-active ligand-mediated Co-Cl bond-forming reactions at cobalt(III)

Addition of 1 equiv  $CCl_4$  or *N*-chlorosuccinimide (NCS) to the blue  $Co^{III}(ap^{Ar})(isq^{Ar})$  complexes in THF gives a color change to



**Fig. 3.** Cyclic voltammograms of 5 mM Na[Co<sup>III</sup>(ap<sup>Ph</sup>)<sub>2</sub>] (red) and Na[Co<sup>III</sup>(ap<sup>iPr</sup>)<sub>2</sub>] (black) in CH<sub>3</sub>CN containing 0.1 M [<sup>n</sup>Bu<sub>4</sub>N][PF<sub>6</sub>] at a 10 mm Pt electrode. Scan rate: 0.5 V s<sup>-1</sup>. Temperature: 25 °C.

blue-green in seconds at ambient temperature. Identical UV-vis spectra are obtained by exposure of  $CH_2Cl_2$  solutions of the  $Co^{III}(a-p^{Ar})$  (isq<sup>Ar</sup>) materials to ambient fluorescent light. The products of all the reactions are the previously reported square pyramidal  $Co^{III}Cl(isq^{Ar})_2$  species containing two iminobenzoseminonate(1–) radical ligands [40,41,51].

As illustrated in Scheme 2, quantitative conversion of Co<sup>III</sup>(ap<sup>Ar</sup>)(isq<sup>Ar</sup>) to Co<sup>III</sup>Cl(isq<sup>Ar</sup>)<sub>2</sub> products occurs by net addition of a chlorine radical. Because the Co-Cl bond-forming reactions are formally a reduction of Cl<sup>•</sup> to Cl<sup>-</sup>, they occur with 1e<sup>-</sup> oxidation of the Co<sup>III</sup>(ap)(isq) fragment, which is ligand centered. Addition of 1 equiv of the radical inhibitor 2,6-di-tert-butyl-4-methylphenol (BHT) to THF solutions containing Co<sup>III</sup>(ap<sup>Ar</sup>)(isq<sup>Ar</sup>) results in a significant decrease in its rate of reactions with CCl<sub>4</sub>: whereas addition of 5 equiv CCl<sub>4</sub> to Co<sup>III</sup>(ap<sup>Ph</sup>)(isq<sup>Ph</sup>) affords quantitative conversion to Co<sup>III</sup>Cl(isq<sup>Ph</sup>)<sub>2</sub> in seconds, with added BHT the same reaction takes hours to reach completion. The origin of this inhibition is apparently a reversible reaction of  $Co^{III}(ap^{Ph})(isq^{Ph})$  with BHT. Accordingly, addition of 1 equiv BHT to Co<sup>III</sup>(ap<sup>Ph</sup>)(isq<sup>Ph</sup>) in THF or CH<sub>3</sub>CN under N<sub>2</sub> affords an immediate color change from blue to olive green. The dark green color is slowly discharged on addition of CCl<sub>4</sub> to afford Co<sup>III</sup>Cl(isq<sup>Ph</sup>)<sub>2</sub>. The nature of the green species is still under investigation.

Reaction of CH<sub>3</sub>CN solutions of the [Co<sup>III</sup>(ap<sup>Ar</sup>)<sub>2</sub>]<sup>-</sup> complexes with 1 equiv 2,3,4,5,6,6-hexachloro-2,4-cyclohexadien-1-one, which serves as a source of electrophilic Cl<sup>+</sup> [52], immediately gives the same Co<sup>III</sup>Cl(isq<sup>Ar</sup>)<sub>2</sub> products. The reaction is quantitative and proceeds without the accumulation of any observable intermediates at 298 K, as evidenced by UV-vis spectroscopy. The rate of Co<sup>III</sup>Cl(isq<sup>Ph</sup>)<sub>2</sub> formation is unaffected by addition of 1 equiv BHT to the reaction mixture. Control reactions confirm that  $[Co^{III}(ap^{Ph})_2]^-$  does not react with added BHT. The bond-forming reaction with net Cl<sup>+</sup> is a 2e<sup>-</sup> redox process, because the electrophilic addition to  $[Co^{III}(ap^{Ar})_2]^-$  formally reduces  $Cl^+$  to Cl<sup>-</sup> (Scheme 2). However, the 2e<sup>-</sup> oxidation of the square planar cobalt(III) fragment is not metal-centered because the redox-active ligands each supply one electron for the reaction. Addition of 1 equiv CCl<sub>4</sub> to CH<sub>3</sub>CN solutions of  $[Co^{III}(ap^{Ph})_2]^-$  gives no reaction over days at ambient temperature, as evidenced by UV-vis spectroscopy.

#### 4. Discussion

The structural and electronic properties of the square planar cobalt electron-transfer pairs reported here are notable in several respects. First, our successful isolation of the Ph complexes demonstrates that, contrary to a previous report [40], steric bulk at the *ortho*-positions of the ligand *N*-aryl group is not a prerequisite for stabilization of a four-coordinate complex. This ability to



Scheme 2.

forego bulky ligands is essential for the development of reaction chemistry at these complexes because it affords substrates better access to the cobalt center.

Second, the X-ray crystallographic data for both the neutral  $S = \frac{1}{2}$  and anionic S = 1 complexes suggest that they are all best formulated as cobalt(III), so addition of an electron to Co<sup>III</sup>(ap<sup>Ar</sup>)(isq<sup>Ar</sup>) complexes occurs at a redox-active ligand. This proposed charge distribution agrees with a recent assignment of a closely related electron-transfer pair containing an ortho-trifluoromethyl substituent on the ligand *N*-aryl group [46]. It should be noted that an alternative electronic structure assignment has been proposed for the charge neutral  $S = \frac{1}{2}$  complexes. Poddel'sky and coworkers argue that these materials may be better formulated as  $Co^{II}(isq^{Ar})_2$ containing a low spin d<sup>7</sup> cobalt(II) ion ligated by two iminobenzoseminonate(1-) radicals that couple antiferromagnetically [25,41]. The basis for this claim are previously reported EPR spectra for two Co<sup>III</sup>(ap<sup>Ar</sup>)(isq<sup>Ar</sup>) complexes that exhibit features expected for an electron localized on the cobalt ion [41,46]. However, the cobalt(III) assignment proposed by Wieghardt and coworkers (described in Section 3.1 above), in fact invokes a metal-centered radical that is consistent with the observed EPR data [46]. Moreover, Poddel'sky and coworkers suggest that the unpaired electrons in an *S* = 1 square planar cobalt(III) center would occupy MOs that derive from the metal  $d_{x^2-v^2}$  and  $d_{z^2}$  orbitals [25], but this is incorrect. Calculations on a very closely related system clearly show that the unpaired electrons are in orbitals of  $b_{2g}$  and  $b_{3g}$  symmetry that are primarily of metal  $d_{xz}$  and  $d_{yz}$  parentage [46]. In this scheme, overlap with the aminophenolate  $\pi$ -donor MOs raises the energy of the metal  $b_{2g}$  and  $b_{3g}$  orbitals and provides a pathway for facile intramolecular ligand-to-metal charge transfer. Because the ligand metrical parameters for Co<sup>III</sup>(ap<sup>Ph</sup>)(isq<sup>Ph</sup>) are indistinguishable from those of the previously reported <sup>i</sup>Pr congener [41], we suggest that all of these complexes are better described as Co<sup>III</sup>(ap<sup>Ar</sup>)(isq<sup>Ar</sup>) in the ground state.

Finally, the ability of the redox-active ligands to accept and store electrons facilitates the preparation of coordinatively-unsaturated cobalt(III) complexes that can deliver multiple electrons at modest reduction potentials. This forms a basis for oxidative bond-forming reactions with chlorine electrophiles at cobalt(III) centers. Identical Co<sup>III</sup>Cl(isq<sup>Ar</sup>)<sub>2</sub> products are obtained from reactions of Co<sup>III</sup>(ap<sup>Ar</sup>)(isq<sup>Ar</sup>) with sources of a net Cl<sup>•</sup>(via a 1e<sup>-</sup> reaction) or by addition of electrophilic  $Cl^+$  to  $[Co^{III}(ap^{Ar})_2]^-$  (via a 2e<sup>-</sup> process). Both the radical addition and electrophilic addition reactions are formally oxidations of the metal fragments, but neither oxidizes the cobalt(III) center because the redox-active ligand manifold acts as a reservoir for electrons. As described above, facile transfer of electrons from the ligand to the metal derives from a high degree of covalency in the metal-ligand bonding that is a result of the close match of the frontier orbital energies of cobalt(III) and the aminophenol-derived ligands [46]. In this way, the ligandmediated Co-Cl bond-forming reactions reported herein are very similar to recent reports of pseudo-oxidative addition reactions of X<sub>2</sub> to redox-active ligand complexes that rely on ligand centered changes in oxidation state to accommodate the transformation



without a formal change in oxidation state at the metal center [27,30,31,37].

Two possible mechanistic pathways were considered for the electrophilic addition reactions at [Co<sup>III</sup>(ap<sup>Ar</sup>)<sub>2</sub>]<sup>-</sup>: (a) direct nucleophilic attack of the cobalt(III) center on the Cl<sup>+</sup> electrophile, resulting in a 2e<sup>-</sup> oxidation of the metal fragment; (b) initial outer-sphere 1e<sup>-</sup> transfer (ET) to generate the radical pair, Co<sup>III</sup>(ap<sup>Ar</sup>)(isq<sup>Ar</sup>) and Cl<sup>•</sup>, followed by coupling with bond formation (Scheme 3). The facile reactions of Co<sup>III</sup>(ap<sup>Ar</sup>)(isq<sup>Ar</sup>) with sources of chlorine radical Cl<sup>•</sup> to generate Co<sup>III</sup>Cl(isq<sup>Ar</sup>)<sub>2</sub> demonstrate that the stepwise mechanism b is viable, but experiments performed in the presence of the radical inhibitor support mechanism a. Namely, the reactions of Co<sup>III</sup>(ap<sup>Ph</sup>)(isq<sup>Ph</sup>) with CCl<sub>4</sub> is retarded by addition of BHT, but the reaction of [Co<sup>III</sup>(ap<sup>Ph</sup>)<sub>2</sub>]<sup>-</sup> with 2,3,4,5,6,6-hexachloro-2,4-cyclohexadien-1-one is unaffected with added BHT. Although the mechanism of this radical inhibition is ill defined, control reactions demonstrate that Co<sup>III</sup>(ap<sup>Ph</sup>)(isq<sup>Ph</sup>) reacts rapidly with BHT under the reaction conditions. Accordingly, mechanisms that invoke formation of a long-lived Co<sup>III</sup>(ap<sup>Ph</sup>)(isq<sup>Ph</sup>) intermediate in the reaction of  $[Co^{III}(ap^{Ph})_2]^-$  with net  $Cl^+$  (including mechanism b) can likely be ruled out.

In sum, the reaction chemistry presented herein suggest that the  $S = \frac{1}{2} \operatorname{Co}^{III}(ap^{Ar})(isq^{Ar})$  complexes behave as efficient radical scavengers but the [Co<sup>III</sup>(ap<sup>Ar</sup>)<sub>2</sub>]<sup>-</sup> complexes react as 2e<sup>-</sup> nucleophiles and do not react efficiently with sources of net Cl<sup>•</sup>. This is somewhat surprising given the S = 1 diradical ground state of the anionic complexes. The reactivity patterns of the [Co<sup>III</sup>(ap<sup>Ar</sup>)<sub>2</sub>]<sup>-</sup> species are therefore more reminiscent of the well-known cobaloxime(I) complexes that are closed-shell d<sup>8</sup> nucleophiles [21]. However, the  $[Co^{III}(ap^{Ar})_2]^-$  complexes reported here are not strong outer-sphere reductants, being oxidized at potentials 200–400 mV less negative than most cobalt(I) materials [21,53–55]. Control of 1e<sup>-</sup> versus 2e<sup>-</sup> reactivity derives from management of ligand electron inventory. This ability to modulate the redox selectivity of the metal center to achieve 2e<sup>-</sup> reactions under gentle conditions is predicated entirely on the redox-activity of the ligands, and is a key design feature for the development of naturally abundant transition metals as catalysts for selective bond-making and bond-breaking reactions.

#### 5. Conclusions

The redox-activity of amidophenolate ligands facilitates selective multielectron reactions at square planar cobalt(III) centers. The cobalt(III) complexes are not strong outer-sphere reductants. Instead bond-forming reactions with substrates occur at the metal center through on-demand, intramolecular delivery of redox equivalents from ligand-based electron reservoirs. Modulation of the ligand oxidation state affords a unique mechanism to select for 2e<sup>-</sup> redox reactivity over potentially competing 1e<sup>-</sup> pathways. Future studies in this area are focused on exploiting this ligandmediated 2e<sup>-</sup> redox capacity for the development of new multielectron catalysis cycles for selective bond-making and bondbreaking transformations of small-molecule organic substrates.

#### Supplementary data

CCDC 730032 and 730033 contain the supplementary crystallographic data for Co<sup>III</sup>(ap<sup>Ph</sup>)(isq<sup>Ph</sup>) and (Cp <sub>2</sub>Co)[Co<sup>III</sup>(ap<sup>iPr</sup>)<sub>2</sub>]. 2CH<sub>3</sub>CN. These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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