Dalton Transactions

Cite this: Dalton Trans., 2012, 41, 3562



Tuning redox potentials of bis(imino)pyridine cobalt complexes: an experimental and theoretical study involving solvent and ligand effects[†]

C. Moyses Araujo,*^a Mark D. Doherty,*^b Steven J. Konezny,^a Oana R. Luca,^a Alex Usyatinsky,^b Hans Grade,^b Emil Lobkovsky,^c Grigorii L. Soloveichik,*^b Robert H. Crabtree^a and Victor S. Batista*^a

Received 16th November 2011, Accepted 14th January 2012 DOI: 10.1039/c2dt12195f

The structure and electrochemical properties of a series of bis(imino)pyridine Co^{II} complexes (NNN) CoX₂ and [(NNN)₂Co][PF₆]₂ (NNN = 2,6-bis[1-(4-R-phenylimino)ethyl]pyridine, with R = CN, CF₃, H, CH₃, OCH₃, N(CH₃)₂; NNN = 2,6-bis[1-(2,6-(iPr)₂-phenylimino)ethyl]pyridine and X = Cl, Br) were studied using a combination of electrochemical and theoretical methods. Cyclic voltammetry measurements and DFT/B3LYP calculations suggest that in solution (NNN)CoCl₂ complexes exist in equilibrium with disproportionation products $[(NNN)_2Co]^{2+} [CoCL_1]^{2-}$ with the position of the equilibrium heavily influenced by both the solvent polarity and the steric and electronic properties of the bis(imino)pyridine ligands. In strong polar solvents (e.g., CH₃CN or H₂O) or with electron donating substituents ($R = OCH_3$ or $N(CH_3)_2$) the equilibrium is shifted and only oxidation of the charged products $[(NNN)_2Co]^{2+}$ and $[CoCl_4]^{2-}$ is observed. Conversely, in nonpolar organic solvents such as CH₂Cl₂ or with electron withdrawing substituents (R = CN or CF₃), disproportionation is suppressed and oxidation of the (NNN)CoCl₂ complexes leads to 18e⁻ Co^{III} complexes stabilized by coordination of a solvent moiety. In addition, the [(NNN)2Co][PF6]2 complexes exhibit reversible Co^{II/III} oxidation potentials that are strongly dependent on the electron withdrawing/donating nature of the N-aryl substituents, spanning nearly 750 mV in acetonitrile. The resulting insight on the regulation of redox properties of a series of bis(imino)pyridine cobalt(II) complexes should be particularly valuable to tune suitable conditions for reactivity.

Introduction

Understanding the redox properties of earth-abundant transition metal complexes is a challenge of great current interest, central to a wide range of applications in electrocatalysis.¹ An important goal is to establish fundamental principles to tune redox potentials and catalytic activity by modifying the ligands, or solvent conditions. In particular, there is a lot of current interest in the development of catalysts for direct organic proton exchange membrane (PEM) fuel cells where oxidation of an organic fuel

^bGeneral Electric Global Research, 1 Research Circle, Niskayuna,

NY 12309. E-mail: doherty@ge.com, soloveichik@ge.com ^cDepartment of Chemistry and Chemical Biology, Cornell University, provides the protons and electrons necessary to drive O_2 reduction to water.² However, the development of electrocatalysts capable of oxidizing organic fuels such as isopropanol or cyclohexane^{2c,d} is hindered by a lack of understanding of the conditions that regulate the redox properties of earth-abundant transition metal complexes. This paper explores a series of Co complexes with bis(imino)pyridine ligands (Chart 1), with emphasis on the analysis of their electrochemical properties as influenced by the solvent, or ligand substituents with electron withdrawing/donating properties.

There is a sizable body of work documenting the utility of various transition metal complexes of bis(imino)pyridine ligands. Independently, Brookhart and Gibson have demonstrated that such complexes, particularly those containing *N*-aryl substituents with halides of iron(π) and cobalt(π), upon activation with methylaluminoxane (MAO) serve as precatalysts for α -olefin homopolymerization,³ dimerization,⁴ oligomerization^{3c,4b,5} and co-polymerization with polar monomers.^{3c,f} Derivatization of the *N*-aryl groups resulted in numerous substitution patterns^{3g} and established the role that steric bulk at the *ortho* positions plays in determining catalysts, polymer molecular weight.^{3b,d,e,h,i} Further studies have focused on preparing reduced iron or cobalt alkyl complexes, particularly methyl

^aDepartment of Chemistry, Yale University, New Haven, CT 06520. E-mail: carlos.araujo@yale.edu, victor.batista@yale.edu

Ithaca, NY 14853

[†] Electronic supplementary information (ESI) available: The supporting information includes X-ray crystallographic files (CIF) for $[(1f)_2Co]$ [CoCl₄] and 2g, a table containing the electrochemical reduction potentials for compounds 2a–d, f, g and 3a, overlaid CV's of 2f and 4f in dichloromethane, ¹H NMR spectra of paramagnetic complexes, gas phase energies, Gibbs free energy upon solvation, and coordinates of the optimized computational structural models. CCDC 854625 (2g) and 854626 ([(1f)_2Co][CoCl_4]). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt12195f



Chart 1 NNN ligands 1a-g, (NNN)Co^{II}X₂ complexes 2a-d, f, g and 3a, and [(NNN)₂Co^{II}][PF₆]₂ complexes 4b-g examined in this work.

complexes, as models of the propagating species present in the olefin polymerization systems described above.⁶ Interest in these reduced compounds has grown to include detailed investigations into the electronic structure, redox properties and reactivity of the iron and cobalt complexes and has established the redox activity of these ligands.^{6e,7}

More recently, several new applications of these bis(imino) pyridine transition metal complexes have been reported including a report by Chirik and co-workers in which they demonstrated C-H bond activation via thermolysis and photolysis of bis(imino) pyridine cobalt azide complexes.⁸ In addition, highly efficient catalytic olefin hydrogenation has been achieved with bis(imino)pyridine iron bis(dinitrogen) complexes.⁹ Related bis (imino)pyridine iron(II) triflate complexes have also shown some activity in the oxidation of cyclohexane with H2O2 to cyclohexanol and cyclohexanone, presumably through a Fenton type free radical mechanism.¹⁰ Therefore, it is natural to expect that a wide range of applications could benefit from fundamental understanding of the dependence of the redox properties of these metal pincer complexes on the nature of the ligands, and on solvent conditions. While previous studies have analyzed the electronic structures associated with various possible oxidation states of cobalt bis(imino)pyridine complexes,^{7c,e} a systematic study of the regulation of redox potentials as influenced by changes in the ligand framework or solvent environment is lacking.

In that context we report here an experimental and theoretical examination of the influence of electrostatic, steric and electronic factors on the redox potentials of a series of $Co(NNN)X_2$ and $[(NNN)_2Co][PF_6]_2$ (NNN is a tridentate bis(imino)pyridine ligand) complexes as shown in Chart 1. We examined ligands with different electron withdrawing or donating substituents and solvents of different polarity ranging from nonpolar to polar protic solvents (*e.g.* CH₂Cl₂, CH₃CN and H₂O). While many studies of these Co^{II} complexes have dealt with their reduction and subsequent chemical reactivity,^{6b,7b,c,8} our interest lies in ultimately being able to oxidize liquid organic fuels for energy storage purposes.^{2a} Therefore we have chosen to focus on the Co^{II/III} redox couple and factors that contribute to one's ability to tune the oxidation potentials of these transition metal complexes.

Results and discussion

Synthesis and electrochemical characterization of (NNN)CoX $_2$ complexes

The (NNN)CoX₂ complexes were prepared in accordance with literature procedures for similar compounds by reaction of equal parts ligand and CoX₂ and the compounds examined in this study are shown in Chart 1 (see Experimental section for details). As expected, complexes **2a–d**, **f** and **g** are high spin and display paramagnetically broadened ¹H NMR spectra, with solution magnetic moments of 3.5–5.3 μ_B at 22 °C (Evans NMR method¹¹), which is consistent with a high spin d⁷ Co^{II} center.^{3d,12}

One method of characterizing the redox activity of bis(imino) pyridine ligands is X-ray crystallography where reduced ligands exhibit bond distortions from neutral ligands. Black needle shaped single crystals suitable for single-crystal X-ray diffraction were obtained by vapor diffusion of diethyl ether into a saturated acetonitrile solution of 2g. The molecular structure is shown in Fig. 1 while the collection and refinement parameters are collected in Table 6. Compound 2g exhibits approximate C_s symmetry about the plane containing the cobalt, pyridyl nitrogen and two chlorine atoms. The geometry around the cobalt is best described as distorted trigonal bipyramidal with the equatorial plane formed by the pyridyl nitrogen and two chlorine atoms with N_{pvridvl}-Co-Cl angles of 130.79(5)° and 112.91(5)° and a Cl-Co-Cl angle of 116.23(3)°. Two axial Co-Nimine bonds fill out the cobalt(II) coordination sphere with an angle of 150.12 (7)°. A bond distance of 2.0344(18) Å for the Co– $N_{pyridyl}$ of 2gis consistent with other para substituted complexes such as those reported for $2c^{13}$ and $2d^{14}$ and shorter than those reported for *ortho* substituted complexes such as 2a.^{3d} As with $2c^{13}$ and $2d^{14}$ the Co-N_{imine} bonds are slightly longer at 2.2093(18) and 2.2289(18) Å, while the Cimine-Nimine distances of 1.289(3) and 1.288(3) Å are typical for C=N double bonds of neutral bis (imino)pyridine ligands coordinated to first row transition metals.^{7e} In addition, C_{imine} - C_{py} bond lengths of 1.488(3) and 1.489(3) Å and C_{py} - N_{py} bond lengths of 1.345(3) and 1.339(3) Å are consistent with the assignment of a neutral bis(imino)pyridine ligand.^{7e} The N-aryl rings of 2g exhibit dihedral angles of



Fig. 1 ORTEP diagram of 2g (40% probability ellipsoids). Hydrogen atoms have been removed for clarity. Selected bond distances (Å) and angles (°): Co(1)–N(1) 2.2093(18), Co(1)–N(2) 2.0344(18), Co(1)–N(3) 2.2289(18), Co(1)–Cl(1) 2.2733(6), Co(1)–Cl(2) 2.2562(6), N(1)–C(2) 1.289(3), C (2)–C(3) 1.488(3), C(3)–N(2) 1.345(3), N(2)–C(7) 1.339(3), C(7)–C(8) 1.489(3), N(3)–C(8) 1.288(2), N(2)–Co(1)–N(1) 75.03(7), N(2)–Co(1)–N(3) 75.55(3), (N1)–Co(1)–N(3) 150.11(7), N(2)–Co(1)–Cl(2) 130.79(5), N(1)–Co(1)–Cl(2) 94.46(5), N(3)–Co(1)–Cl(2) 100.75(5), N(2)–Co(1)–Cl(1) 112.91(5), N(1)–Co(1)–Cl(1) 99.53(5), N(3)–Co(1)–Cl(1) 96.58(5), Cl(2)–Co(1)–Cl(1) 116.23(3).

Table 1 Electrochemical data for **2a–d**, **f**, **g** and **3a** in acetonitrile and dichloromethane (0.1 M [Bu₄N][BF₄] supporting electrolyte) *vs*. $Cp_2Fe^{0/+}$ at 0.1 V s⁻¹ at a glassy carbon working electrode (d = 3 mm)

	CH ₃ CN		CH_2Cl_2			
	$\operatorname{Co}^{\operatorname{II/III}}(\operatorname{V})^{a}$	$\Delta E (\mathrm{mV})$	$\operatorname{Co}^{\operatorname{II/III}}(\operatorname{V})^{a}$	$\Delta E (\mathrm{mV})$	$\Delta \text{Co}^{\text{II/III}}(\text{V})^{b}$	
2a	+0.56	120	+0.70	152	+0.14	
3a	$+0.35^{\circ}$	N/A	$+0.69^{c}$	N/A	+0.34	
2b	$+0.44^{c}$	N/A	$+0.82^{c}$	N/A	+0.38	
2c	$+0.40^{\circ}$	N/A	$+0.81^{c}$	N/A	+0.41	
2d	+0.11	80	$+0.67^{c}$	N/A	+0.56	
2f	-0.01	70	-0.04	120	-0.03	
2g	-0.19	60	-0.21	75	-0.02	
<i>a</i> Ha	lf wave poten	tials, $E_{1/2}$,	unless otherw	ise indicated	$b \Delta Co^{II/III} =$	

Co^{II/III}_{DCM}-Co^{II/III}_{MeCN}, c Irreversible oxidation, E_{PA} .

113.1 and 56.8° relative to the plane of the pyridine ring, which is consistent with those observed for other complexes lacking steric bulk at the *ortho* positions of the *N*-aryl ring 2d.¹⁴

Cyclic voltammograms of 1 mM solutions of **2a–d**, **f** and **g** and **3a** exhibit $Co^{II/III}$ oxidation waves between -0.25 and +1.0 V vs. $Cp_2Fe^{0/+}$ in acetonitrile or dichloromethane (see Table 1). Replacing the chloride ligands with bromide ligands results in a Co^{II} center that is more easily oxidized (**2a** vs. **3a**), however, whereas **2a** exhibits a quasi-reversible oxidation wave in both solvents, oxidation of **3a** is electrochemically reversible in

acetonitrile but irreversible in dichloromethane. Except for **2f** and **2g**, changing from acetonitrile to dichloromethane induces an anodic shift in the Co^{II/III} oxidation potentials of +0.05 to +0.55 V, which we attribute to decreased stabilization of the developing cationic charge upon oxidation in a low polarity solvent such as dichloromethane. The slight cathodic shift of less than 50 mV observed for **2f** and **2g** upon moving to dichloromethane was unexpected and prompted a more detailed investigation.

Analysis of 2g by matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry from an HBMacetonitrile matrix (see Experimental section for details) revealed the presence of a species (ca. 15%) with m/z = 857 in addition to the expected m/z = 493 corresponding to $[2g \neg Cl]^+$. This minor component, which does not contain any chlorine atoms, corresponds instead to $[(1g)_2Co]^+$. Similar analysis of 2f showed the expected $[2\mathbf{f} \neg \mathrm{Cl}]^+$ (m/z = 467) ions as well as the high m/zspecies with m/z = 805 corresponding to $[(1f)_2Co]^+$, which in this case is the major component at ca. 60%. Mass spectrometry analysis of 2d showed only a minor amount of the high m/zspecies ($<5\% m/z = 685 [(1d)_2Co]^+$, 95% $m/z = 407 [2d \neg Cl]^+$) whereas 2c and 2b contained only the expected $[2c \neg Cl]^+$ (m/z)= 543) and $[2b \neg Cl]^+$ (m/z = 457), respectively. As expected, complexes 2a and 3a exhibited only the anticipated $[2a \neg Cl]^{\dagger}$ (m/z = 575) and $[3a \neg C1]^+$ (m/z = 621) ions by mass spectrometry as a result of the steric bulk imparted by the ortho *i*-propyl groups that prohibit formation of any bis-ligand species.



Fig. 2 Cyclic voltammograms of 1 mM solutions of (a) **2f** (—) and **4f** (- -) and (b) $[Bu_4N]_2[CoCl_4]$ (- -), **2f** (—) and $CoCl_2$ (— · ·) in acetonitrile with 0.1 M $[Bu_4N][BF_4]$ as supporting electrolyte and v = 0.1 Vs⁻¹ at a glassy carbon working electrode (d = 3 mm).

Close examination of the cyclic voltammogram (CV) of 2f recorded in acetonitrile and comparison with literature data for $4\mathbf{f}^{7e}$ and the CV of an authentic sample of $4\mathbf{f}$ (vide infra) shown in Fig. 2a indicates the presence of the $[(1f)_2Co]^{2+}$ dication in acetonitrile solutions of 2f. In addition, anodic scans to higher potential reveal two electrochemically irreversible oxidations at +0.68 V and +1.17 V vs. $Cp_2Fe^{0/+}$. Given the reaction stoichiometry of 1 : 1 1f: CoCl₂, the presence of a $[(1f)_2Co]^{2+}$ dication suggests either outer sphere chloride anions and excess CoCl₂ or the formation of a tetrachlorocobaltate dianion, $[CoCl_4]^{2-}$ (eqn (1)). A cyclic voltammogram of [Bu₄N]₂[CoCl₄] is shown in Fig. 2b overlaid with a CV of 2f in acetonitrile, and shows two electrochemically irreversible oxidation waves at +0.72 V and +1.19 V vs. $Cp_2Fe^{0/+}$, which agrees with the assignment of a $[CoCl_4]^{2-}$ dianion. On the other hand, $CoCl_2$ (— · · in Fig. 2b) exhibits a sharp electrochemically irreversible oxidation at +1.54 V vs. $Cp_2Fe^{0/+}$ under similar conditions. Additional evidence for the formation of $[(1f)_2Co][CoCl_4]$ in acetonitrile solutions of 2fcan be gleaned from a comparison of the peak current densities

for the Co^{II/III} oxidation wave at +0.03 V. For a one electron transfer process with equimolar concentrations of **4f** and **2f**, the ratio of peak current densities, $i_{4f}/i_{2f} = 1$. Ligand redistribution of a 1 mM solution of **2f** to form 0.5 mM [(**1f**)₂Co][CoCl₄] and comparison with a 1 mM solution of **4f** should give a ratio of peak current densities, $i_{4f}/i_{2f} = 2$. As illustrated in Fig. 2a, the ratio of peak current densities for 1 mM solutions of **4f** ($i_{PA} = 0.273 \text{ mA cm}^{-2}$) and **2f** ($i_{PA} = 0.135 \text{ mA cm}^{-2}$), i_{4f}/i_{2f} is equal to 2 and is therefore most consistent with ligand disproportionation of **2f** to form [(**1f**)₂Co][CoCl₄] in acetonitrile solution. A similar comparison of the CV of **2f** and **4f** in dichloromethane with 0.1 M [Bu₄N][BF₄] as the supporting electrolyte indicates this ligand disproportionation reaction also occurs in dichloromethane (see Fig. S1 in ESI⁺).

$$2(\text{NNN})\text{CoCl}_2 \rightleftharpoons [(\text{NNN})_2\text{Co}][\text{CoCl}_4]$$
(1)

Attempts to obtain single crystals of 2f by vapor diffusion of diethyl ether into a concentrated acetonitrile solution of 2f resulted instead in red plate like crystals of the ion pair comprised of $[(1f)_2Co]^{2+}$ and $[CoCl_4]^{2-}$, the molecular structure of which is shown in Fig. 3 (see Table 6 for crystallographic data). Tetrahalometallate salts of $[(NNN)_2M]^{n+}$ have been observed previously for iron(II) complexes bearing NNN ligands that lack significant steric bulk in the 2,6 positions of the N-aryl rings (e.g. 2,2';6',2"-terpyridine¹⁵ or 2,6-bis(2-(2-fluorophenylimino) ethyl)pyridine¹⁶). As expected the [CoCl₄]²⁻ anion exhibits a slightly distorted tetrahedral geometry with nearly uniform Co-Cl bond lengths of 2.2759(10)-2.2867(10) Å and Cl-Co-Cl angles ranging from 105.74(4)° to 113.43(4)°. Although the $[(\mathbf{1f})_2 \mathrm{Co}]^{2^+}$ cation has been structurally characterized previously as the hexafluorophosphate salt there are some significant differences in the metrical parameters of the cations in $4\mathbf{f}^{7e}$ and $[(1f)_2Co][CoCl_4]$ reported here as shown in Table 2. Both structures display distorted octahedral geometries with two meridionally coordinated bis(imino)pyridine ligands with mutually trans pyridine nitrogens. The C_{py}-N_{py}, C_{imine}-C_{py} and C_{imine}-N_{imine} bond distances of the ligands in $[(1f)_2Co][CoCl_4]$ and 4f do not show any substantial deviations from one another and are in agreement with the previous assignment of neutral bis(imino) pyridine ligands in the dication.^{7e} However, the bis(imino)pyridine ligands are bound tighter in [(1f)₂Co][CoCl₄] than in 4f. One of the Co-N_{pv} and three of the Co-N_{imine} distances are between 0.03 and 0.08 Å shorter in [(1f)₂Co][CoCl₄] (1.913(2), 1.996(2), 1.989(2) and 2.135(2) Å) than in 4f (1.991(2), 2.009 (2), 2.021(2) and 2.165(2) Å) while the remaining Co- N_{py} distance is equal.

Whereas the intraligand N_{py} -Co- N_{imine} and N_{imine} -Co- N_{imine} angles are in general only slightly larger (0.3 to 0.6°) in [(1f)₂Co][CoCl₄] than in 4f, important differences between the structures of these two cations are apparent upon comparison of the interligand N_{py} -Co- N_{py} , N_{py} -Co- N_{imine} and N_{imine} -Co- N_{imine} angles. The N_{py} -Co- N_{py} angle in [(1f)₂Co][CoCl₄] (175.39(10)°) is farther from linearity than in 4f (178.48(8)°). The average interligand N_{py} -Co- N_{imine} angles for 4f and [(1f)₂Co][CoCl₄] are 100.97(8)° and 100.73(10)°, respectively, however in 4f each ligand is tilted slightly toward the Co- N_{py} bond of the other ligand and contains one large angle (N(2)-Co (1)-N(6) at 103.46(8)° and N(5)-Co(1)-N(3) at 100.91(8)°) and



Fig. 3 ORTEP diagram of $[(1f)_2Co][CoCl_4]$ (40% probability ellipsoids). Hydrogen atoms and a molecule of acetonitrile have been removed for clarity. Metrical parameters for the cation are collected in Table 2 while selected bond distances (Å) and angles (°) for the anion follow: Co(2)–Cl(1) 2.2792(10), Co(2)–Cl(2) 2.2759(10), Co(2)–Cl(3) 2.2774(9), Co(2)–Cl(4) 2.2867(10), Cl(2)–Co(2)–Cl(3) 112.57(4), Cl(2)–Co(2)–Cl(1) 109.72(4), Cl (3)–Co(2)–Cl(1) 106.79(4), Cl(2)–Co(2)–Cl(4) 105.74(4), Cl(3)–Co(2)–Cl(4) 108.70(4), Cl(1)–Co(2)–Cl(4) 113.43(4).

one small angle (N(2)-Co(1)-N(4) at 100.97(8)° and N(5)-Co (1)–N(1) at 98.52(8)°). One ligand of $[(1f)_2Co][CoCl_4]$ is tilted more strongly toward the Co-N_{py} bond of the other ligand (N (2)-Co(1)-N(4) at 106.61(10)° and N(2)-Co(1)-N(6) at 97.20 $(10)^{\circ}$) while the imine nitrogens of the other ligand are virtually equidistant from N(5) (N(5)–Co(1)–N(1) at 99.92(10)° and N (5)-Co(1)-N(3) at 99.18(10)°). Finally, the N_{imine}-Co-N_{imine} angles show the most significant structural deviations between 4f and [(1f)₂Co][CoCl₄]. As with the N_{pv}-Co-N_{imine} angles, there are two large (N(1)-Co(1)-N(6) at 97.79(8)° and N(3)-Co(1)-N (4) at 97.11(8)°) and two small (N(1)-Co(1)-N(4) at 87.60(8)° and N(3)-Co(1)-N(6) at 85.73(8)°) N_{imine}-Co-N_{imine} angles in **4f**. These angles in $[(1f)_2Co][CoCl_4]$ differ from those in **4f** by 5.4° to 5.9° and are much closer to right angles (N(1)-Co(1)-N (4) at 93.47(9)°, N(1)–Co(1)–N(6) at 92.06(10)°, N(3)–Co(1)–N (4) at 91.21(9)° and N(3)-Co(1)-N(6) at 91.11(9)°) suggesting that the two bis(imino)pyridine ligands in $[(1f)_2Co][CoCl_4]$ are virtually orthogonal to one another and that the distortion from an ideal octahedral geometry is less pronounced than in 4f.

Synthesis and electrochemical characterization of [(NNN)₂Co] [PF₆]₂ complexes

In order to fully evaluate the contribution of the $[(NNN)_2Co]^{2+}$ ions to the electrochemical behavior of **2b–d**, **f** and **g**, the

corresponding [(NNN)2Co][PF6]2 complexes were prepared using the method reported by de Bruin^{7e} for **4f** and are shown in Chart 1. The addition of two equivalents of ligand to CoCl₂ in methanol followed by excess ammonium hexafluorophosphate precipitates the product, which was collected by filtration, washed with cold methanol and air dried. As with 2a-d, f and g these cobalt(II) complexes exhibit paramagnetically shifted ¹H NMR spectra, however the solution magnetic moments at 22 °C for 4b-g are considerably smaller than those measured for the dichloride complexes and increase with decreasing electron donating ability from 2.1 μ_B for 4g to 3.5 μ_B for 4b. These data are consistent with a low spin d⁷ Co^{II} center with $S = \frac{1}{2}$ as previously observed for $4f^{7e}$ except for 4b, which is better described as having a high spin $S = \frac{3}{2}$ ground state. This change in spin state is most likely the result of the strongly electron withdrawing 4-CN substituent in 4b ($\sigma_p = 0.66$), which serves to stabilize the e_g (M–L σ^*) orbitals and decrease the ligand field splitting. As will be discussed in more detail later, this also causes the half wave potential of 4b to shift to more positive potentials relative to 4c-g as it becomes more difficult to remove an electron from the stabilized σ^* orbital.

As evidenced by the cyclic voltammograms shown in Fig. 4 and the data collected in Table 3, complexes **4b–g** exhibit much simpler redox chemistry. Each complex shows a reversible one-electron metal centered oxidation $(Co^{II/III})$ and one (**4c** and **e**) or

two (4b, d, f and g) reversible one-electron reductions. In accordance with previous electrochemical assignments for $4f^{7e}$,

Table 2 Selected bond distances (Å) and bond angles (°) for $[(1f)_2Co]$ [CoCl₄] and **4f** and the minimum energy structure of **4f** obtained in the gas phase and at the B3LYP/lacvp-6-31g level of theory

	$[(\mathbf{1f})_2 \text{Co}][\text{CoCl}_4]$	$4\mathbf{f}^{7e}$	4f(DFT)
	Bond distance		
	Co-N _{pv}		
Co(1) - N(2)	1.852(2)	1.852(2)	1.899
Co(1) - N(5)	1.913(2)	1.991(2)	1.929
	Co-N _{imine}		
Co(1) - N(1)	1.996(2)	2.009(2)	2.146
Co(1) - N(3)	1.989(2)	2.021(2)	2.149
Co(1) - N(4)	2.191(2)	2.145(2)	2.236
Co(1) - N(6)	2.135(2)	2.165(2)	2.228
	C _{imine} -N _{imine}		
N(1)-C(2)	1.297(4)	1.298(3)	1.311
N(3) - C(8)	1.300(4)	1.305(3)	1.311
N(4) - C(25)	1.294(4)	1.289(3)	1.306
N(6)–N(31)	1.287(4)	1.289(3)	1.307
	C _{imine} –Ć _{pv}		
C(2)-C(3)	1.469(4)	1.472(4)	1.476
C(7) - C(8)	1.476(4)	1.476(3)	1.477
C(25)–C(26)	1.487(4)	1.487(3)	1.482
C(30) - C(31)	1.487(4)	1.485(3)	1.481
	C _{pv} -N _{pv}		
N(2)-C(3)	1.349(4)	1.347(3)	1.356
N(2) - C(7)	1.347(4)	1.350(3)	1.358
N(5)-C(26)	1.348(4)	1.347(3)	1.359
N(5)-C(30)	1.346(4)	1.350(3)	1.359

Bond Angle

	Dona / High	·			
N _{nv} -Co-N _{nv} (trans)					
N(2)-Co(1)-N(5)	175.39(10)	178.48(8)	179.30		
	N _{imine} -Co-N _{imine}	(trans)			
N(1)-Co(1)-N(3)	160.88(10)	160.56(8)	156.22		
N(4)-Co(1)-N(6)	156.14(9)	155.54(8)	158.42		
	N _{nv} -Co-N _{imine} (cis-in	traligand)			
N(2)-Co(1)-N(1)	80.04(10)	80.42(8)	77.99		
N(2)-Co(1)-N(3)	80.86(10)	80.42(8)	78.27		
N(5)-Co(1)-N(4)	78.00(10)	77.45(8)	79.32		
N(5)-Co(1)-N(6)	78.19(10)	78.16(8)	79.10		
	N _{nv} -Co-N _{imine} (cis-in	terligand)			
N(2)-Co(1)-N(4)	106.61(10)	100.97(8)	101.36		
N(2) - Co(1) - N(6)	97.20(10)	103.46(8)	100.20		
N(5)-Co(1)-N(1)	99.92(10)	98.52(8)	102.05		
N(5)-Co(1)-N(3)	99.18(10)	100.91(8)	101.68		
	Nimine-Co-Nimine	(cis)			
N(1)-Co(1)-N(4)	93.47(9)	87.60(8)	88.42		
N(1) - Co(1) - N(6)	92.06(10)	97.79(8)	96.02		
N(3) - Co(1) - N(4)	91.21(9)	97.11(8)	94.73		
N(3) - Co(1) - N(6)	91.11(9)	85.73(8)	89.10		
		× /			

we assign the first reduction between -0.6 and -1.1 V vs. $Cp_2Fe^{0/+}$ as a metal centered reduction to $[Co^{I}(NNN^{0})_{2}]^{+}$, and the second reduction to a ligand centered process resulting in $[Co^{I}(NNN^{0})(NNN^{-1})]^{0}$. The Co^{II/III} oxidation potential and first reduction potential (e.g. $[ML_2]^{+/2+}$) also show a strong correlation with the Hammett parameter¹⁷ for the substituents in the para position of the N-aryl groups on the ligands as shown in Fig. 5. Replacing the *p*-H ($\sigma_p = 0.00$) on the *N*-aryl rings of 4d with an electron withdrawing substituent induces an anodic shift of the Co^{II/III} oxidation potential by as much as +0.28 V for 4b with a *p*-CN ($\sigma_p = 0.66$). As highlighted previously, this is the result of stabilization afforded by the electron withdrawing substituents, which increases the potential required to remove an electron from the singly occupied e_{σ} orbitals. Conversely, replacing the p-H with a donating substituent such as p-NMe2 results in a cathodic shift of the Co^{II/III} oxidation potential of approximately the same magnitude (-0.31 V, $\sigma_p = -0.83$) for 4g. Here the destabilization provided by the electron donating substituents raises the energy of the singly occupied e_g orbitals allowing the oxidation to occur at much lower potentials.

Using the electrochemical data for **4b**–**g** as a point of reference it is now possible to reexamine the data in Table 1 for evidence of ligand redistribution to form $[(NNN)_2Co]^{2+}$ with **2b**–**d**, **f** and **g**. As with **2f** and in agreement with the mass spectrometry results (*vide supra*) the *N*,*N*-dimethylamino substituted **2g** also exhibits redox waves consistent with the formation of $[(1g)_2Co]$ [CoCl₄] in acetonitrile (*cf*. Table 1: Co^{II/III} = (-0.19 V and



Fig. 4 Overlay of cyclic voltammograms of 1 mM solutions of **4b–g** recorded in acetonitrile with 0.1 M [Bu₄N][BF₄] as supporting electrolyte and v = 0.1 Vs⁻¹ at a glassy carbon working electrode (d = 3 mm).

Table 3 Electrochemical data for 4b–g in acetonitrile (0.1 M [Bu₄N][BF₄] supporting electrolyte) vs. $Cp_2Fe^{0/+}$ at 0.1 V s⁻¹ at a glassy carbon working electrode (d = 3 mm)

	$[ML_2]^{0/+}$	$\Delta E (\mathrm{mV})$	$[ML_2]^{+/2+}$	$\Delta E (\mathrm{mV})$	$[ML_2]^{2+/3+}$	$\Delta E (\mathrm{mV})$	$\sigma_{ m p}{}^a$
4b	-1.59	70	-0.65	70	+0.39	75	0.66
4c	-1.69^{c}	N/A	-0.70	90	+0.35	110	0.54
4d	-1.88	75	-0.87	70	+0.11	70	0.00
4e	-1.52°	N/A	-0.92	85	+0.03	80	-0.17
4f	-1.92	75	-0.94	70	-0.01	75	0.27
$4g^b$	-1.99	80	-1.05	70	-0.20	75	-0.83
0							

^a See ref. 17. ^b This work and ref. 7e. ^c Irreversible reduction, E_{PC}.

Table S1[†]: $E_{RED} = -1.13$ V for **2g** and Table 3: $[ML_2]^{2+/3+} = -0.20$ V and $[ML_2]^{+/2+} = -1.05$ V for **4g** vs. $Cp_2Fe^{0/+}$) as well as dichloromethane (cf. Table 1: $Co^{II/III} = -0.21$ V and Table S1[†]: $E_{RED} = -1.02$ V for **2g** vs. $Cp_2Fe^{0/+}$). In contrast, the CVs of **2b** and **2c** bearing strong electron withdrawing substituents do not exhibit any significant contributions from $[(1b)_2Co]^{2+}$ or $[(1c)_2Co]^{2+}$ in acetonitrile or dichloromethane, an observation that is also consistent with the mass spectrometry results. Interestingly, the CV of **2d**, which does not contain strongly donating or accepting substituents on the bis(imino)pyridine ligand, shows complete conversion to $[(1d)_2Co]^{2+}$ in acetonitrile (cf. Table 1: $Co^{II/III} = +0.11$ V and Table S1[†]: $E_{RED} = -0.88$ V for **2d** and Table 3: $[ML_2]^{2+/3+} = +0.11$ V and $[ML_2]^{+/2+} = -0.87$ V for **4d** vs. $Cp_2Fe^{0/+}$) but not in dichloromethane (cf. Table 1: $Co^{II/III} = +0.67$ V and Table S1[†]: $E_{RED} = -0.87$ V for **4d** vs. $Cp_2Fe^{0/+}$) but not in dichloromethane (cf. Table 1: $Co^{II/III} = +0.67$ V and Table S1[†]: $E_{RED} = -0.87$ V for **4d** vs. $Cp_2Fe^{0/+}$) but not in dichloromethane (cf. Table 1: $Co^{II/III} = +0.67$ V and Table S1[†]: $E_{RED} = -0.87$ V for **4d** vs. $Cp_2Fe^{0/+}$) but not in dichloromethane (cf. Table 1: $Co^{II/III} = +0.67$ V and Table S1[†]: $E_{RED} = -0.87$ V for **4d** vs. $Cp_2Fe^{0/+}$) but not in dichloromethane (cf. Table 1: $Co^{II/III} = +0.67$ V and Table S1[†]: $E_{RED} = -0.87$ V for **4d** vs. $Cp_2Fe^{0/+}$) but not in dichloromethane (cf. Table 1: $Co^{II/III} = +0.67$ V and Table S1[†]: $E_{RED} = -0.87$ V for **4d** vs. $Cp_2Fe^{0/+}$) but not in dichloromethane (cf. Table 1: $Co^{II/III} = +0.67$ V and Table S1[†]: $E_{RED} = -0.87$ V for **4d** vs. $Cp_2Fe^{0/+}$) but not in dichloromethane (cf. Table 1: $Co^{II/III} = +0.67$ V and Table S1[†]: $E_{RED} = -0.87$ V for **4d** vs. $Cp_2Fe^{0/+}$) but not in dichloromethane (cf. Table 1: $Co^{II/III} = +0.$



Fig. 5 Hammett plot correlating the (a) $[ML_2]^{2+/3+}$ (*e.g.* Co^{II/III}) and (b) $[ML_2]^{+/2+} E_{1/2}$ with σ_p for the ligand *N*-aryl *para* substituents.

-0.08 V for **2d** *vs*. Cp₂Fe^{0/+}). While conversion of the (NNN) CoCl₂ complexes to the [(NNN)₂Co][CoCl₄] salts appears to be more facile in acetonitrile than in dichloromethane, the electronic effects exerted by the bis(imino)pyridine substituents are also important and in the case of **2b** and **2c** the electronic effects are strong enough to prevent this ligand disproportionation.

Theoretical evaluation of electrochemical properties of (NNN) CoX₂ complexes

We have carried out a thorough analysis of the ligand binding free energies and redox potentials at the DFT/B3LYP level (Fig. 6), using the computational methodology based on implicit solvation models (see Experimental section for details).¹⁸ We investigated (NNN)Co^{II}Cl₂ and [(NNN)Co^{III}Cl₂]⁺ complexes in three solvents of increasing polarity (CH₂Cl₂: $\varepsilon = 8.9$, CH₃CN: ε = 37.5 and H₂O: ε = 80.4) and considered various reaction pathways involving solvent-ligand exchange and disproportionation. The results reported in Fig. 6 correspond to 2d as a representative example for 2a-d, f and g. Table 4 compares the bond lengths and angles obtained for the calculated minimum energy structure of 2d to the corresponding X-ray structure obtained by Gong et. al.14 The bond lengths and angles involving the bis (imino)pyridine ligand and the cobalt center in the DFT optimized structure of 2d agree very well with the reported structure¹⁴ (largest difference of *ca*. 0.03 Å and 0.1°, respectively) and are consistent with a neutral bis(imino)pyridine ligand environment.^{7e} Although the bond lengths and angles involving the chloride ligands show substantial deviations from the reported structure by *ca*. 0.09 Å and $5-20^\circ$, respectively, these are likely the result of crystal packing forces not accounted for in the calculated structure. In agreement with experimental data, 2d was calculated to be a $17e^{-1}$ high spin Co^{II} quartet ground state (d⁷, $S = \frac{3}{2}$ with a trigonal bipyramidal geometry, while the singlet



Fig. 6 The reaction pathways calculated for 2d (L = 1d) in CH₂Cl₂ (DCM), CH₃CN (AN), and H₂O, respectively. Free-energy changes ΔG are reported in kcal mol⁻¹ and redox potentials, E° in V vs. Cp₂Fe^{0/+}.

Table 4 Selected bond distances (Å) and bond angles (°) for **2d** and the minimum energy structure of **2d** obtained in the gas phase at the DFT B3LYP/lacvp-6-31G level of theory (elements labeled according to the reported structure)¹⁴

	$2d^{14}$	2d(DFT)
	Bond distance	
	Co-N _{pv}	
Co(1)-N(2)	2.031(18)	2.050
	Co-N _{imine}	
Co(1) - N(1)	2.213(18)	2.241
Co(1) - N(3)	2.222(18)	2.242
	Co-Cl	
Co(1)-Cl(1)	2.268(6)	2.356
Co(1) - Cl(2)	2.261(6)	2.353
	C _{imine} -N _{imine}	
C(14)–N(2)	1.281(3)	1.299
C(6) - N(3)	1.281(3)	1.300
	C _{imine} -C _{pv}	
C(1)–C(6)	1.494(3)	1.492
C(5) - C(14)	1.496(3)	1.487
	C _{nv} -N _{nv}	
C(1)-N(1)	1.347(3)	1.350
C(5)–N(1)	1.335(3)	1.348
	Bond angle	
	N _{imine} CoN _{imine}	
N(1)-Co(1)-N(3)	150.88(7)	151.40
	N _{nv} -Co-N _{imine}	
N(2)-Co(1)-N(1)	75.29(7)	75.22
N(2) - Co(1) - N(3)	75.64(7)	75.26
N _{nv} –Co–Cl		
N(2)-Co(1)-Cl(1)	118.36(5)	108.35
N(2) - Co(1) - Cl(2)	123.78(5)	112.54
	N _{imine} -Co-Cl	
N(1)-Co(1)-Cl(1)	97.85(5)	94.83
N(1) - Co(1) - Cl(2)	95.86(5)	90.50
N(3) - Co(1) - Cl(1)	97.31(5)	95.92
N(3) - Co(1) - Cl(2)	98.80(5)	99.66
	Cl–Co–Cl	
Cl(1)-Co(1)-Cl(2)	117.84(3)	138.70

state containing a low spin $16e^{-}$ Co^{III} ion (d⁶, S = 0) was determined to be the ground state electronic configuration for 2d⁺.

Fig. 6 shows that the direct oxidation of 2d without changing the coordination sphere at cobalt (Fig. 6, $2d \rightarrow 2d^+$) would require a significantly higher potential (+0.90, +0.99 and +0.93 V vs. Cp₂Fe^{0/+} for CH₂Cl₂, CH₃CN and H₂O, respectively) than observed experimentally (+0.67, +0.11 and +0.02 V vs. $Cp_2Fe^{0/+}$ for CH₂Cl₂, CH₃CN and H₂O, respectively). This is likely because direct oxidation, without changing the coordination sphere of the metal center, produces a relatively unstable 16-electron complex. In contrast, coordination of a solvent molecule (e.g., CH_3CN or CH_2Cl_2) upon oxidation of **2d** to form the 18e⁻ low spin octahedral Co^{III} -species **2d(solv)**⁺ at potentials of +0.06 V (CH₃CN) and +0.54 V (CH₂Cl₂) vs. $Cp_2Fe^{0/+}$ (bold in Fig. 6) is in good agreement with the experimental data reported in Table 1. In H₂O, however, the comparison is less favorable and suggests that neither of the two reaction pathways discussed so far are the predominant mechanisms for oxidation of 2d in water.

To analyze alternative reaction pathways for oxidation in water, we have explored the feasibility of Cl^-/H_2O ligand exchange (Fig 6, $2d \rightarrow 5d$, 6d, 7d) as well as the possibility of disproportionation (Fig 6, $2d \rightarrow 4d$) where two neutral 2d

Table 5 Calculated free energies, ΔG° in kcal mol⁻¹ for disproportionation of **2b**, **d**, **f** to [(**1b**, **d**, **f**)₂Co][CoCl₄]

Solvent	2f ($R = 4$ -OCH ₃)	2d (R = 4-H)	2b (R = 4-CN)
H ₂ O	-3.7	-0.8	1.6
CH ₃ CN	-0.9	2.3	6.4
CH ₂ Cl ₂	16.9	21.7	28.3

complexes react to form the ions $[(NNN)_2C0]^{2+}$ and $[CoCl_4]^{2-}$ that comprise **4d'**. To investigate these pathways, we have calculated the Gibbs free energies and the results are shown in Fig. 6. Replacement of one chloride ligand by a solvent moiety to form **5d** was found to be thermodynamically disfavored, demanding Gibbs free-energy changes of 6.1 and 18.9 kcal mol⁻¹ for H₂O and CH₃CN, respectively. Similar 'uphill' free-energy changes are predicted for the substitution of both chloride ligands by a single solvent moiety in **6d**, or exchange of both chloride ligands by water in **7d**. These results suggest that none of the ligand-exchange reactions are thermodynamically favored, leaving disproportionation to **4d'** as the most likely reaction in water. It should also be mentioned that ion pairing was not considered for this calculation *i.e.* the free energy of the ions $[(L)_2Co_A]^{2+}$ and $[Co_BCl_4]^{2-}$ were evaluated separately.

We have also investigated the effect of solvent polarity on the disproportionation reaction shown in Fig. 6 $(2d \rightarrow 4d')$ in an effort to further investigate such a reaction mechanism. The calculated free-energy changes are collected in Table 5 and indicate that such a disproportionation is spontaneous in water ΔG = -0.8 kcal mol⁻¹ and very likely to be observed to some extent even in acetonitrile $\Delta G = 2.3$ kcal mol⁻¹ ($K_{eq} = 0.13$). However, in non-polar or weakly polar solvents (e.g., CH2Cl2) the reaction is predicted to be non-spontaneous, with a significant freeenergy penalty of 21.7 kcal mol⁻¹. Furthermore, the Co^{II/III} oxidation potential calculated for $[(NNN)_2Co^{II}]^{2+}$ in 4d' in water (+0.13 V vs. $Cp_2Fe^{0/+}$) is only ca. 0.1 V higher than that determined experimentally (+0.02 V vs. $Cp_2Fe^{0/+}$) suggesting that in water 2d disproportionates prior to oxidation. In contrast, oxidation in CH₂Cl₂ must follow the pathway where the 18e⁻ Co^{III} cation is stabilized by coordination of a CH₂Cl₂ moiety upon $Co^{II/III}$ oxidation (*i.e.* $2d \rightarrow 2d(solv)^+$). Finally, in polar organic solvents (e.g., CH₃CN) although oxidation to the solvated Co^{III} species $(2d \rightarrow 2d(solv)^+)$ is calculated to be thermodynamically more favored, both pathways are likely accessible at equilibrium. These results agree nicely with the experimental observation of disproportionation of 2d to 4d' in acetonitrile but not in dichloromethane (vide supra).

In addition to the analysis of the effect of solvent polarity on the underlying reaction mechanism, we have explored the effect of ligand substituents on the resulting free-energy profiles. As can be seen from the data in Table 5 a similar effect of solvent polarity on the disproportionation is observed for **2b** and **2f**, with the reaction in water being the most favorable, while disproportionation in dichloromethane is least favorable. The effect of ligand substituents on the reaction is also in very good agreement with experimental observations as the data in Table 5 indicates that disproportionation is favored for electron donating substituents and disfavored for electron withdrawing substituents relative to the unsubstituted complex **2d**. The electron donating

	$[(\mathbf{1f})_2 \mathrm{Co}][\mathrm{CoCl}_4]$	2g
Formula	C48H49Cl4C02N7O4	C25H29Cl2CoN5
Formula weight	1047.60	529.36
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
Cell dimensions		
a (Å)	17.8237(15)	12.3191(4)
b (Å)	15.3342(14)	15.1565(5)
<i>c</i> (Å)	19.2414(16)	14.1316(5)
α (°)	90	90
β (°)	113.367(3)	107.0280(10)
γ (°)	90	90
$V(Å^3)$	4827.6(7)	2522.90(15)
Ζ	4	4
$D_{\text{calc}} (\text{Mg m}^{-3})$	1.441	1.394
μ (Mo K _{α}) (mm ⁻¹)	0.960	0.915
Crystal dimensions (mm ³)	$0.30 \times 0.30 \times 0.03$	0.50 imes 0.20 imes
		0.05
$T(\mathbf{K})$	173(2)	173(2)
θ range (°)	1.76 to 27.10	1.93 to 28.28
No. of rflns	42 880	24 507
No. of indep reflns	10 559	6267
$R_1 (I > 2\sigma(I))$	0.0480	0.0375
wR_2 (all data)	0.1372	0.1094
GOF	1.094	1.003
Largest diff. peak, hole $(eÅ^{-3})$	1.643, -0.836	1.252, -0.358

Table 6 Crystallographic data and structural refinement parameters for $[(1f)_2Co][CoCl_4]$ and 2g

effect of the methoxy substituent is strong enough in **2f** to make disproportionation spontaneous in water and acetonitrile, while the electron withdrawing effect of the cyano group is strong enough to discourage disproportionation in dichloromethane and acetonitrile.

These results are therefore consistent with oxidation of the (NNN)CoX₂ complexes in water following disproportionation to [(NNN)₂Co][CoCl₄]. In contrast, 18e⁻ solvated Co^{III} cations are formed upon oxidation of the (NNN)CoX₂ complexes in CH₂Cl₂ and coordination of a solvent moiety (*e.g.* formation of **2d** (**solv**)⁺ in Fig. 6). Finally, in polar organic solvents (*e.g.*, CH₃CN) both pathways are accessible *via* the equilibrium shown in equation 1, although formation of the solvated Co^{III} species [(NNN)CoX₂(solv)]⁺ is predicted to be thermodynamically more favored.

Conclusions

The electrochemical properties of a series of (NNN)CoX₂ and [(NNN)₂Co][PF₆]₂ complexes have been investigated for ligands with various electron donating/withdrawing substituents, in solvents of low (CH₂Cl₂), high (CH₃CN) and very high (H₂O) polarity. Experimental and theoretical results show clear evidence of the regulation of Co^{II/III} oxidation potentials using ligand effects and/or solvent polarity, affecting not only the electronic properties but also the stability of the complexes. Introducing substituents in the *para* position of the *N*-aryl ring allows one to vary the Co^{II/III} oxidation potential of the [(NNN)₂Co] [PF₆]₂ complexes by up to 750 mV in acetonitrile.

Calculations show that oxidation of the $(NNN)CoX_2$ complexes in CH_2Cl_2 and CH_3CN leads to expansion of the

coordination sphere of the metal to accommodate a solvent molecule. However, complexes lacking bulky substituents in the ortho positions of the N-aryl rings (2b-d, f and g) are in equilibrium with [(NNN)₂Co][CoCl₄] resulting from disproportionation, with the equilibrium constant heavily influenced by solvent polarity and ligand electronic effects. In acetonitrile, complexes bearing electron donating or neutral substituents (2d, 2f and 2g) form the bis-ligand complexes almost exclusively, while those bearing electron withdrawing substituents (2b and 2c) have equilibria predominantly displaced towards the (NNN)CoCl₂ species, with only minor amounts (~5%) of [(NNN)₂Co][CoCl₄]. In agreement with our DFT results, oxidation of the latter two complexes follows a different reaction pathway which likely involves coordination of a solvent molecule as in $2d(solv)^+$. These results are also in agreement with the CV data of 4b-g, mass spectrometry data for 2b-d, f and g, and the single-crystal X-ray structure of [(2f)₂Co][CoCl₄] (obtained from crystallizing $[(1f)_2Co][CoCl_4]$ from CH₃CN/Et₂O). In dichloromethane, the disproportionation is observed only for 2f and 2g complexes with strong electron donating substituents, while 2b-d do not show any evidence for disproportionation.

Therefore, we conclude that although increasing the solvent polarity can reduce the oxidation potential by as much as 600 mV (+0.67 V, +0.11 and +0.02 V vs. CpFe^{0/+} for CH₂Cl₂, CH₃CN, H₂O) the stability of the complexes (NNN)CoX₂ is jeopardized by polar solvents such as H₂O or CH₃CN. This ultimately leads to disproportionation into coordinatively saturated $[(NNN)_2Co][CoCl_4]$ salts, which may not have the desired catalytic properties. A safer way of modulating the redox potentials is by moving to more electron-donating groups in the substituents of the pincer ligands (e.g., $R = NMe_2$ as in 2g), increasing the electron-density at the metal center, thus generating a more easily oxidized Co^{II} center, while electron-withdrawing groups $(e.g., \mathbf{R} = \mathbf{CN} \text{ as in } \mathbf{2b})$ produce the opposite effect. A caveat to such a strategy, however, is that steric effects (or lack thereof) imparted by ligand substituents may affect any potential catalytic activity.

Experimental methods

General considerations

Acetonitrile and dichloromethane were dried by passage over activated molecular sieves and degassed prior to use. Bu₄NBF₄ was recrystallized three times from ethanol and dried under vacuum at 120 °C over P2O5 for 3 d. Elemental analyses were performed by Galbraith Laboratories, Inc., in Knoxville, TN. All ¹H and ¹³C $\{^{1}H\}$ NMR spectra were recorded on a Bruker 400 MHz Avance spectrometer and referenced to residual CHCl₃ (δ 7.27) or CHD₂CN (δ 1.94) for ¹H and CDCl₃ (δ 77.16) for $^{13}C{^{1}H}$. Spectra of the paramagnetic complexes can be found in the ESI.[†] Solution magnetic moments were determined by Evans NMR method¹¹ using the residual solvent signal as the reference and although these are generally the result of a single experiment, in several cases the values obtained were checked against multiple independent experiments and found to be in agreement ($\pm 0.1 \mu_{\rm B}$). MALDI time-of-flight mass spectra were acquired with an Applied Biosystems Voyager-DE STR mass spectrometer utilizing a nitrogen laser ($\lambda = 334$ nm) to ionize a dried residue consisting of the analyte mixed with the HBM– acetonitrile matrix (20 mg mL⁻¹) from a polished stainless steel plate (HBM = 4-hydroxybenzylidenemalononitrile). Electrochemical measurements were conducted on an IviumStat Electrochemical Interface & Impedance Analyzer from Ivium Technologies and were carried out under an inert Ar or N₂ atmosphere using 0.1 M tetrabutylammonium tetrafluoroborate as the supporting electrolyte in acetonitrile or dichloromethane. Cyclic voltammetry experiments were performed in a beaker type cell with a working volume of 5 mL using a standard threeelectrode cell with a glassy carbon disk (d = 3 mm) working electrode, platinum wire counter electrode and a homemade reference electrode consisting of Ag wire immersed in a 10 mM AgNO₃/0.1 M Bu₄NBF₄ electrolyte in acetonitrile separated from the bulk solution by a "thirsty" VycorTM frit.

Single crystals suitable for X-ray diffraction were transferred from a crystallization vessel into a drop of viscose organic oil, transferred to a nylon loop and mounted on a Bruker X8 APEX II diffractometer (Mo K α radiation) and cooled to -100 °C. Data collection and reduction were done using Bruker APEX2 and SAINT + software packages and corrected for absorption using SADABS. Structures were solved by direct methods and refined on F^2 by full matrix least-squares techniques using SHELXTL software package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were found in a difference Fourier map and refined isotropically (Table 6).

Theoretical methods

The computational methods implemented in this study have been described previously.¹⁸ Here, we outline the methodology only briefly.

The standard reduction potentials are obtained, as follows:

$$E^{\circ} = -\frac{\Delta G_{(\text{solv})}(\text{Red})}{nF} \tag{2}$$

where *F* and *n* are the Faraday constant (23.06 kcal mol⁻¹ V⁻¹) and the number of electrons involved in the redox reaction, respectively, by evaluating the reduction free energies ΔG (red) using the Born–Haber thermodynamic cycle (illustrated in Scheme 1), as follows:

$$\Delta G_{(\text{solv})}(\text{Red}) = \Delta G_{(g)}(\text{Red}) + \Delta G_{(s)}(\text{Red}) - \Delta G_{(s)}(\text{Ox}) \quad (3)$$

with $\Delta G_{(g)}(\text{Red}) = \Delta U_{(g)}(\text{Red}) + \text{PV} - T\Delta S_{(g)}(\text{Red})$. The vibrational, rotational and translational contributions (statistical mechanics contributions) were included in the calculation of internal energy and entropy. The solvation free energies of the oxidized and reduced species, $\Delta G_{(s)}(\text{Ox})$ and $\Delta G_{(s)}(\text{Red})$, were calculated using the PBF method as described below, except for





the Cl⁻ ion and the hydration of H₂O, for which we have used experimental results.¹⁹

$$G = E_{\text{elect}} + G_{\text{solv}} + ZPVE + \sum_{\nu} \frac{h\nu}{e^{h\nu/kT} - 1} + \frac{n}{2}kT - T(S_{\text{vib}} + S_{\text{rot}} + S_{\text{trans}})$$
(4)

where n = 8 accounts for the internal energies of the translational and rotational modes and the PV term. Calculated redox potentials are reported relative to Cp₂Fe^{0/+}, calculated at the same level of theory, to eliminate systematic differences due to the nature of the solvent, electrolyte and working electrode conditions.

All quantum chemistry calculations were carried out within the framework of density functional theory, using the hybrid density functional B3LYP²⁰ as implemented in the Jaguar 7.7 software package.²¹ For geometry optimization and vibration calculations, we have employed a hybrid basis set where Co ions were described by LACVP effective core potential²² and basis set (ECP), using the double- ζ contraction of valence functions, while the other elements (Cl, C, N and H) were treated in the level of 6-31G basis set.²³ Single-point calculations were also performed with a larger basis set cc-PVTZ(-f).²⁴

Solvation energies were calculated using the Poisson–Boltzmann self-consistent reaction field method (PBF)²⁵ to represent the solvents with dielectric constant (effective radius) equal to 8.93 (2.33), 37.5 (2.19) and 80.37 (1.40) for dichloromethane (CH₂Cl₂), acetonitrile (CH₃CN) and water, respectively. Here, we have employed B3LYP/LACVP_cc-PVTZ(-f) theory level.

Synthetic procedures

Ligands 1a, 3d,i 1c, 13 1d, 13,26 1e, 27 and $1f^{26}$ and complexes 2a, 3d,i 2c, 13 2d, ${}^{13-14,26}$ 2f, 26 $3a^{3b}$ and $4f^{7e}$ were prepared as reported previously while new ligands and complexes were prepared using modifications of these published procedures, the details of which are described below.

2,6-Bis[1-(4-cyanophenylimino)ethyl]pyridine, (1b)

2,6-Diacetylpyridine (2.00 g, 12.26 mmol, 1.0 equiv.), p-aminobenzonitrile (3.04 g, 25.75 mmol, 2.1 equiv.) and p-toluenesulfonic acid (0.010 g, 0.053 mmol, 0.05 equiv.) were dissolved in 70 mL of toluene and heated to reflux under N2 with constant stirring and removal of water using a Dean-Stark trap. After 2 d, the reaction mixture was cooled to room temperature and the volatiles were removed by evaporation to give an orange-red residue. The addition of methanol and filtration of the resultant pale yellow solid, followed by washing with ethyl ether and petroleum ether gave 1.20 g (3.31 mmol, 27%) of a pale yellow powder. ¹H NMR (CDCl₃, 400.13 MHz, 24.4 °C) δ 8.36 (d, 2H, py-H_{meta}, ${}^{3}J_{HH} = 7.8$ Hz), 7.93 (t, 1H, py-H_{para}, ${}^{3}J_{HH} = 7.8$ Hz), 7.69 (d, 4H, *N*-Ar-H_{meta}, ${}^{3}J_{HH} = 8.5$ Hz), 6.92 (d, 4H, *N*-Ar- H_{ortho} , ${}^{3}J_{HH} = 8.5 \text{ Hz}$, 2.41 (s, 6H, C(Me) = N). ${}^{13}C{}^{1}H$ NMR (CDCl₃, 100.6 MHz, 22.0 °C) δ 167.9, 155.3, 154.7, 137.2, 133.4, 123.1, 119.8, 119.2, 107.1, 16.6. MALDI MS, m/z: 364 $[1b + H]^+$.

2,6-Bis[1-(4-dimethylaminophenylimino)ethyl]pyridine, (1g)

2,6-Diacetylpyridine (2.00 g, 12.26 mmol, 1.0 equiv.), N,Ndimethyl-1,4-phenylene diamine (3.51 g, 25.75 mmol, 2.1 equiv.) and p-toluenesulfonic acid (0.010 g, 0.053 mmol, 0.05 equiv.) were dissolved in 70 mL of toluene and heated to reflux under N₂ with constant stirring and removal of water using a Dean-Stark trap. After 1 d, the reaction mixture was cooled to room temperature and the volatiles were removed by evaporation to give an orange-red residue. Addition of methanol and filtration of the resultant dark yellow solid, followed by washing with ethyl ether and petroleum ether gave 2.88 g (7.22 mmol, 59%) of a dark yellow powder. ¹H NMR (CDCl₃, 400.13 MHz, 24.4 °C) δ 8.32 (d, 2H, py-H_{meta}, ${}^{3}J_{HH} = 7.8$ Hz), 7.84 (t, 1H, py-H_{para}, ${}^{3}J_{HH} = 7.8$ Hz), 6.87 (d, 4H, N-Ar-H_{meta}, ${}^{3}J_{HH} = 9.1$ Hz), 6.81 (d, 4H, *N*-Ar-H_{ortho}, ${}^{3}J_{HH} = 9.1$ Hz), 2.98 (s, 12H, N (Me₂)), 2.49 (s, 6H, C(*Me*) = N). ${}^{13}C{}^{1}H{}$ NMR (CDCl₃, 100.6 MHz, 22.0 °C) δ 166.5, 156.0, 147.7, 141.0, 136.6, 121.8. 121.4, 113.2, 41.1, 16.3. MALDI MS, m/z: 400 $[1g + H]^+$.

2,6-Bis[1-(4-cyanophenylimino)ethyl]pyridine cobalt(11) chloride, (2b)

1b (0.75 g, 2.07 mmol, 1.001 equiv.) and CoCl₂ (0.27 g, 2.06 mmol, 1.0 equiv.) were combined in 65 mL of THF and stirred under N₂ overnight at room temperature. The reaction mixture was then poured into 125 mL of ethyl ether and the resulting precipitate was isolated by vacuum filtration, washed with ethyl ether and petroleum ether and air dried to give 1.02 g (2.06 mmol, 99%) of a green powder. Elemental analysis calcd for C₂₃H₁₇Cl₂CoN₅: C, 56.00; H, 3.47; N, 14.20. Found: C, 55.19; H, 3.49; N, 13.66.²⁸ MALDI MS, *m/z*: 457 [**2b** – Cl]⁺. Magnetic susceptibility (acetonitrile-d₃, 297 K): $\mu_{\text{eff}} = 5.1 \,\mu_{\text{B}}$.

2,6-Bis[1-(4-dimethylaminophenylimino)ethyl]pyridine cobalt(II) chloride, (2g)

1g (1.00 g, 2.50 mmol, 1.0 equiv.) and CoCl₂ (0.33 g, 2.50 mmol, 1.0 equiv.) were combined in 70 mL of THF and stirred under N₂ overnight at room temperature. The reaction mixture was then poured into 150 mL of ethyl ether and the resulting precipitate was isolated by vacuum filtration, washed with ethyl ether and petroleum ether and air dried to give 1.18 g (2.23 mmol, 89%) of a brown powder. Elemental analysis calcd for C₂₅H₂₉Cl₂CoN₅: C, 56.72; H, 5.52; N, 13.23. Found: C, 57.00; H, 5.63; N, 13.01. MALDI MS, *m*/*z*: 493 [**2**g – Cl]⁺, 857 [(**1**g)₂Co]⁺. Magnetic susceptibility (acetonitrile-d₃, 297 K): $\mu_{\text{eff}} = 3.5 \,\mu_{\text{B}}$.

Bis{2,6-Bis[1-(4-cyanophenylimino)ethyl]pyridine}cobalt(II) hexafluorophosphate, 4b

1b (0.26 g, 0.71 mmol, 2.01 equiv.) and $CoCl_2$ (0.046 g, 0.35 mmol, 1.00 equiv.) were dissolved in 20 mL of methanol and the mixture was stirred at room temperature for 30 minutes before excess NH₄PF₆ (0.78 g, 4.82 mmol, 13.6 equiv.) was added to precipitate the product. The brick-red solid was collected by filtration, washed with ice cold methanol and air dried

to give 0.382 g (0.35 mmol, 100%) of **4b**. Elemental analysis calcd for C₄₆H₃₄CoF₁₂N₁₀P₂: C, 51.36; H, 3.19; N, 13.02. Found: C, 50.90; H, 3.34; N, 12.55.²⁸ MALDI MS, *m/z*: 785 [**4b** – 2 PF₆]⁺. Magnetic susceptibility (acetonitrile-d₃, 297 K): $\mu_{\rm eff} = 3.5 \,\mu_{\rm B}$.

Bis{2,6-Bis[1-(4-trifluoromethylphenylimino)ethyl]pyridine} cobalt(11) hexafluorophosphate, 4c

2c (0.30 g, 0.67 mmol, 2.04 equiv.) and CoCl₂ (0.042 g, 0.33 mmol, 1.00 equiv.) were dissolved in 25 mL of methanol and the mixture was stirred at room temperature for 30 minutes before excess NH₄PF₆ (0.81 g, 4.99 mmol, 15.3 equiv.) was added. The solution was dried under reduced pressure and the resulting red residue was taken up in dichloromethane, washed with water and the organic phase was dried with Na₂SO₄ and filtered. The filtrate was dried under reduced pressure and 0.38 g (0.30 mmol, 92%) of a red powder was obtained after trituration from a 1 : 1 diethyl ether : hexane mixture. Elemental analysis calc. for C₄₆H₃₄CoF₂₄N₆P₂: C, 44.28; H, 2.75; N, 6.74. Found: C, 44.13; H, 2.84; N, 6.39. MALDI MS, *m/z*: 957 [**4c** – 2 PF₆]⁺, 1104 [**4c** – PF₆]⁺. Magnetic susceptibility (acetonitrile-d₃, 297 K): $\mu_{eff} = 2.7 \mu_{B}$.

Bis{2,6-Bis[1-(phenylimino)ethyl]pyridine}cobalt(II) hexafluorophosphate, 4d

1d (0.14 g, 0.45 mmol, 2.3 equiv.) and CoCl₂ (0.025 g, 0.19 mmol, 1.00 equiv.) were dissolved in 20 mL of methanol and the mixture was stirred at room temperature for 30 minutes before excess NH₄PF₆ (0.52 g, 3.17 mmol, 16.5 equiv.) was added to precipitate the product. The brown crystalline solid was collected by filtration, washed with ice cold methanol and air dried to give 0.143 g (0.15 mmol, 76%) of **4d**. Elemental analysis calcd for C₄₂H₃₈CoF₁₂N₆P₂: C, 51.70; H, 3.93; N, 8.61. Found: C, 51.99; H, 3.98; N, 8.66. MALDI MS, *m/z*: 685 [**4d** - 2 PF₆]⁺. Magnetic susceptibility (acetonitrile-d₃, 297 K): $\mu_{eff} = 2.6 \mu_{B}$.

Bis{2,6-Bis[1-(4-methylphenylimino)ethyl]pyridine}cobalt(11) hexafluorophosphate, 4e

1e (0.30 g, 0.88 mmol, 2.24 equiv.) and CoCl₂ (0.051 g, 0.39 mmol, 1.00 equiv.) were dissolved in 20 mL of methanol and the mixture was stirred at room temperature for 30 minutes before excess NH₄PF₆ (1.00 g, 6.17 mmol, 15.7 equiv.) was added to precipitate the product. The brick-red solid was collected by filtration, washed with ice cold methanol and air dried to give 0.258 g (0.25 mmol, 64%) of **4e**. Elemental analysis calcd for C₄₆H₄₆CoF₁₂N₆P₂: C, 53.55; H, 4.49; N, 8.15. Found: C, 53.04; H, 4.50; N, 8.02. MALDI MS, *m/z*: 741 [**4e** – 2 PF₆]⁺. Magnetic susceptibility (acetonitrile-d₃, 297 K): $\mu_{eff} = 2.7 \mu_{B}$.

Bis{2,6-Bis[1-(4-dimethylaminophenylimino)ethyl]pyridine} cobalt(11) hexafluorophosphate, 4g

1g (0.39 g, 0.98 mmol, 2.02 equiv.) and $CoCl_2$ (0.063 g, 0.48 mmol, 1.00 equiv.) were dissolved in 20 mL of methanol

and the mixture was stirred at room temperature for 30 minutes before excess NH₄PF₆ (1.14 g, 7.03 mmol, 14.5 equiv.) was added to precipitate the product. The brick-red solid was collected by filtration, washed with ice cold methanol and air dried to give 0.346 g (0.30 mmol, 62%) of **4g**. Elemental analysis calcd for C₅₀H₅₈CoF₁₂N₁₀P₂: C, 52.31; H, 5.09; N, 12.20. Found: C, 51.31; H, 5.14; N, 11.98.²⁸ MALDI MS, *m/z*: 857 [**4g** \neg 2 PF₆]⁺, 1002 [**4g** \neg PF₆]. Magnetic susceptibility (acetonitrile-d₃, 297 K): $\mu_{eff} = 2.1(4) \mu_{B}$.

Acknowledgements

This material is based upon work supported as part of the Center for Electrocatalysis, Transport Phenomena, and Materials (CETM) for Innovative Energy Storage, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC00001055.

References

- 1 G. Jerkiewicz, *Electrocatalysis*, 2010, 1, 1.
- 2 (a) R. H. Crabtree, Energy Environ. Sci., 2008, 1, 134–138;
 (b) G. L. Soloveichik, J. P. Lemmon, J. -C. Zhao (General Electric Company), USA Pat., 2008/0248339, 2008; (c) N. Kariya, A. Fukuoka and M. Ichikawa, Chem. Commun., 2003, 690–691; (d) N. Kariya, A. Fukuoka and M. Ichikawa, Phys. Chem. Chem. Phys., 2006, 8, 1724–1730; (e) D. L. DuBois and R. M. Bullock, Eur. J. Inorg. Chem., 2011, 1017–1027; (f) A. D. Wilson, R. H. Newell, M. J. McNevin, J. T. Muckerman, M. R. DuBois and D. L. duBois, J. Am. Chem. Soc., 2006, 128, 358–366; (g) B. R. Galan, J. Schoffel, J. C. Linehan, C. Seu, A. M. Appel, J. A. S. Roberts, M. L. Helm, U. J. Kilgore, J. Y. Yang, D. L. DuBois and C. P. Kubiak, J. Am. Chem. Soc., 2011, 133, 12767–12779.
- 3 (a) C. C. H. Atienza, C. Milsmann, E. Lobkovsky and P. J. Chirik, Angew. Chem., Int. Ed., 2011, 50, 8143-8147; (b) A. M. A. Bennett (DuPont), WO Pat., 98/27124, 1998; (c) C. Bianchini, G. Giambastiani, I. G. Rios, G. Mantovani, A. Meli and A. M. Segarra, Coord. Chem. Rev., 2006, 250, 1391-1418; (d) G. J. P. Britovsek, M. Bruce, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. Mastroianni, S. J. McTavish, C. Redshaw, G. A. Sloan, S. Stromberg, A. J. P. White and D. J. Williams, J. Am. Chem. Soc., 1999, 121, 8728-8740; (e) G. J. P. Britovsek, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. J. McTavish, G. A. Solan, A. J. P. White and D. J. Williams, Chem. Commun., 1998, 849-850; (f) G. J. P. Britovsek, V. C. Gibson, S. K. Spitzmesser, K. P. Tellmann, A. J. P. White and D. J. Williams, J Chem. Soc., Dalton Trans., 2002, 1159-1171; (g) V. C. Gibson, C. Redshaw and G. A. Solan, Chem. Rev., 2007, 107, 1745-1776; (h) B. L. Small and M. Brookhart, Macromolecules, 1999, 32, 2120-2130; (i) B. L. Small, M. Brookhart and A. M. A. Bennett, J. Am. Chem. Soc., 1998, 120, 4049-4050.
- 4 (a) B. L. Small, Organometallics, 2003, 22, 3178–3183;
 (b) K. P. Tellmann, V. C. Gibson, A. J. P. White and D. J. Williams, Organometallics, 2005, 24, 280–286.
- 5 (a) B. L. Small and M. Brookhart, J. Am. Chem. Soc., 1998, 120, 7143– 7144; (b) B. L. Small, R. Rios, E. R. Fernandez and M. J. Carney, Organometallics, 2007, 26, 1744–1749.
- 6 (a) M. W. Bouwkamp, S. C. Bart, E. J. Hawrelak, R. J. Trovitch, E. Lobkovsky and P. J. Chirik, *Chem. Commun.*, 2005, 3406–3408; (b) M. J. Humphries, K. P. Tellmann, V. C. Gibson, A. J. P. White and D. J. Williams, *Organometallics*, 2005, **24**, 2039–2050; (c) T. M. Kooistra, Q. Knijnenburg, J. M. M. Smits, A. D. Horton, P. M. Budzelaar and A. W. Gal, *Angew. Chem., Int. Ed.*, 2001, **40**, 4719–4722; (d) J. Scott, S. Gambarotta, I. Korobkov and P. M. Budzelaar, *Organometallics*, 2005,

24, 6298; (e) A. M. Tondreau, C. Milsmann, A. D. Patrick, H. M. Hoyt, E. Lobkovsky, K. Wieghardt and P. J. Chirik, *J. Am. Chem. Soc.*, 2011, 132, 15046–15059.

- 7 (a) S. C. Bart, K. Chlopek, E. Bill, M. W. Bouwkamp, E. Lobkovsky, F. Neese, K. Wieghardt and P. J. Chirik, J. Am. Chem. Soc., 2006, 128, 13901–13912; (b) A. C. Bowman, C. Milsmann, C. C. H. Atienza, E. Lobkovsky, K. Wieghardt and P. J. Chirik, J. Am. Chem. Soc., 2010, 132, 1676–1684; (c) A. C. Bowman, C. Milsmann, E. Bill, E. Lobkovsky, T. Weyhermuller, K. Wieghardt and P. J. Chirik, Inorg. Chem., 2010, 49, 6110–6123; (d) P. M. Budzelaar, B. de Bruin, A. W. Gal, K. Wieghardt and J. L. van Lenthe, Inorg. Chem., 2001, 40, 4649–4655; (e) B. de Bruin, E. Bill, E. Bothe, T. Weyhermuller and K. Wieghardt, Inorg. Chem., 2000, 39, 2936–2947.
- 8 C. C. H. Atienza, A. C. Bowman, E. Lobkovsky and P. J. Chirik, J. Am. Chem. Soc., 2010, 132, 16343–16345.
- 9 (a) H. Nakazawa and M. Itazaki, in *Topics in Organometallic Chemistry: Iron Catalysis Fundamentals and Applications*, ed. B. Plietker, Springer, New York, NY, Editon edn, 2011, vol. 33, pp. 27–81; (b) R. J. Trovitch, E. Lobkovsky, E. Bill and P. J. Chirik, *Organometallics*, 2008, 27, 1470–1478; (c) R. J. Trovitch, E. Lobkovsky and P. J. Chirik, *J. Am. Chem. Soc.*, 2008, 130, 11631–11640; (d) S. C. Bart, E. Lobkovsky and P. J. Chirik, *J. Am. Chem. Soc.*, 2004, 126, 13794– 13807.
- 10 G. J. P. Britovsek, J. England, S. K. Spitzmesser, A. J. P. White and D. J. Williams, J. Chem. Soc., Dalton Trans., 2005, 945–955.
- 11 (a) D. F. Evans, J. Chem. Soc., 1959, 2003–2005; (b) S. K. Sur, J. Magn. Reson., 1989, 82, 169–173.
- 12 R. S. Drago, *Physical Methods for Chemists*, Surfside Scientific Publishers, Gainesville, FL, 2nd edn, 1992.
- 13 D. Gong, B. Wang, H. Cai, X. Zhang and L. Jiang, J. Organomet. Chem., 2011, 696, 1584–1590.
- 14 D. Gong, B. Wang, C. Bai, J. Bi, F. Wang, W. Dong, X. Zhang and L. Jiang, *Polymer*, 2009, **50**, 6259–6264.
- 15 W. M. Reiff, N. E. Erickson and W. A. Baker Jr, *Inorg. Chem.*, 1969, 8, 2019–2021.
- 16 Y. Chen, R. Chen, C. Qian, X. Dong and J. Sun, *Organometallics*, 2003, 22, 4312–4321.
- (a) D. H. McDaniel and H. C. Brown, J. Org. Chem., 1958, 23, 420–427;
 (b) W. G. Herkstroeter, J. Am. Chem. Soc., 1973, 95, 8686–8691.
- 18 (a) T. Wang, G. Brudvig and V. S. Batista, J. Chem. Theory Comput., 2010, 6, 755–760; (b) T. Wang, G. Brudvig and V. S. Batista, J. Chem. Theory Comput., 2010, 6, 2395–2401.
- (a) C. P. Kelly, C. J. Cramer and D. G. Truhlar, J. Phys. Chem. B, 2007, 111, 408–422; (b) J. Sefcik and W. A. Goddard III, Geochim. Cosmochim. Acta, 2001, 65, 4435–4443.
- 20 (a) A. D. Becke, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1988, 38, 3098–3100; (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, 37, 785–789; (c) A. D. Becke, *J. Chem. Phys.*, 1993, 98, 5648–5652.
- 21 Jaguar, Schrodinger, LLC, New York, NY, Editon edn., 2010.
- 22 P. J. Hay and W. R. Wadt, J. Chem. Phys., 1985, 82, 299-310.
- (a) W. J. Hehre, R. Ditchfield and J. A. Pople, J. Chem. Phys., 1972, 56, 2257–2261; (b) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees and J. A. Pople, J. Chem. Phys., 1982, 77, 3654–3665.
- (a) T. H. Dunning Jr, J. Chem. Phys., 1989, 90, 1007–1023;
 (b) R. A. Kendall, T. H. Dunning Jr and R. J. Harrison, J. Chem. Phys., 1992, 96, 6796–6806;
 (c) D. E. Woon and T. H. Dunning Jr, J. Chem. Phys., 1994, 100, 2975–2988.
- 25 (a) D. J. Tannor, B. Marten, R. Murphy, R. A. Friesner, D. Sitkoff, A. Nicholls, M. Ringnalda, W. A. Goddard III and B. Honig, *J. Am. Chem. Soc.*, 1994, **116**, 11875–11882; (b) B. Marten, K. Kim, C. Cortis, R. A. Friesner, R. B. Murphy, M. N. Ringnalda, D. Sitkoff and B. Honig, *J. Phys. Chem.*, 1996, **100**, 11775–11788.
- 26 D. A. Edwards, S. D. Edwards, W. R. Martin, T. J. Pringle and P. Thornton, *Polyhedron*, 1992, **11**, 1569–1573.
- 27 J. Granifo, S. J. Bird, K. G. Orrell, A. G. Osborne and V. Sik, *Inorg. Chim. Acta*, 1999, **295**, 56–63.
- 28 Despite repeated attempts to obtain better elemental analysis data, the low oxidation potential of this compound resulted in lower than expected C and N values.