

## Electronically Flexible Ligands for Realizing the Cluster-Surface Analogy

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Characterization methods for metallic surfaces are limited. This has historically inspired the cluster-surface analogy, in which well-defined molecular cluster compounds are used to model heterogeneous catalysts.<sup>1</sup> Because of the large quantity of characterization methods available for homogeneous systems, studying homogenous complexes that mimic metal surfaces would allow for a better understanding of the activity of heterogeneous metallic catalysts. However, classical metal clusters are generally supported by strong-field ligands (carbonyls, phosphines and hydrides). These ligands lead to electronic structures that are poor mimics of metal surfaces. To this end, we envisioned that macrocycles with redox-active ligands would be excellent candidates for studying the cluster-surface analogy, since redox-active ligands are known to exhibit metal-like character in the way they bind to other metal centers.<sup>2</sup>

We have been particularly interested in the <sup>3</sup>PDI<sub>2</sub> macrocyclic ligands (Figure 1),<sup>3</sup> derived from pyridinediimine (PDI) moieties, which are well-established redox-active ligands used in polymer and organic synthesis. The <sup>3</sup>PDI<sub>2</sub> macrocycle is synthesized as a strontium complex via an alkaline earth metal templated [2+2] condensation reaction.<sup>4</sup> This complex can then be transmetallated to transition metals for further studies. Following the synthesis of a series of bimetallic complexes <sup>3</sup>PDI<sub>2</sub>M<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>(μ-Cl)(OTf)<sub>x</sub> ([M<sub>2</sub>Cl]<sup>x+</sup>, M = Fe, Co, Ni; x = 1, 2, 3), we observed unexpected variations in the metal-metal distances and the extent of reduction of the redox-active macrocycle (Figure 1). These prompted an investigation into the interdependence of M–M bonding and ligand-based redox-activity.<sup>5</sup>

The formal shortness ratio (FSR) is the distance between two metal centers divided by the sum of their atom radii. This parameter has been used for decades as a qualitative measure of the bond order between two metal centers. The FSR values of [M<sub>2</sub>Cl]<sup>x+</sup> complexes are listed in Table 1. The isoelectronic 34 e<sup>-</sup> species [Fe<sub>2</sub>Cl]<sup>+</sup> and [Co<sub>2</sub>Cl]<sup>3+</sup> show the smallest FSR values (1.138) across the series and are consistent with the presence of a metal-metal single bond. The one electron reduction of [Co<sub>2</sub>Cl]<sup>3+</sup> to form the 35 e<sup>-</sup> species [Co<sub>2</sub>Cl]<sup>2+</sup> results in a slight increase in FSR to 1.207. Further reduction to [Co<sub>2</sub>Cl]<sup>+</sup> (36 e<sup>-</sup>) results in a more drastic increase in FSR to 1.349. This trend suggests that the LUMO of [Co<sub>2</sub>Cl]<sup>3+</sup> contains significant Co-Co antibonding character. This antibonding orbital is singly occupied in [Co<sub>2</sub>Cl]<sup>2+</sup> and doubly occupied in [Co<sub>2</sub>Cl]<sup>+</sup> (Figure 2).

Interestingly, the added electrons also increase the extent of reduction of the <sup>3</sup>PDI<sub>2</sub> ligand. This may be inferred from the Δ value for each complex. The Δ value has been formulated by Wieghardt and coworkers to describe the oxidation state of the ligand based on characteristic bond lengths in the ligand's backbone.<sup>6</sup> Higher Δ values indicate less electron density on the ligand and *vice versa*. In this case, one-electron reduction of [Co<sub>2</sub>Cl]<sup>3+</sup> not only partially cleaves the Co–Co bond but also causes a change from a (<sup>3</sup>PDI<sub>2</sub>)<sup>1-</sup> to (<sup>3</sup>PDI<sub>2</sub>)<sup>1.5-</sup> oxidation state (Figure 1). This trend continues on reduction of [Co<sub>2</sub>Cl]<sup>2+</sup> to [Co<sub>2</sub>Cl]<sup>+</sup>, the latter of which exhibits a ligand-based oxidation state of (<sup>3</sup>PDI<sub>2</sub>)<sup>3-</sup>. These data indicate that the Co–Co (anti-)bonding system is heavily mixed with the redox-active manifold on the

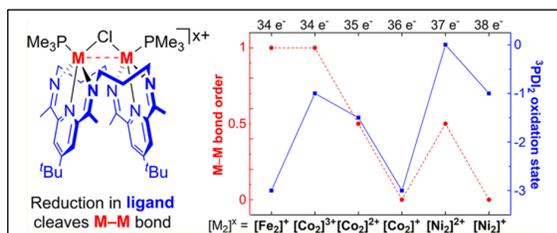


Figure 1.

Table 1. Selected calculated and experimental parameters of bimetallic complexes

Complex (EAN)	FSR		$\Delta / \text{\AA}$	
	Exp.	Calc.	Exp.	Calc.
[Fe <sub>2</sub> Cl] <sup>+</sup> (34 e <sup>-</sup> )	1.138	1.138	0.086	0.090
[Co <sub>2</sub> Cl] <sup>3+</sup> (34 e <sup>-</sup> )	1.138	1.127	0.134	0.122
[Co <sub>2</sub> Cl] <sup>2+</sup> (35 e <sup>-</sup> )	1.207	1.260	0.119	0.107
[Co <sub>2</sub> Cl] <sup>+</sup> (36 e <sup>-</sup> )	1.349	1.356	0.085	0.082
[Ni <sub>2</sub> Cl] <sup>2+</sup> (37 e <sup>-</sup> )	1.181	1.202	0.163	0.156
[Ni <sub>2</sub> Cl] <sup>+</sup> (38 e <sup>-</sup> )	1.397	1.392	0.138	0.134

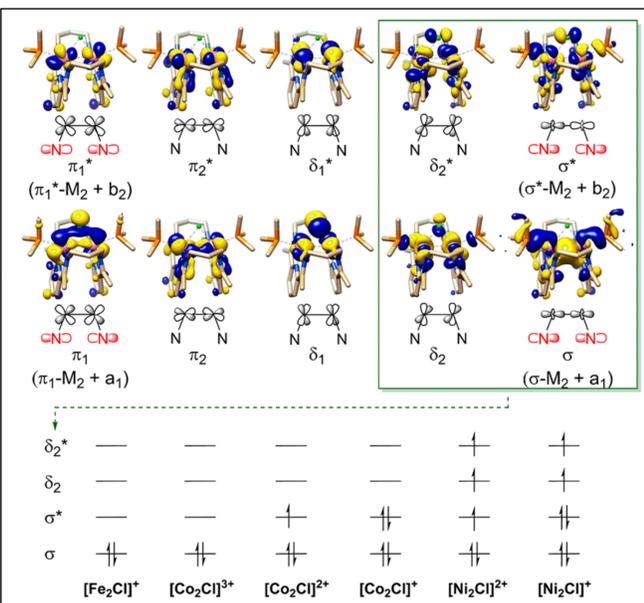


Figure 2. Valence manifold orbitals and occupation numbers.

<sup>3</sup>PDI<sub>2</sub> ligand. This conclusion was supported by DFT computational work, and the extension of this series to a pair of dinickel complexes further validated the electronic structure model (Figure 2).

Aside from bridging chloride complexes, we also discovered an interesting metal-metal interaction in a bridging thiophenolate complex, <sup>3</sup>PDI<sub>2</sub>Fe<sub>2</sub>(SPh)<sub>2</sub>(μ-SPh)(OTf) ([Fe<sub>2</sub>(SPh)<sub>3</sub>]<sup>+</sup>, Scheme 1).<sup>7</sup> The <sup>3</sup>PDI<sub>2</sub> ligand in [Fe<sub>2</sub>(SPh)<sub>3</sub>]<sup>+</sup> adopts a folded geometry much like that in [M<sub>2</sub>Cl]<sup>2+</sup>. The large FSR value of 1.259 for this complex is similar to that of [Co<sub>2</sub>Cl]<sup>+</sup> and [Ni<sub>2</sub>Cl]<sup>+</sup>, indicative of little Fe-Fe interaction, and the Δ value of 0.176 Å is consistent with neutral PDI moieties. At room temperature, the μ<sub>eff</sub> of [Fe<sub>2</sub>(SPh)<sub>3</sub>]<sup>+</sup> is 4.66 μ<sub>B</sub> by Evans' method, as expected for a quartet state, but SQUID data for the complex (Figure 3) revealed that [Fe<sub>2</sub>(SPh)<sub>3</sub>]<sup>+</sup> has a singlet ground state, as indicated by its effective magnetic moment of 0.80 μ<sub>B</sub> at 2 K.

The gradual increase of the effective magnetic moment with temperature is a result of the thermal population of one-or-more excited states with higher spin multiplicities. We envisioned that the two Fe(II) centers in [Fe<sub>2</sub>(SPh)<sub>3</sub>]<sup>+</sup> may be antiferromagnetically coupled in the singlet ground state, which could result in a shorter Fe-Fe distance. In its higher multiplicity states, however, the interaction between the iron centers would be disrupted, resulting in larger Fe-Fe distances. To investigate this hypothesis, we performed variable temperature crystallography studies (Figure 3). Indeed, VT-X-ray studies on [Fe<sub>2</sub>(SPh)<sub>3</sub>]<sup>+</sup> revealed an increase of the Fe-Fe distance from 3.1726(5) Å at 100K to 3.2344(8) Å at 250K.

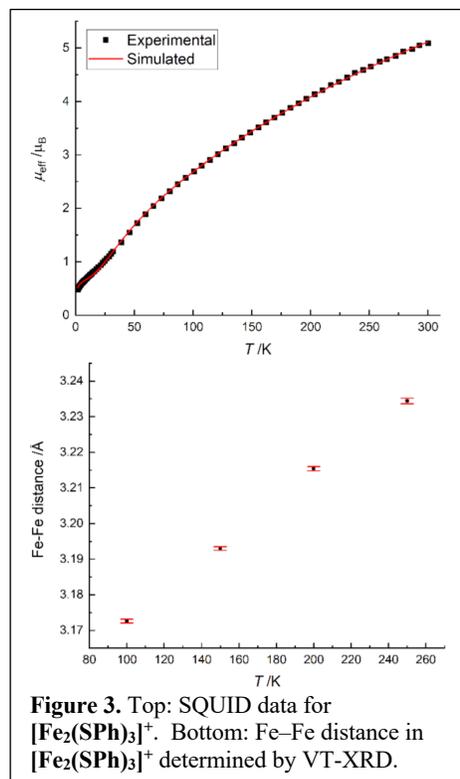
Finally, [Fe<sub>2</sub>(SPh)<sub>3</sub>]<sup>+</sup> was shown to be a member of a series of complexes that were used to highlight the geometric flexibility of the <sup>3</sup>PDI<sub>2</sub> ligand scaffold.<sup>7</sup> As shown in Scheme 1, the extent of ligand folding was controlled by substitution and reduction chemistry. This unique and dramatic variation in the geometry of the <sup>3</sup>PDI<sub>2</sub> ligand is currently under investigation for its ability to stabilize bridging atoms in a variety of geometries. These include bridging nitrides, carbides, and oxides – all of which have been proposed to play critical roles in surface-mediated catalytic cycles.

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**Figure 3.** Top: SQUID data for [Fe<sub>2</sub>(SPh)<sub>3</sub>]<sup>+</sup>. Bottom: Fe-Fe distance in [Fe<sub>2</sub>(SPh)<sub>3</sub>]<sup>+</sup> determined by VT-XRD.

