TRIS(THIOETHER)-SUPPORTED
BASE METAL COMPLEXES WITH REDOX-ACTIVE
DIOXOLENE AND α-DIIMINE LIGANDS

by

Peng Wang

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy with a major in Chemistry and Biochemistry

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ABSTRACT

The examination of transition metal complexes containing redox-active ligands such as \( \alpha \)-diimines and \( o \)-dioxolenes are important research topics due to their relevance to biochemistry, electronic functional materials and catalysis. They also provide interesting challenges for the comprehensive understanding of the electronic structures, which are of fundamental import to their reactivity.

In this context, tris(thioether)-supported \( \alpha \)-diiminato-iron complexes \([\kappa^2-\text{PhTt}^{tBu}]\text{Fe(AdNCHCHNAd)}\) (\(\text{PhTt}^{tBu} \equiv \text{phenyltris(}((\text{tert-butylthio})\text{methyl})\text{borate; Ad = adamantyl})\) and \([\kappa^2-\text{PhTt}^{tBu}]\text{Fe(CyNCHCHNCy)}\) (\(\text{Cy = cyclohexyl}\)) were prepared through reduction of \([\text{PhTt}^{tBu}]\text{FeCl}\) in the presence of \(\text{AdNCHCHNAd}\) and \(\text{CyNCHCHNCy}\), respectively. Both complexes were characterized by liquid injection field desorption ionization (LIFDI) mass spectroscopy, single crystal X-ray diffraction, \(^1\)H NMR spectroscopy, solution magnetic moment measurements, electronic spectroscopy, cyclic voltammetry (CV) and differential pulse voltammetry (DPV). In addition, \([\kappa^2-\text{PhTt}^{tBu}]\text{Fe(AdNCHCHNAd)}\) was also characterized by Mössbauer spectroscopy. The combined spectroscopic and magnetic data suggest \([\kappa^2-\text{PhTt}^{tBu}]\text{Fe(RNCHCHNR)}\) (\(R = \text{Ad or Cy}\)) are best described as high-spin ferrous complexes with antiferromagnetically coupled \( \alpha \)-diiminato \( \pi \)-radicals. This assignment is further supported by the single-point DFT calculations of \([\kappa^2-\text{PhTt}^{tBu}]\text{Fe(AdNCHCHNAd)}\) using the broken-symmetry (BS) approach. By comparing the structural and spectroscopic features of \([\kappa^2-\text{PhTt}^{tBu}]\text{Fe(AdNCHCHNAd)}\)
PhTt\textsuperscript{Bu}Fe(AdNCHCHNAd) to those of its isoelectronic analogue, $[\kappa^2$-PhTt\textsuperscript{Bu}Fe(AdNNNNAd)] prepared by M. T. Mock, it is further concluded that $[\kappa^2$-PhTt\textsuperscript{Bu}Fe(AdNNNNAd)] contains a high-spin ferrous center that is antiferromagnetically coupled to the dialkyltetraazadiene π-radical anion.

A series of tris(thioether)-supported metal iodide complexes $[\text{PhTt}^\text{Bu}]MI$ ($M = \text{Mn, Fe, Co, Ni}$) were prepared and characterized by LIFDI mass spectroscopy, X-ray crystallography, $^1$H NMR spectroscopy, magnetic measurements and electronic spectroscopy. In two representative cases, the iodide complexes are better synthetic precursors compared to the corresponding chloride analogues, due to iodide lability. First, $[\text{PhTt}^\text{Bu}]\text{CoI}$ was a better synthetic precursor compared to $[\text{PhTt}^\text{Bu}]\text{CoCl}$ in preparing $[\text{PhTt}^\text{Bu}]\text{Co}(3,5$-DBCatH). Second, $[\text{PhTt}^\text{Bu}]\text{FeI}$ reacted with CO in the presence of a reductant ($\text{KC}_8$) affording $[\text{PhTt}^\text{Bu}]\text{Fe(CO)}_2$, whereas $[\text{PhTt}^\text{Bu}]\text{FeCl}$ did not react with CO in the presence of $\text{KC}_8$.

Furthermore, $[\text{PhTt}^\text{Bu}]MI$ ($M = \text{Mn, Fe, Co, Ni}$) were utilized to generate $M^{\text{III}}$-semiquinonate complexes $[\text{PhTt}^\text{Bu}]M(\text{phenSQ})$ ($M = \text{Mn, Fe, Co, Ni}$) and $[\text{PhTt}^\text{Bu}]M(3,5$-DBSQ) ($M = \text{Co, Ni}$), interesting synthetic targets because of their relevance to the proposed or observed intermediates in the catalytic cycles of the catechol dioxygenases. These $M^{\text{III}}$-semiquinonate complexes were studied by comprehensive spectroscopic techniques in conjunction with the broken-symmetry DFT calculations. Interestingly, $[\text{PhTt}^\text{Bu}]\text{Co(phenSQ)}$ exhibited temperature-induced spin-crossover phenomenon, as supported by variable temperature X-ray diffraction analysis, variable temperature electronic spectroscopy, and variable temperature magnetic susceptibility measurements. $[\text{PhTt}^\text{Bu}]\text{Co}(3,5$-DBSQ) also exhibited spin-crossover behavior. However, its spin transition occurred at a higher temperature,
making [PhTt\textsubscript{Bu}]Co(3,5-DBSQ) stay mostly low-spin at room temperature. Reaction of [PhTt\textsubscript{Bu}]M(phenSQ) (M = Fe, Co) and [PhTt\textsubscript{Bu}]M(3,5-DBSQ) (M = Co, Ni) with O\textsubscript{2} was studied by \textsuperscript{1}H NMR, electronic and mass spectroscopies. [PhTt\textsubscript{Bu}]Fe(phenSQ) and [PhTt\textsubscript{Bu}]Co(3,5-DBSQ) exhibited O\textsubscript{2}-promoted intradiol cleavage. [PhTt\textsubscript{Bu}]Co(phenSQ) reacted with O\textsubscript{2} forming mostly the autoxidation product phenanthrenequinone (phenQ). [PhTt\textsubscript{Bu}]Ni(3,5-DBSQ) did not react with O\textsubscript{2}. It is thus concluded that the metal ion, the dioxolene ligands, and the spin state of the complex play vital roles in affecting the intradiol dioxygenase reactivity. Based on the \textsuperscript{1}H NMR, electronic, and mass spectroscopic data, plausible mechanisms are provided for the O\textsubscript{2} reactivity of [PhTt\textsubscript{Bu}]Fe(phenSQ) and [PhTt\textsubscript{Bu}]Co(phenSQ). O\textsubscript{2} addition to [PhTt\textsubscript{Bu}]Co(phenSQ) forms a Co\textsuperscript{III}-superoxo species. The thermal decay of this species led to the formation of phenQ instead of diphenic anhydride, an intradiol product, through one-electron oxidation of phenSQ. On the other hand, O\textsubscript{2} addition to [PhTt\textsubscript{Bu}]Fe(phenSQ) forms an Fe\textsuperscript{III}-superoxo species. The thermal decay of this species leads to the formation of phenQ and diphenic anhydride. The results provide the first direct experimental evidence that the Fe\textsuperscript{II}-semiquinonate species may be responsible for the intradiol reactivity.
Chapter 1

INTRODUCTION

The oxidation state assignment of a metal ion in a coordination environment has been a central theme in inorganic chemistry. Such assignment can help classify coordination compounds and explain and/or predict spectroscopic features, chemical stabilities, and reactivity patterns of the coordination compounds.\(^1,\)\(^2\) While in many cases the oxidation state assignment is straightforward and textbook procedures have been described,\(^3\) it is not intuitive nor obvious when the coordinated ligands are “redox-noninnocent” or “redox-active,” meaning that the ligands can access multiple oxidation levels.\(^1,\)\(^2\) In these cases the physical or spectroscopic oxidation state, which is directly associated with the d\(^{\text{n}}\) electron configuration is usually different from the formal oxidation state derived by counting covalent bonds and ionic charges. Thus, it is challenging for inorganic chemists to provide the best descriptions of the electronic structures of metal complexes with redox-active ligands.\(^1,\)\(^2\)

Besides raising challenges in determining the electronic structures of coordination compounds, redox-active ligands have also grown into an interesting design concept for catalysis research.\(^4\) Serving as electron or hole reservoirs, the redox-active ligands can enable multi-electron processes with earth-abundant transition metals such as iron and cobalt, making these metals function like noble metals.\(^5,\)\(^6\) It is also worth mentioning that such a catalyst design strategy is not uniquely associated with synthetic catalysts, but is also observed in some of the metalloenzyme that are able to promote multi-electron processes. For example, in the
catalytic cycle of cytochrome P-450, the highly oxidizing intermediate known as compound I is an Fe$^{IV}$ d$^4$ oxo with a one-electron-oxidized heme thiolate.$^7$ Compound I is a two-electron oxidizing reagent promoting C-H bond hydroxylation.$^7$ Incorporation of the heme thiolate ligand radical avoids reaching an unusual oxidation state of Fe (Fe$^V$) and lowers the activation barrier for the catalyst.

Inspired by the design of some metalloenzyme such as catechol dioxygenases where the combinations of redox-innocent ancillary ligands and redox-active ligands are found in the active-sites to achieve the enzymatic functions,$^{8-10}$ we initiated this research project aiming to synthesize new first-row transition metal complexes that involve a tris(thioether)borate ligand, [PhTt$^{tBu}$] (PhTt$^{tBu}$ = phenyltris((tert-butylthio)methyl)borate), as the ancillary ligand and a redox-active ligand. In this chapter, we describe our motivation behind these synthetic efforts. We also introduce a multitechnique approach that probes the electronic structures of transition metal complexes with redox-active ligands. As a demonstration, we examine one example in the literature where the multitechnique approach was used towards this goal.

1.1 Catechol Dioxygenases: Metalloenzymes Featuring Redox-Active Dioxolene Ligands

1.1.1 An Overview

We drew our inspiration for the synthetic work from a family of metalloenzymes called catechol dioxygenases.$^{8-10}$ They are found in a diverse range of soil bacteria and are responsible for the last step in the biodegradation of aromatic molecules in the environment.$^8$ These enzymes catalyze the oxidative cleavage of a
C=C double bond in a catechol molecule in the presence of O\textsubscript{2}.\textsuperscript{8} Based on the regioselectivity on the ring cleavage, catechol dioxygenases are split into two families: the intradiol catechol dioxygenases, which cleave the carbon-carbon bond of the enediol moiety, and the extradiol catechol dioxygenases, which cleave the carbon-carbon bond adjacent to the enediol, Scheme 1.1.\textsuperscript{8}

Scheme 1.1. Intradiol versus extradiol cleavage reaction.

1.1.2 Intradiol Catechol Dioxygenases and Model Complexes

Protein crystallography revealed that the substrate-bound form of the intradiol catechol dioxygenases contains a five-coordinate Fe\textsuperscript{III} center in the active site.\textsuperscript{11} Two histidines and one tyrosinate bind to the Fe\textsuperscript{III} center in a facial mode and the catecholate coordinates in a bidentate fashion as a dianion, Figure 1.1.\textsuperscript{8} Although the exact O\textsubscript{2} activation mechanism still remains controversial,\textsuperscript{12-16} it has been frequently proposed based on the redox activity of the catecholate ligand that the activity of this Fe\textsuperscript{III}-catecholate species contributes to the partial Fe\textsuperscript{II}-semiquinonate (SQ) character mixed in the ground state, which results in the formation of a Fe\textsuperscript{III}-alkylperoxy intermediate upon addition of O\textsubscript{2}, Scheme 1.2.\textsuperscript{8,13-17}
Figure 1.1. Active site of protocatechuate 3,4-dioxygenase (3,4-PCD) in the substrate-bound form.

Scheme 1.2. Proposed mechanism for the intradiol catechol dioxygenases.
Some of the evidence in support of the involvement of an Fe$^{II}$-semiquinonate state in the O$_2$ activation mechanism come from the study of synthetic model complexes. In the late 1980s and early 1990s, Que and co-workers reported systematic studies of a series of tripodal ligand supported Fe$^{III}$(3,5-DBC) complexes (3,5-DBC = 3,5-di-tert-butyl-catecholate), Figure 1.2. They found that by varying the supporting ligand so that the Lewis acidity of the ferric center was increased, the O$_2$ reactivity of the complex was enhanced. The highest reactivity was observed for [TPA]Fe$^{III}$(3,5-DBC) which afforded intradiol products in 98% yield. The increase in the Lewis acidity of the ferric center is correlated with the increase in the semiquinone character on the catecholate ligand, which is manifested by the decrease in the energy of catecholate-to-Fe$^{III}$ charge transfer bands and the increase in the redox potential of the 3,5-DBSQ/3,5-DBC couple. These results suggest that the electronic tautomeric state of the Fe$^{III}$-catecholate species, i.e. the Fe$^{II}$-semiquinonate state, is contributing to the intradiol reactivity of the model complexes.

Figure 1.2. Some tripodal ligands used by Que and coworkers in their studies of the synthetic models for the intradiol catechol dioxygenases.
Theoretical work is also supportive of an Fe$^{II}$-semiquinonate state mixing into the Fe$^{III}$-catecholate ground state. Recently, Sakaki and co-workers employed a multistate complete active space second-order perturbation theory (MS-CASPT2) to investigate a native intradiol dioxygenase and its functional models, Figure 1.3.\textsuperscript{18}

Figure 1.3. The active site of the protocatechuate 3,4-dioxygenase (a native intradiol catechol dioxygenase) and three model complexes based on the tripodal TPA ligand. The calculated weight of Fe$^{III}$-catecholate configuration in the ground state is labeled in red and the weight of Fe$^{II}$-semiquinonate configuration is labeled in blue.
They found that the MS-CASPT2 calculated LMCT energies agree well with the experimental values, suggesting that this method is excellent for calculating both the ground and excited states. Furthermore, they found that the ground state mainly consists of Fe\textsuperscript{III}-catecholate configuration and moderately of the Fe\textsuperscript{II}-semiquinonate configuration for both the enzyme active site and the model complexes. For those model complexes, the higher the weight of the Fe\textsuperscript{II}-semiquinonate configuration is, the higher O\textsubscript{2} reactivity it shows. These studies show that the Fe\textsuperscript{II}-semiquinonate configuration may be relevant to the intradiol cleavage reactivity of the enzyme and model complexes.

In spite of the implications that the Fe\textsuperscript{II}-semiquinonate state may be relevant for O\textsubscript{2} activation in the intradiol catechol dioxygenase and its model complexes, well characterized Fe\textsuperscript{II}-semiquinonate species are very rare. Recently, the Fiedler research group reported the isolations and characterizations of an mononuclear Fe\textsuperscript{II}-\textit{p}-semiquinonate complex,\textsuperscript{19} a semiquinonate-bridged dinuclear Fe\textsuperscript{II} complex,\textsuperscript{20} and a mononuclear Fe\textsuperscript{II}-(imino)benzosemiquinonate complex, Figure 1.4.\textsuperscript{21} In general, they attribute the successful stabilization of these species to the utilization of the tridentate Tp ligand (Tp = hydrotrispyrazolylborate), which allows the formation of five-coordinate iron centers. Compared to the tripodal ligand supported six-coordinate Fe\textsuperscript{III}-catecholate complexes, these five-coordinate Fe-dioxolene complexes favor the Fe\textsuperscript{II}-semiquinonate states over the Fe\textsuperscript{III}-catecholate states.\textsuperscript{21} The fact that they used \textit{p}-dioxolene or nitrogen-analogue of \textit{o}-dioxolene (\textit{o}-aminophenol) instead of \textit{o}-dioxolene may also contribute to their success. Nevertheless, since the Fe\textsuperscript{II}-\textit{o}-semiquinonate species is the most relevant to the intradiol dioxygenase and its model complexes, it is highly desirable to isolate and characterize such species.
A systematic study by Hikichi and co-workers highlights the challenge for stabilizing the Fe\textsuperscript{II}-o-semiquinonate species. They prepared a series of [Tp\textsuperscript{R2}]M(o-dioxolene) complexes (M = Fe, Mn, Co; R = iPr (M = Fe, Mn) or Me (M = Co)), Figure 1.5.\textsuperscript{22-24} They found that for M = Mn, Co the electronic structures of the complexes are best described as M\textsuperscript{II}-semiquinonate.\textsuperscript{23, 24} For M = Fe the electronic structure is best described as Fe\textsuperscript{III}-catecholate.\textsuperscript{22} Interestingly, the Fe\textsuperscript{III}-catecholate complex crystallizes as purple crystals in a pseudo-octahedral geometry with one acetonitrile molecule occupying the sixth position. Upon switching the solvent to toluene, a blue solution was obtained and a red shift of LMCT band in toluene (612 nm) vs. in acetonitrile (574 nm) was observed, suggesting that in toluene the complex
becomes five-coordinate and has more Fe\textsuperscript{II}-semiquinonate character than the six-coordinate analogue does.\textsuperscript{22}

Figure 1.5. Thermal ellipsoid plots for $[\text{Tp}^{i\text{Pr}2}]\text{M}(\text{o-dioxolene})$ (M = Fe, Mn) and $[\text{Tp}^{\text{Me}3}]\text{Co}(\text{o-dioxolene})$. $[\text{Tp}^{\text{Me}3}]\text{Co}(\text{o-dioxolene})$ is an analogue of $[\text{Tp}^{\text{Me}2}]\text{Co}(\text{o-dioxolene})$. All complexes crystallize with an acetonitrile molecule occupying the sixth position.

Despite of similar ligand environment and geometric structures, the $\text{O}_2$ reactivity patterns of $[\text{Tp}^{R2}]\text{M}(\text{o-dioxolene})$ complexes are quite different. The Fe analogue exhibits high reactivity towards both intradiol (33%) and extradiol (67%) cleavage reactions.\textsuperscript{22} The Mn analogue exhibits a low intradiol reactivity (10-12% intradiol product per mol of dioxolene)\textsuperscript{24} and the Co analogue has no catechol
cleavage reactivity. These results suggest the importance of the metal ion in effecting catechol dioxygenase reactivity. The observations of the metal ion effect in the extradiol catechol dioxygenases, however, contrast those observed in the model complexes (vide infra).

1.1.3 Extradiol Catechol Dioxygenases and Key Intermediates

The substrate-bound form of the extradiol catechol dioxygenase contains five-coordinate Fe$^{II}$ or Mn$^{II}$ in the active site, Figure 1.6. Its O$_2$ activation mechanism is analogous to many non-heme Fe$^{II}$ enzyme in which O$_2$ binds to the Fe$^{II}$ center to form a putative Fe$^{III}$-superoxo species. Electron transfer from the redox-active catecholate ligand to the Fe$^{III}$ center affords a superoxo-Fe$^{III}$-semiquinonate species which has been trapped crystallographically by Lipscomb and co-workers during the catalytic turnover. Interestingly, Lipscomb and co-workers have also shown that by substituting the Fe$^{II}$ center in the active site of the native enzyme with Mn$^{II}$ or Co$^{II}$ ions, comparable extradiol cleavage activities were obtained in spite of the differences in the redox potentials of these metal ions. These results suggest a universal mechanism for the extradiol dioxygenase, Scheme 1.3. The results also highlight that M$^{II}$-semiquinonate (M = Fe, Mn, Co) may be a common motif in the catalytic intermediates of the extradiol catechol dioxygenase.
Figure 1.6. Active site of 2,3-dihydroxybiphenyl 1,2-dioxygenase (BphC) in the substrate-bound form.

Scheme 1.3. Proposed mechanism for the native Fe$^{II}$ and Mn$^{II}$ or Co$^{II}$ substituted extradiol catechol dioxygenases.
1.2 Multitechnique Approach for the Study of Electronic Structures of Transition Metal Complexes with Redox-Active Ligands

As discussed earlier, reliable approaches are indispensable in understanding the electronic structures of transition metal complexes with redox-active ligands. A well recognized approach is the so-called multitechnique approach which includes a comprehensive study of the molecular structures, spectroscopic features, and magnetic properties. These experimental data are then to be used to guide and evaluate the state-of-the-art computational work, which affords the electronic structure descriptions of the transition metal complexes.

To demonstrate how such an approach can be used to determine the electronic structures, we examine herein a classic example from the Wieghardt laboratory in Germany. They studied a series of homoleptic bis(α-diimine)iron complexes using the multitechnique approach, Figure 1.7 (complexes 3, 5, 6). These complexes were previously described either as zerovalent iron complexes ($S = 1$) with two neutral α-diimine ligands or intermediate-spin ferrous complexes ($S = 1$) with a dianionic diamagnetic enediamide and a neutral diamagnetic α-diimine. For comparative purposes, Wieghardt and coworkers also studied well-defined high-spin ferrous complexes ($S = 2$) with neutral α-diimine ligands (complexes 2, 4) or monoanionic N-tert-butylquinolinolinamide ligand (complex 1).
Figure 1.7. Homoleptic bis(α-diimine)iron complexes (3, 5, 6), high-spin ferrous complexes (S = 2) with neutral α-diimine ligands (2, 4), and high-spin ferrous complex with monoanionic N-tert-butylquinolinylamide ligand (1) studied by Wieghardt and co-workers.

Scheme 1.4 contains the metric parameters derived from crystallographic studies, validated by DFT calculations, of Zn complexes for neutral α-diimine, monoanionic α-diiminato π-radical, and the dianionic diamide. These are the benchmark parameters for distinguishing among different oxidation levels of the α-diimine ligands. Figure 1.8 shows the high-quality crystal structures of complexes 1, 2 and 6. In complex 6, the average C–N distance is 1.342 Å which agrees nicely with the monoanionic α-diiminato π-radical description (C–N: 1.35 Å). Similarly, the average C–C distance at 1.408 Å also agrees excellently with the monoanionic π-radical description (C–C: 1.41 Å). The average Fe–N distance for 6 (2.02 Å) is intermediate between Fe$^{II}$–Namide distance (1.986 Å) for 1 and the average Fe$^{II}$–N distance (2.112 Å) for 2, consistent with the high-spin ferrous center in 6. Thus, the
metric parameter analysis suggests that the best description of the electronic structure of 6 is a high-spin ferrous complex with two monoanionic π-radical ligands.

Scheme 1.4. Metric parameters for α-diimine ligands at different oxidation levels.

Figure 1.8. Crystal structures of complexes 1, 2, 6.
Further, they collected the variable temperature variable field (VTVH) magnetic susceptibility data using SQUID susceptometer. The ground state for complexes 3, 5, 6 is $S = 1$ due to intramolecular antiferromagnetic coupling between the high-spin ferrous center and two $\alpha$-diiminato $\pi$-radicals. They also simulated the VTVH data and obtained the molecular zero-field splitting parameters $D_t$. Interestingly, when the molecular zero-field splitting parameters $D_t$ for complexes 3, 5 and 6 were converted to the intrinsic zero-field splitting parameters of the central iron ion $D_{Fe}$, they found that the values match very well with those of the well-define high-spin ferrous complexes 2 and 4. Therefore, it is further confirmed that complexes 3, 5 and 6 all have high-spin ferrous ions.

Mössbauer and electronic spectroscopies also help elucidate the electronic structures of the bis($\alpha$-diimine)iron complexes 3, 5 and 6. The isomer shift values of 3, 5 and 6 were observed in the narrow range 0.50–0.70 mm/s. These data point again to the presence of high-spin ferrous ions. Complexes 3, 5 and 6 all exhibit weak electronic absorptions between 1100 nm and 1320 nm. These absorption features were assigned as ligand-to-ligand charge transfer (LLCT) bands, which are absence in complexes 1, 2 and 4. Thus, these LLCT bands are considered to be a spectroscopic marker for the presence of two ligand-based $\pi$-radicals.

Finally, DFT calculations using the broken-symmetry (BS) approach were performed to further assess the experimentally derived electronic structure descriptions. These calculations are validated by the excellent match of the calculated structural and Mössbauer parameters with the experimental values. All different $S = 1$ models they calculated converged to the same isoenergetic and isostructural solution.
of the BS (4,2) minimum, indicating that four unpaired electrons on the ferrous center are antiferromagnetically coupled to two $\alpha$-diiminato $\pi$-radicals.$^{31}$

1.3 Summary and Research Proposal

In summary, due to the implications for the catalytic mechanisms of the intradiol and extradiol catechol dioxygenases, Fe$^{II}$-semiquinonate and other M$^{II}$-semiquinonate (M = Co, Mn, etc) species are very interesting synthetic targets. Previous synthetic work on the Tp system suggests that in order to stabilize Fe$^{II}$-semiquinonate species, five-coordinate geometries are preferred over six-coordinate geometries. Thus, we propose to use the tris(thioether)borate ligand, [PhTt$^{tBu}$], developed in this laboratory some twenty years ago.$^{34}$ This ligand provides a tridentate, truly soft donor set, i.e. high polarizability, that should stabilize the Fe$^{II}$-semiquinonate state over the Fe$^{III}$-catecholate state. Besides the redox-active dioxolene ligands, we are also interested in preparing [PhTt$^{tBu}$] supported Fe complexes with $\alpha$-diimine ligands. Reasons for making these molecules are detailed in Chapter 2.

Through close collaborations with spectroscopic and computational groups, we have been able to perform multitechnique spectroscopic and computational analyses on the compounds to elucidate their electronic structures.
Chapter 2

EXPERIMENTAL SECTION

2.1 General Procedures  All air and moisture sensitive reactions were performed either under N$_2$ using standard Schlenk techniques or carried out under an Ar or N$_2$ atmosphere in a Vacuum Atmospheres glovebox equipped with a gas purification system.

2.2 Materials

Unless otherwise noted, all reagents were purchased from commercial sources and were used without further purification. MnI$_2$ (anhydrous flakes) purchased from Sigma-Aldrich was a gift from Professor Louise Liable-Sands at Widener University. Anhydrous FeI$_2$ and CoI$_2$ were purchased from Strem Chemical. THF, diethyl ether, pentane, acetonitrile and toluene were dried by passing through activated alumina, sparged with N$_2$, and cannula transferred into bottles. THF and acetonitrile were further dried over 4 Å or 3 Å molecular sieves. Deuterated solvents were purchased from Cambridge Isotope Laboratories and stored over 4 Å molecular sieves. [PhTt$^{tBu}$]Tl, Tl(phenSQ), Tl(3,5-DBSQ), [PhTt$^{tBu}$]FeCl, [PhTt$^{tBu}$]Fe(PMe$_3$), [PhTt$^{tBu}$]CoCl, [PhTt$^{tBu}$]Co(PMe$_3$), AdN=CH-CH=NA and CyN-CH=CH-NCy were prepared following the published procedures. Tl(3,5-DBCatH) was prepared by reacting 3,5-DBCatH$_2$ (1.0 eq) with TlOEt (1.0 eq) in THF for 30 min, and then
removing solvent in vacuo. K(3,5-DBCatH) was prepared in situ by mixing KH (1.0 eq) and 3,5-DBCatH₂ (1.0 eq) in THF and stirring for 30 min.

2.3 Physical Methods

NMR spectra were recorded on a Bruker AVIII 400 spectrometer. Chemical shifts (δ) were referenced to residual protons in the deuterated solvent. FT-IR spectra were recorded Magna-IR ESP 560 spectrometer. Electronic absorption spectra were recorded on a Varian Cary 50 UV-vis spectrophotometer using screw-top quartz cuvettes with a 1-cm path length. Low temperature electronic absorption experiments were conducted using a Unisoku Scientific Instruments cryostat coupled to a Varian Cary 50 UV-vis spectrophotometer. Solution state magnetic moments were determined using the Evans method.³⁹⁻⁴¹ Liquid injection field desorption ionization (LIFDI) mass spectroscopy in positive ion mode, high resolution electron ionization (EI) mass spectroscopy and chemical ionization (CI) mass spectroscopy were performed on a Waters GCT Premier mass spectrometer.

In collaboration with Dr. Mohamed Saber and Professor Kim R. Dunbar, Texas A&M University, the static magnetic properties of [PhTt(Bu)]CoI, [PhTt(Bu)]Fe(phenSQ), [PhTt(Bu)]Ni(phenSQ), [PhTt(Bu)]Co(phenSQ), [PhTt(Bu)]Ni(3,5-DBSQ) and [PhTt(Bu)]Co(3,5-DBSQ) were measured on samples of crushed crystals using a Quantum Design MPMS-XL SQUID magnetometer operating in the temperature range, 1.8-400 K at 1000 Oe DC field. The data were corrected for the diamagnetic contribution using Pascal constants.

In collaboration with Professor Codrina V. Popescu, Colgate University, low-field (0.04 T), variable temperature (5 K–200 K) Mössbauer spectra were recorded on
a closed-cycle refrigerator spectrometer, model CCR4K, equipped with a 0.04 T permanent magnet, maintaining temperatures between 5 and 300 K. The samples consisted of solid powders (or crystalline material) suspended in nujol and placed in Delrin 1.00 mL cups, then frozen in liquid nitrogen. The isomer shifts are quoted at 5 K with respect to iron metal spectra recorded at 298 K. Mössbauer spectra were analyzed using the software WMOSS (Thomas Kent, SeeCo.us, Edina, MN), using equation (1), where the symbols have their standard definitions.

$$\hat{H}_Q = \frac{eQ_{zz}}{12} \left[ \tilde{I}_{z,l}^2 - \frac{15}{4} + \eta (\tilde{I}_{x,l}^2 - \tilde{I}_{y,l}^2) \right]$$  \hspace{1cm} (1)

In collaboration with graduate student Tian Qiu and Professor Joel Rosenthal, University of Delaware, electrochemistry was performed using a CHI-620D potentiostat/galvanostat under N₂ atmosphere. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed using a standard three-electrode configuration. The working electrode was a polished glassy carbon electrode (GCE, 3.0 mm diameter CH Instruments). The auxiliary electrode was a piece of platinum wire. The Ag/Ag⁺ couple was used as a reference electrode. Decamethylferrocene (Fc*, 1 mM) was used as the internal standard and all potentials were referenced to Fc⁺/Fc through the relationship of Fc⁺/Fc = 427 mV + Fc*+/Fc*. 
2.4 Computational Methods

2.4.1 Computational Details for Metal(II)-Semiquinonate Complexes

In collaboration with graduate student Mickie Killian and Professor Thomas C. Brunold, University of Wisconsin–Madison, computational models were generated for each M(II)SQ complex and analyzed against the available experimental data. Unless otherwise stated, initial atomic coordinates for each M(II)SQ model were imported from crystallographic data. Density functional theory (DFT) geometry optimizations and energy calculations were performed with the ORCA v. 2.9.0 or 2.9.1 software package developed by Dr. Frank Neese.\(^{42}\) In light of experimental magnetic susceptibility and electronic absorption data, both high-spin and low-spin M(II) models of each complex with a semiquinone radical ligand were considered and the multiplicity of the complex was specified, rather than metal and ligand oxidation states. Metal atoms and the immediately-ligated oxygen and sulfur atoms were described with Ahlrich’s polarized triple-\(\zeta\)-valence (TZVP)\(^{43}\) basis set, while the remaining atoms were modeled with the polarized split-valence (SVP) basis set.\(^{44}\) For each spin state, computations were carried out using the spin-unrestricted formalism and either Becke’s three-parameter hybrid functional for exchange along with the Lee-Yang-Parr functional for correlation (B3LYP)\(^ {45,46}\) or Becke’s functional for exchange along with Perdew’s functional for correlation (BP86).\(^ {47-49}\) Tight SCF convergence criteria were specified with an integration grid of 302 Lebedev points. Single point DFT and time-dependent DFT (TD-DFT) calculations were performed on the optimized geometries. The TD-DFT results were used to simulate absorption spectra, whereby each of the 40 computed transitions was modeled as a Gaussian band with a full width at half maximum of 1500 cm\(^{-1}\).
[PhTt\textsuperscript{Bu}]Fe(phenSQ)

Starting coordinates for the initial models of the [PhTt\textsuperscript{Bu}]Fe(phenSQ) complex were taken from X-ray crystallographic data. Because the magnetic susceptibility ($\mu_{\text{eff}} = 4.65(2) \mu_\text{B}$) and electronic absorption data indicate a high-spin metal center, the spin state of this complex was set to $S = 3/2$ (high-spin Fe(II) coupled antiferromagnetically to an SQ$^-$ ligand radical, models LFephenSQ1 [B3LYP] and LFephenSQ2 [BP86]). Because the LFephenSQ1 model converged to an unreasonable electronic structure, a third $S = 3/2$ model was generated using the optimized geometry and MO descriptions from LFephenSQ2 as the starting point for a geometry optimization with the B3LYP functional (model LFephenSQ3). Mössbauer parameters were derived for LFephenSQ3 from DFT calculations. The DFT calibration for the isomer shift in mm/s relative to $\alpha$-iron at 295 K (eq. 2) was performed using experimental data for a test set of molecules as was described previously.\textsuperscript{50}

$$\delta = \alpha (\rho_\text{o}-C)+\beta = -0.298 (\rho_\text{o} - 11580) + 1.118$$ (2)

Charge density at the iron nucleus, $\rho(0)$, for LFephenSQ3 from these calculations was 11581.097075, which after substitution yields $\delta$ value of 0.791 mm/s. The same DFT calculations yielded a quadrupole splitting, $\Delta E_Q$, of 2.486 mm/s.

[PhTt\textsuperscript{Bu}]Ni(phenSQ)

Starting coordinates for the initial models of the [PhTt\textsuperscript{Bu}]Ni(phenSQ) complex were taken from X-ray crystallographic data. Since the magnetic susceptibility measurement ($\mu_{\text{eff}} = 2.20 \mu_\text{B}$) indicates an $S = 1/2$ system, the spin state of the complex was $S = 1/2$ (high-spin Ni(II) coupled antiferromagnetically to an SQ$^-$ ligand radical or
low-spin Ni(II) coordinated by SQ\(^-\), models LNiphenSQ1 [B3LYP] and LNiphenSQ2 [BP86]). Because the LNiphenSQ1 model converged to an unreasonable electronic structure, a third \(S = 1/2\) model was generated using the optimized geometry and MO descriptions from LNiphenSQ2 as the starting point for a geometry optimization with the B3LYP functional (model LNiphenSQ3).

\[\text{[PhTt}^\text{Bu}]\text{Ni(DBSQ)}\]

Starting coordinates for models of the \([\text{PhTt}^\text{Bu}]\text{Ni(3,5-DBSQ)}\) complex were taken directly from the X-ray crystallographic data. The spin state of this complex was set to \(S = 1/2\) (high-spin Ni(II) coupled antiferromagnetically to an SQ\(^-\) ligand radical or low-spin Ni(II) coordinated by SQ\(^-\), models LNiDBSQ1 [B3LYP] and LNiDBSQ2 [BP86]). Because the LNiDBSQSQ1 model converged to an unreasonable electronic structure, a third \(S = 1/2\) model was generated using the optimized geometry and MO descriptions from LNiDBSQSQ2 as the starting point for a geometry optimization with the B3LYP functional (model LNiDBSQSQ3).

2.4.2 Computational Details for [κ2-PhTt^Bu]Fe(AdNCHCHNAd)

In collaboration with Professor Christopher C. Scarborough, Emory University, the ORCA program package\(^{51}\) was employed for all calculations. In each case, the TPSSh functional\(^{52}\) was employed in line with previous studies that identified this functional as particularly useful for calculation of Mössbauer parameters\(^{53}\). Alrichs all-electron basis\(^{43, 45, 46}\) sets were employed: triple-\(\zeta\)-quality basis sets with one set of polarization functions (TZVP) were applied to the iron atom and the atoms directly coordinated to it (sulfur and nitrogen); the remaining atoms were described by
slightly smaller polarized split-valence SVP basis sets that are double-\(\zeta\)- quality in the valence region and contain a polarizing set of d functions on the non-hydrogen atoms.\textsuperscript{45, 46} Auxiliary basis sets for the expansion of the electron density were chosen to match the orbital basis. The radial integration accuracy for all calculations was improved by setting the radial resolution parameters to 10 for the iron atoms and 5 for all other atoms. The SCF calculations were tightly converged (\(1 \times 10^{-8}\) E\(_h\) in energy, \(1 \times 10^{-7}\) E\(_h\) in the density change, and \(1 \times 10^{-7}\) in maximum element of the DIIS error vector). Unrestricted corresponding orbitals (UCOs)\textsuperscript{54} and quasi-restricted orbitals (QROs)\textsuperscript{55} (iso-electron density surfaces = \(95\%\)) were plotted with the program Molekel, version 5.4.\textsuperscript{56} Single-point calculations on the crystallographic geometry without truncation of the ligand were run, consistent with previous results demonstrating that single-point calculations on the crystal structure geometry, without ligand truncation, provided the best matches between experimental and theoretical Mössbauer parameters.\textsuperscript{57, 58}

The broken symmetry (BS) approach\textsuperscript{59-63} was employed to describe the computational results based on the following notation. The system was divided into two fragments. The notation BS(m,n) refers to a broken symmetry state with \(m\) unpaired \(\alpha\)-spin electrons largely localized on fragment 1 and \(n\) unpaired \(\beta\)-spin electrons largely localized on fragment 2, where fragments 1 and 2 correspond to the iron and the \(\alpha\)-diimine ligand, respectively. In this notation the standard high-spin, open-shell solution is written as BS(m + n,0). The BS(m,n) notation refers to the initial guess to the wave function. The variational process does, however, have the freedom to converge to a solution of the form BS(m – n,0) in which the \(n\) \(\beta\)-spin
electrons pair up with \( n < m \) \( \alpha \)-spin electrons on the partner fragment. Such a solution is then a standard \( M_s \approx (m - n)/2 \) spin-unrestricted Kohn-Sham solution.

Mössbauer isomer shift and quadrupole splitting (\( \delta \) and \( \Delta E_Q \), Table 2.1) were calculated using the TPSSh functional\(^{52} \) and the basis sets described above by applying the computed electron densities at the iron center as described previously.\(^{50} \) Satisfactory isomer shifts and quadrupole splittings were calculated using the TZVP basis set for iron; employing the CP(PPP) basis set for iron was not found to improve the results (Table 2.1).\(^{64, 65} \) The differences between experimental and computational values for the Mössbauer parameters are within acceptable limits.\(^{50, 64, 65} \)

<table>
<thead>
<tr>
<th>Basis set at Fe</th>
<th>( \delta ) (mm/s)</th>
<th>( \Delta E_Q ) (mm/s)</th>
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<tr>
<td>TZVP</td>
<td>0.45</td>
<td>-3.11</td>
</tr>
<tr>
<td>CP(PPP)</td>
<td>0.29</td>
<td>-3.74</td>
</tr>
</tbody>
</table>

Table 2.1. DFT-calculated Mössbauer parameters. Experimental values of \( \delta \) and \( \Delta E_Q \) are 0.60 mm/s and -4.03 mm/s, respectively.

2.5 Preparation of \([\kappa^2-\text{PhTt}^{\text{tBu}}]\text{Fe(RNCHCHNR)} \) (R = 1-adamantyl or cyclohexyl)

2.5.1 \([\kappa^2-\text{PhTt}^{\text{tBu}}]\text{Fe(AdNCHCHNAd)} \) (Ad = 1-adamantyl)

To the solution of \([\text{PhTt}^{\text{tBu}}]\text{FeCl} \) (147 mg, 0.3 mmol) in 1 mL THF and 30 mL diethyl ether was added \( \text{AdN}=\text{CHCH}=\text{NAd} \) (97 mg, 0.3 mmol) in small portions. A pink-purple precipitate was formed. The reaction mixture was stirred for 1 hr. \( \text{KC}_8 \) (45 mg, 0.33 mmol) was then added slowly into the reaction mixture over about 10 min. The color of the solution turned brown. After stirring for 3 hr, the mixture was filtered
through a pad of Celite and solvent was removed under vacuum. The residue was washed with pentane (2 × 4 mL), dissolved in 4 mL of benzene and passed through a small plug of APTS-coated silica gel to remove impurities. After removing benzene under vacuum, the residue was washed with pentane (2 × 2 mL) and dried under vacuum to obtain a yellow brown powder (84 mg, 36%). Single crystals suitable for X-ray crystallography were obtained by slow evaporation of the pentane/diethyl ether solution (v: v = 1: 1) of the product at room temperature. \(^1\)H NMR (C\(_6\)D\(_6\)): \(\delta\) 126.2 (s, NCH), 31.3 (s, Ad), 29.7 (s, Ad), 8.8 (br, C(CH\(_3\))\(_3\)S), 7.8 (s, (C\(_6\)H\(_3\))B), 6.9 (s, (C\(_6\)H\(_3\))B), 5.1 (s, Ad), 4.5 (s, Ad), 3.2 (s, C(CH\(_3\))\(_3\)S (free)), 1.4 (s, Ad), -1.3 (s, CH\(_3\)S\(_{\text{Bu}}\)), -11.2 (s, Ad), -11.5 (s, Ad). UV-vis (THF): \(\lambda_{\text{max}}\) (\(\varepsilon\), M\(^{-1}\) cm\(^{-1}\)) 289 (9748), 402 (7983), 456 (sh), 613 (380), 1007 (188). LIFDI-MS: \(m/z\) calcd. for C\(_{43}\)H\(_{70}\)BFeN\(_2\)S\(_3\) (M)\(^+\) 777.4144, found (M)\(^+\) 777.4152 (100%). \(\mu_{\text{eff}}\) (C\(_6\)D\(_6\)) = 3.9(1) \(\mu_B\).

2.5.2 \([\kappa^2-\text{PhTt}^{\text{Bu}}]\)Fe(CyNC\(_2\)HCH=NCy) (Cy = cyclohexyl)

To the solution of \([\text{PhTt}^{\text{Bu}}]\)FeCl (147 mg, 0.3 mmol) in 8 mL THF and 16 mL diethyl ether was added CyN=CHCH=NCy (66 mg, 0.3 mmol) in small portions. A dark blue solution was obtained. The reaction mixture was stirred for 1 hr. KC\(_8\) (45 mg, 0.33 mmol) was then added slowly into the reaction mixture over about 10 min. The color of the solution turned brown. After stirring for 3 hr, the mixture was filtered through a pad of Celite and solvent was removed under vacuum. The residue was washed with pentane (2 × 4 mL), dissolved in 4 mL of benzene and passed through a small plug of APTS-coated silica gel to remove impurities. After removing benzene under vacuum, the residue was washed with pentane (2 × 2 mL) and dried under vacuum to obtain a yellow brown powder (90 mg, 45%). Single crystals suitable for
X-ray crystallography were obtained by slow evaporation of a concentrated diethyl ether solution of the product at room temperature. $^1$H NMR (C$_6$D$_6$): $\delta$ 139.5 (s, NCH), 29.1 (s, Cy), 27.0 (s, Cy), 8.9 (br, C(CH$_3$)$_3$S), 7.9 (s, (C$_6$H$_5$)B), 6.8 (s, (C$_6$H$_5$)B), 5.2 (s, Cy), 2.6 (s, C(CH$_3$)$_3$S (free)), -1.1 (s, CH$_2$S$i$Bu), -8.5 (s, Cy), -9.9 (s, Cy). UV-vis (THF): $\lambda_{max}$ ($\varepsilon$, M$^{-1}$ cm$^{-1}$) 294 (8400), 401 (6816), 458 (sh), 615 (285), 984 (195). LIFDI-MS: m/z calcd. for C$_{35}$H$_{62}$BFeNS$_3$ (M)$^+$ 673.3518, found (M)$^+$ 673.3542 (100%). $\mu_{eff}$ (C$_6$D$_6$) = 3.9(1) $\mu_B$.

2.6 Preparation of [PhTt$^{ibu}$]MI (M = Fe, Mn, Ni and Co)

2.6.1 [PhTt$^{ibu}$]FeI

Anhydrous FeI$_2$ (310 mg, 1.0 mmol) was dissolved in 50 mL of CH$_3$CN. [PhTt$^{ibu}$]Tl (602 mg, 1.0 mmol) was added in small portions to the stirring solution of FeI$_2$. TlI precipitated immediately as a yellow solid and the color of the solution changed to pale yellowish brown. After stirring for 2 hr, the reaction mixture was filtered through Celite removing TlI and the solvent was removed in vacuo. The residue was extracted with pentane/diethyl ether (v:v = 10:1) and was filtered through Celite. Removing the solvent under reduced pressure afforded a pale green solid. Recrystallization by slow evaporation of the pentane solution afforded yellow crystals (87 mg, 15%). $^1$H NMR (C$_6$D$_6$): $\delta$ 14.6 (27H, br, C(CH$_3$)$_3$S), 14.2 (2H, s, m-(C$_6$H$_5$)B), 9.1 (1H, s, p-(C$_6$H$_5$)B), 8.2 (2H, s, o-(C$_6$H$_5$)B). UV-vis (THF): $\lambda_{max}$ ($\varepsilon$, M$^{-1}$ cm$^{-1}$) 264 (3620), 315 (3140), 368 (sh, 1730). FTIR (KBr): 3058, 3040, 2961, 2894, 2861, 1456, 1426, 1399, 1366, 1260, 1160, 1027, 951, 893, 869, 748, 700, 576, 506. LIFDI-MS: m/z calcd. for C$_{25}$H$_{38}$BFeS$_3$ (M)$^+$ 580.0627, found (M)$^+$ 580.0632 (100%). $\mu_{eff}$ (C$_6$D$_6$) = 5.35(3) $\mu_B$. 

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2.6.2 [PhTt^{tBu}]MnI

Anhydrous MnI$_2$ (309 mg, 1.0 mmol) was dissolved in 50 mL of CH$_3$CN. [PhTt^{tBu}]Tl (602 mg, 1.0 mmol) was added in small portions to the stirring solution of MnI$_2$. TlI precipitated immediately as a yellow solid. After stirring for 2 hr, the reaction mixture was filtered through Celite to remove TlI and the solvent was removed in vacuo. Extracting the colorless residue with pentane/diethyl ether (v:v = 5:1) followed by filtering through Celite afforded a colorless solution. Removing the solvent in vacuo afforded a white solid (498 mg, 86%). Slow evaporation of concentrated pentane/diethyl ether solution (v: v = 1: 1) provided colorless crystals suitable for X-ray crystallography. $^1$H NMR (C$_6$D$_6$): $\delta$ 22.5 (br, C(CH$_3$)$_3$S), 10.0 (br), 7.5 (s), 6.6 (s). FTIR (KBr): 3058, 3040, 2958, 2894, 2858, 1456, 1426, 1402, 1366, 1260, 1163, 1069, 1024, 945, 899, 869, 751, 703, 582, 506. LIFDI-MS: m/z calcd. for C$_{21}$H$_{38}$BMnIS$_3$ (M)$^+$ 579.0658, found (M)$^+$ 579.0652 (100%). $\mu_{eff}$ (C$_6$D$_6$) = 5.9(1) $\mu_B$.

2.6.3 [PhTt^{tBu}]NiI

Anhydrous NiI$_2$ (1.250 g, 4.0 mmol) was ground into a fine powder and suspended in 100 mL of THF. After stirring for 6 hr, [PhTt^{tBu}]Tl (1.204 g, 2.0 mmol) was added in small portions. After stirring for 16 hr, the reaction mixture was filtered through Celite to remove TlI and the solvent was removed in vacuo. The residue was extracted with pentane (2 $\times$ 40 mL) and the resulting red solution was filtered through Celite. Removing the solvent under reduced pressure afforded a brown solid. (919 mg, 69%) $^1$H NMR (C$_6$D$_6$): $\delta$ 15.2 (27H, br, C(CH$_3$)$_3$S), 11.1 (2H, s, $m$-(C$_6$H$_5$)B), 8.5 (2H,
s, o-(C₆H₅)B), 8.3 (1H, s, p-(C₆H₅)B). UV-vis (toluene): λ_max (ε, M⁻¹ cm⁻¹) 311 (1518), 375 (sh), 413 (sh), 452 (6036), 567 (972), 841 (427), 903 (432). Anal. Calcd. for C₂₁H₃₈BINiS₃: %C, 43.26; %H, 6.57. Found: %C, 43.50; %H, 6.80.

2.6.4  [PhTt₄Bu]CoI

Anhydrous CoI₂ (313 mg, 1.0 mmol) was dissolved in 50 mL of THF. [PhTt₄Bu]Tl (602 mg, 1.0 mmol) was added in small portions resulting in precipitation of a yellow solid, TII. After stirring for 6 hr, the reaction mixture was filtered through Celite separating TII. The solvent was then removed in vacuo affording a green solid (500 mg, 86%). Slow evaporation of a concentrated diethyl ether solution afforded green crystals suitable for X-ray crystallography. ¹H NMR (C₆D₆): δ 14.1 (27H, br, C(CH₃)₃S), 9.0 (1H, s, p-(C₆H₅)B), 7.4 (2H, s, m/o-(C₆H₅)B). UV-vis (THF): λ_max (ε, M⁻¹ cm⁻¹) 314 (3600), 369 (4070), 665 (sh), 712 (1410), 986 (412). FTIR (KBr): 3061, 3037, 2964, 2894, 2861, 1456, 1423, 1396, 1366, 1260, 1160, 1024, 948, 899, 866, 748, 706, 576, 503. LIFDI-MS: m/z calcd. for C₂₁H₃₈BCoIS₃ (M)+ 583.0610, found (M)+ 583.0637 (100%). μ_eff (C₆D₆) = 4.58(3) μ_B.

2.7  Synthetic Applications of [PhTt₄Bu]MI (M = Fe, Mn, Ni, Co)

2.7.1  Preparation of [PhTt₄Bu]Co(3,5-DBCatH)

A yellow solution of Tl(3,5-DBCatH) (94 mg, 0.22 mmol) in 40 mL THF was added dropwise to a stirring solution of [PhTt₄Bu]CoI (117 mg, 0.20 mmol) in 10 mL THF over 30 min, during which a yellow precipitate formed and the color of the solution changed from green to brown. The mixture was stirred for 6 hr and filtered
through a pad of Celite. Solvent was removed in vacuo and the residue was extracted with pentane. The pentane solution was filtered through a pad of Celite and the solvent was slowly removed in vacuo until 1-2 mL of solution was left in the vial. The solution was decanted and the orange-brown residue was dried under vacuum (67 mg, 49%). Cooling a concentrated diethyl ether/pentane solution to -30 °C provided orange crystals suitable for X-ray crystallography. \(^1\)H NMR (C\(_6\)D\(_6\)): \(\delta\) 15.7 (2H, s, \(m/o-(C_6H_5)B\)), 10.5 (27H, br, C(CH\(_3\))\(_3\)S), 9.7 (1H, s, \(p-(C_6H_5)B\)), 8.5 (2H, s, \(o/m-(C_6H_5)B\)), 4.8 (9H, s, 3/5-tBu), -2.1 (9H, s, 5/3-tBu), -43.6 (1H, s). UV-vis (THF): \(\lambda_{\text{max}}\) (\(\varepsilon\), M\(^{-1}\) cm\(^{-1}\)) 287 (8444), 336 (sh, 2437), 427 (2069), 565 (sh, 565), 664 (430), 718 (426), 792 (364). LIFDI-MS: \(m/z\) calcd. for C\(_{35}\)H\(_{59}\)BCoO\(_2\)S\(_3\) (M\(^+\)) 677.3102, found (M\(^+\)) 677.3073 (100%).

2.7.2 Preparation of [PhTt\(^{tBu}\)]Fe(CO)\(_2\)

This molecule was originally prepared and characterized by M. T. Mock.\(^{36}\) In an Ar-filled glovebox, 158 mg of [PhTt\(^{tBu}\)]FeI (0.272 mmol), 48 mg of KC\(_8\) (0.354 mmol), and 10 mL diethyl ether were added to a 50-mL Schlenk flask charged with a stir bar. The Schlenk flask was removed from the glovebox and the solution was degassed by two freeze-pump-thaw cycles. 1 atm of dry CO gas was transferred into the flask. The reaction mixture was stirred at -78 °C (dry ice-acetone bath) for 6 hr. Then, the reaction was warmed to room temperature and stirred overnight. Solvent was removed under vacuum and the Schlenk flask was brought into the glovebox. 20 mL of diethyl ether was added to the flask to extract the product and the solution was filtered through a pad of Celite. Diethyl ether was removed under vacuum to afford a brown solid, which was dissolved in 5 mL of benzene and passed through APTS-coated silica gel to remove impurities. Removing benzene under vacuum afforded an
orange-brown powder (78 mg, 56%). The $^1$H NMR spectrum of the product agreed with the previously reported $^1$H NMR spectrum of [PhTt$^{tBu}$]Fe(CO)$_2$.$^{36}$

2.7.3 Preparation of [PhTt$^{tBu}$]M(PhenSQ) (M = Fe, Mn, Ni, Co)

2.7.3.1 [PhTt$^{tBu}$]Fe(PhenSQ)

**Method A:** A suspension of Tl(PhenSQ) (43 mg, 0.10 mmol) in 20 mL THF was added dropwise to a stirring solution of [PhTt$^{tBu}$]FeI (60 mg, 0.10 mmol) in 10 mL THF. The addition lasted for 30-40 min, during which time a yellow precipitate formed and the color of the solution changed from light yellow to dark greenish brown. The mixture was stirred for 2-3 additional hr and filtered through Celite. Solvent was removed in vacuo and the residue was extracted with pentane/diethyl ether ($v:v = 1:1$). Filtering the solution through Celite followed by removing the solvent in vacuo yielded a dark greenish brown solid (65 mg, 95%). Cooling a concentrated diethyl ether/pentane solution to -30 °C provided yellow brown crystals suitable for X-ray crystallography. $^1$H NMR ($C_6D_6$): $\delta$ 115.6 (2H, br, C$_{14}H_8O_2$), 108.1 (2H, s, C$_{14}H_8O_2$), 20.4 (2H, s, m-(C$_6H_5$)B), 12.1 (2H, s, o-(C$_6H_5$)B), 11.4 (1H, s, p-(C$_6H_5$)B), -3.2 (27H, br, C(CH$_3$)$_3$S), -5.6 (2H, s, C$_{14}H_8O_2$), -13.0 (2H, s, C$_{14}H_8O_2$).

**UV-vis (THF):** $\lambda_{max}$ ($\varepsilon$, M$^{-1}$ cm$^{-1}$) 246 (28200), 268 (24900), 321 (5310), 401 (5230), 465 (sh), 496 (sh), 600 (868), 935 (539). **FTIR (KBr):** 3058, 3043, 2958, 2891, 1596, 1574, 1538, 1469, 1456, 1402, 1363, 1290, 1163, 1027, 951, 863, 757, 703, 576, 542. **LIFDI-MS:** $m/z$ calcd. for C$_{35}$H$_{46}$BFeO$_2$S$_3$ (M)$^+$ 661.2109, found (M)$^+$ 661.2100 (100%). $\mu_{eff}$ ($C_6D_6$) = 4.65(2) $\mu_B$. 

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**Method B:** 9,10-phenanthrenequinone (33 mg, 0.16 mmol) in 50 mL diethyl ether was added dropwise to a stirring solution of [PhTt$^{tBu}$]Fe(PMe$_3$) (83 mg, 0.16 mmol) in 20 mL of pentane over approximately 1 hr, during which time the color of the solution changed from blue to dark greenish brown. The reaction mixture was stirred an additional hr and the solvent was removed in vacuo. The solid residue was extracted with pentane and the solution was filtered through Celite. Removing the solvent under vacuum provided a dark greenish brown solid (68 mg, 65%).

2.7.3.2 [PhTt$^{tBu}$]Mn(PhenSQ)

A suspension of Tl(PhenSQ) (86 mg, 0.21 mmol) in 30 mL THF was added dropwise to a stirring solution of [PhTt$^{tBu}$]MnI (116 mg, 0.20 mmol) in 15 mL THF over 40 min, during which a yellow precipitate formed and the color of the solution changed from green to brown. The mixture was stirred for 2 more hr and filtered through Celite. Solvent was removed in vacuo and the residue was extracted with pentane/diethyl ether (v:v = 1:1). Filtering the solution through Celite followed by removing the solvent in vacuo yielded a brown solid (119 mg, 90%). Cooling a concentrated diethyl ether/pentane solution to -30 °C provided brown crystals suitable for X-ray crystallography. $^1$H NMR (C$_6$D$_6$): $\delta$ 12.8 (br, C(CH$_3$)$_3$S), 9.4 (br), 7.8 (br), -25.1 (br), -29.7 (br). UV-vis (THF): $\lambda_{max}$ ($\varepsilon$, M$^{-1}$ cm$^{-1}$) 257 (28300), 278 (31200), 310 (6130), 322 (8370), 408 (9020), 467 (sh), 500 (3350). FTIR (KBr): 3058, 2958, 2891, 2861, 1674, 1647, 1593, 1556, 1511, 1472, 1426, 1402, 1363, 1290, 1160, 1031, 954, 754, 710, 648, 580, 545. LIFDI-MS: $m/z$ calcd. for C$_{35}$H$_{46}$BMnO$_2$S$_3$ (M)$^+$ 660.2140, found (M)$^+$ 660.2155 (100%). $\mu_{eff}$ (C$_6$D$_6$) = 5.01(6) $\mu$B.
2.7.3.3 [PhTt\textsuperscript{Bu}]Ni(PhenSQ)

A suspension of Tl(PhenSQ) (83 mg, 0.20 mmol) in 30 mL THF was added dropwise over 20-30 min to a stirring solution of [PhTt\textsuperscript{Bu}]NiI (117 mg, 0.20 mmol) in 10 mL THF. A yellow precipitate gradually formed and the color of the solution turned from orange-red to purple. The mixture was stirred for 6 hr and then filtered through a pad of Celite. THF was removed in vacuo and the residue was washed with pentane (2 × 4 mL) and then extracted with pentane/diethyl ether (v: v = 1: 1). Filtering the extract through a Celite pad followed by removing the solvent in vacuo yielded a dark purple powder (106 mg, 80%). Slow evaporation of a concentrated pentane/diethyl ether (v: v = 2: 1) solution of the product yielded crystals suitable for X-ray diffraction analysis. \(^1\)H NMR (C\(_6\)D\(_6\)): \(\delta\) 52.6 (br), 9.4 (br, C(CH\(_3\))\(_3\)S), -4.1 (br). UV-vis (toluene): \(\lambda_{\text{max}}\) (\(\varepsilon\), M\(^{-1}\) cm\(^{-1}\)) 316 (9131), 398 (12877), 536 (11375), 586 (10011), 846 (710), 966 (sh). LIFDI-MS: \(m/z\) calcd. for C\(_{35}\)H\(_{46}\)BNiO\(_2\)S\(_3\) (M)\(^+\) 663.2113, found (M)\(^+\) 663.2093 (100%). \(\mu_{\text{eff}}\) (C\(_6\)D\(_6\)) = 2.20 \(\mu_B\). Anal. Calcd. for C\(_{35}\)H\(_{46}\)BNiO\(_2\)S\(_3\): \%C, 63.27; \%H, 6.98. Found: \%C, 63.31; \%H, 7.18.

2.7.3.4 [PhTt\textsuperscript{Bu}]Co(PhenSQ)

**Method A**: A suspension of Tl(PhenSQ) (74 mg, 0.18 mmol) in 30 mL THF was added dropwise to a stirring solution of [PhTt\textsuperscript{Bu}]CoI (100 mg, 0.17 mmol) in 15 mL THF over 40 min, during which a yellow precipitate formed and the color of the solution changed from green to orange-brown. The mixture was stirred for 2 more hr and then, filtered through Celite. Solvent was removed in vacuo and the residue was extracted with pentane/diethyl ether (v:v = 1:1). Filtering the solution through Celite followed by removing the solvent in vacuo yielded an orange-brown solid (102 mg,
89%). Cooling a concentrated diethyl ether/pentane solution to -30 °C provided green brown crystals suitable for X-ray crystallography. \(^1\)H NMR (C\(_6\)D\(_6\)): \(\delta \) 109.9 (2H, s, C\(_{14}\)H\(_8\)O\(_2\)), 101.4 (2H, s, C\(_{14}\)H\(_8\)O\(_2\)), 32.3 (2H, s, \(m\)-(C\(_6\)H\(_5\))B), 17.3 (2H, s, \(o\)-(C\(_6\)H\(_5\))B), 15.3 (1H, s, \(p\)-(C\(_6\)H\(_5\))B), 2.6 (2H, s, C\(_{14}\)H\(_8\)O\(_2\)), -11.3 (2H, s, C\(_{14}\)H\(_8\)O\(_2\)), -21.8 (27H, br, C(CH\(_3\))\(_3\)). UV-vis (THF): \(\lambda_{\text{max}} \right) / (\varepsilon, \text{M}^{-1} \text{cm}^{-1}) \) 257 (31800), 268 (32100), 393 (7830), 508 (7610), 683 (1310), 803 (1290). FTIR (KBr): 3061, 3046, 2958, 2922, 2891, 2864, 1671, 1590, 1574, 1469, 1447, 1390, 1363, 1341, 1299, 1260, 1160, 1108, 1036, 954, 869, 800, 751, 700, 663, 603, 566. LIFDI-MS: \(m/z \) calcd. for C\(_{35}\)H\(_{46}\)BCoO\(_2\)S\(_3\) (M)\(^+\) 664.2092, found (M)\(^+\) 664.2104 (100%). \(\mu_{\text{eff}} \right) \text{(C}_6\text{D}_6) = 3.43(3) \mu_B \). Anal. Calcd. for C\(_{35}\)H\(_{46}\)BCoO\(_2\)S\(_3\): \%C, 63.24; \%H, 6.98. Found: \%C, 62.88; \%H, 6.95.

**Method B:** 9, 10-phenanthrenequinone (33 mg, 0.16 mmol) in 50 mL diethyl ether was added dropwise to a stirring solution of [PhTt\(^{\text{tBu}}\)]Co(PMe\(_3\)) (84 mg, 0.16 mmol) in 20 mL of pentane over approximately 1 hr, after which the color of the solution changed from pale green to orange-brown. The reaction mixture was stirred an additional hour and the solvent was removed in vacuo. The solid residue was extracted with pentane and the solution was filtered through Celite. Removing the solvent provided an orange-brown solid (73 mg, 70%).

### 2.7.4 Preparation of [PhTt\(^{\text{tBu}}\)]M(3,5-DBSQ) (M = Ni, Co)

#### 2.7.4.1 [PhTt\(^{\text{tBu}}\)]Ni(3, 5-DBSQ)

A solution of Tl(3,5-DBSQ) (178 mg, 0.42 mmol) in 50 mL THF was added dropwise over 30 min to a stirring solution of [PhTt\(^{\text{tBu}}\)]Ni (233 mg, 0.40 mmol) in 20 mL diethyl ether. A yellow precipitate gradually formed and the color of the solution
turned from orange-red to red-purple. The mixture was stirred for 6 hr and then filtered through a pad of Celite. The solvent was removed in vacuo and the residue was extracted with pentane. Filtering the extract through Celite followed by removing the solvent in vacuo yielded a dark brown powder (230 mg, 85%). Slow evaporation of a concentrated pentane solution of the product yielded crystals suitable for X-ray diffraction analysis. $^1$H NMR (C$_6$D$_6$): $\delta$ 10.3 (sh), 9.2 (br, C(CH$_3$)$_3$S), -7.1 (br). UV-vis (toluene): $\lambda_{max}$ ($\epsilon$, M$^{-1}$ cm$^{-1}$) 300 (7328), 366 (sh), 460 (sh, 3057), 522 (5811), 566 (sh, 5040), 842 (823), 966 (sh). LIFDI-MS: m/z calcd. for C$_{35}$H$_{58}$BNiO$_2$S$_3$ (M)$^+$ 675.3052, found (M)$^+$ 675.3093 (100%). $\mu_{eff}$ (C$_6$D$_6$) = 2.25 $\mu$B

2.7.4.2 [PhTt$^{Bu}$]Co(3, 5-DBSQ)

A solution of Tl(3,5-DBSQ) (134 mg, 0.32 mmol) in 20 mL THF was added dropwise to a stirring solution of [PhTt$^{Bu}$]CoI (175 mg, 0.30 mmol) in 40 mL diethyl ether over 40 min, during which time a yellow precipitate formed and the color of the solution changed from green to dark reddish brown. The mixture was stirred for 2 more hr and filtered through Celite. Solvent was removed in vacuo and the residue was extracted with pentane. Filtering the solution through Celite followed by removing the solvent in vacuo yielded a dark reddish brown solid (182 mg, 90%). Cooling a concentrated pentane/toluene solution to -30 °C provided dark green brown crystals suitable for X-ray crystallography. $^1$H NMR (C$_6$D$_6$): $\delta$ 75.4 (6H, br, BCH$_2$), 30.5 (1H, s, 4/6-DBSQ-H), 21.3 (2H, s, m-(C$_6$H$_5$)B), 12.9 (2H, s, o-(C$_6$H$_5$)B), 11.7 (1H, s, p-(C$_6$H$_5$)B), 3.6 (9H, s, 3/5-DBSQ-C(CH$_3$)$_3$), -2.1 (9H, s, 3/5-DBSQ-C(CH$_3$)$_3$), -11.8 (27H, br, C(CH$_3$)$_3$S). UV-vis (THF): $\lambda_{max}$ ($\epsilon$, M$^{-1}$ cm$^{-1}$) 298 (9940), 495 (4120), 784 (5470). FTIR (KBr): 3063, 3041, 2959, 2893, 2862, 1578, 1523, 1462, 1394,
LIFDI-MS: \( m/z \) calcd. for C\(_{35}\)H\(_{58}\)BCoO\(_2\)S\(_3\) (M)\(^+\) 676.3030, found (M)\(^+\) 676.3026 (100\%). \( \mu_{\text{eff}}(\text{C}_6\text{D}_6) = 2.91(2) \mu_B \).

2.8 Reactivity of [PhTt\(^{tBu}\)]Fe(PhenSQ) with O\(_2\)

2.8.1 Reaction of [PhTt\(^{tBu}\)]Fe(PhenSQ) with O\(_2\) Monitored by Electronic Absorption Spectroscopy

In an Ar-filled glovebox, [PhTt\(^{tBu}\)]Fe(PhenSQ) (2.0 mg, 0.0030 mmol) was dissolved in 10 mL toluene. 3 mL of the solution was transferred to a cryostat UV-vis cuvette charged with a magnetic stir bar. The cuvette was sealed with a rubber septum and removed from the glovebox. With gentle stirring, the solution was exposed to a stream of dry O\(_2\) at -90 °C for 15 seconds. Spectra were collected every minute until no further spectral changes were observed at -90 °C. The temperature was then raised to 0°C for 5 min to monitor the time course of the thermal decay. After spectral changes ceased, the sample was cooled back to -90 °C to collect the spectrum of the final products.

2.8.2 Study of the [PhTt\(^{tBu}\)]Fe(PhenSQ) + O\(_2\) Intermediates and Products by LIFDI Mass Spectroscopy

In an Ar-filled glovebox, [PhTt\(^{tBu}\)]Fe(PhenSQ) (3.0 mg, 0.0045 mmol) was dissolved in 10 mL toluene. 4 mL of the solution was transferred to a 20-mL scintillation vial charged with a magnetic stir bar. The vial was then sealed with a rubber septum and removed from the glovebox. The solution was degassed by two freeze-pump-thaw cycles and the vial was then immersed in dry ice-acetone bath (-78
°C). With stirring, the solution was exposed to 1 atm of dry O₂ at -78 °C. The color of the solution changed from greenish brown to yellow brown. After 5 min, a LIFDI mass spectrum was collected on an aliquot of the solution at -78 °C. The solution was then warmed to room temperature and another LIFDI mass spectrum was taken.

2.8.3 Study of the Products of the Reaction of [PhTt(Bu)]Fe(PhenSQ) with O₂ by ¹H NMR Spectroscopy

In an Ar-filled glovebox, [PhTt(Bu)]Fe(PhenSQ) (30 mg, 0.045 mmol) was dissolved in 10 mL toluene in a 100 mL Schlenk flask charged with a stirring bar. The solution was removed from the glovebox and degassed by two freeze-pump-thaw cycles. Then, the flask was immersed in dry ice-acetone bath (-78 °C) and 1 atm of dry O₂ was added through a needle. The solution was stirred at -78 °C for 30 min and then, warmed to room temperature and stirred for 30 min (pressure of O₂ was released as the sample warmed-up). The solution was concentrated to 2-3 mL in vacuo and Na₂EDTA (19 mg, 0.051 mmol) in 10 mL H₂O was added to deligate the metal. After stirring the mixture for 10 min, 15 mL of H₂O was added and the sample was extracted with ethyl acetate (3 × 20 mL). The organic layer was combined and dried with anhydrous Na₂SO₄. The products were obtained after removing ethyl acetate in vacuo. The production of diphenic anhydride was confirmed by ¹H NMR spectroscopy in CDCl₃.
2.9 Reactivity of [PhTt\textsc{Bu}]Co(PhenSQ) with O\textsubscript{2}

2.9.1 Reaction of [PhTt\textsc{Bu}]Co(PhenSQ) with O\textsubscript{2} Monitored by Electronic Absorption Spectroscopy

In an Ar-filled glovebox, [PhTt\textsc{Bu}]Co(PhenSQ) (6.0 mg, 0.0090 mmol) was dissolved in 100 mL toluene. 3 mL of the solution was transferred to a cryostat UV-vis cuvette charged with a magnetic stir bar. The cuvette was sealed with a rubber septum and removed from the glovebox. With gentle stirring, the solution was exposed to a stream of dry O\textsubscript{2} at -90 °C for 15 seconds. Spectra were collected every minute until no further spectral changes were observed at -90 °C. The temperature was then raised to 20 °C for 10 min to monitor the time course of the ambient temperature decay. After spectral changes ceased, the sample was cooled back to -90 °C to collect the spectrum of the final products.

2.9.2 Study of the Intermediates and Products by LIFDI Mass Spectroscopy

In an Ar-filled glovebox, [PhTt\textsc{Bu}]Co(PhenSQ) (3.0 mg, 0.0045 mmol) was dissolved in 10 mL toluene. 4 mL of the solution was transferred to a 20-mL scintillation vial charged with a magnetic stirring bar. The vial was then sealed with a rubber septum and removed from the glovebox. The solution was degassed by two freeze-pump-thaw cycles and the vial was then immersed in dry ice-acetone bath (-78 °C). With stirring, the solution was exposed to 1 atm. of dry O\textsubscript{2} at -78 °C. The color of the solution changed from dark orange brown to yellow. After 5 min, LIFDI mass spectrum was collected on the solution sample at -78 °C. The solution was then warmed to room temperature and another LIFDI mass spectrum was taken.
2.9.3 Study of O$_2$ Binding and Release by [PhTt$^{tBu}$]Co(PhenSQ)

In an Ar-filled glovebox, [PhTt$^{tBu}$]Co(PhenSQ) (10.0 mg, 0.015 mmol) was dissolved in 100 mL toluene. 3 mL of the solution was transferred to a cryostat UV-vis cuvette charged with a magnetic stir bar. The cuvette was sealed with a rubber septum and removed from the glovebox. Electronic spectra were collected at both room temperature and -80 °C. With gentle stirring, the solution was exposed to a stream of dry O$_2$ at -80 °C for 1 min. The electronic spectrum was then collected. The cuvette was removed from the cryostat and immediately immersed in dry ice-acetone bath. Dry N$_2$ was bubbled through the solution for 4 min. Then the cuvette was warmed to room temperature under N$_2$ atmosphere and an electronic spectrum of the solution was collected at room temperature.

2.9.4 Examination of the Reaction of [PhTt$^{tBu}$]Co(PhenSQ) with O$_2$ by $^1$H NMR Spectroscopy

In an Ar-filled glovebox, [PhTt$^{tBu}$]Co(PhenSQ) (40 mg, 0.060 mmol) was dissolved in 10 mL THF in a 100 mL Schlenk flask charged with a stirring bar. The solution was removed from the glovebox and degassed by two freeze-pump-thaw cycles. Then, the flask was immersed in dry ice-acetone bath (-78 °C) and 1 atm of dry O$_2$ was added through a needle. The solution was stirred at -78 °C for 30 min and then, warmed to room temperature and stirred for 2 hr (pressure of O$_2$ was released as the sample warmed-up). The solution was concentrated to 2-3 mL in vacuo and Na$_2$EDTA (25 mg, 0.066 mmol) in 10 mL H$_2$O was added to deligate the metal. After stirring the mixture for 10 min, 15 mL of H$_2$O was added and the sample was extracted with ethyl ether (3 × 25 mL). The organic layers were combined and dried with anhydrous MgSO$_4$. The products were obtained after removing ethyl ether in
vacuo. The production of 9,10-phenanthrenequinone was confirmed by $^1$H NMR spectroscopy in CDCl$_3$. The NMR yield was calculated as 43% by comparison against a 9,10-phenanthrenequinone sample with TMS (0.05% v/v) as the internal standard.

2.10 Reaction of [PhTt$_{tBu}$]Co(3, 5-DBSQ) with O$_2$

2.10.1 O$_2$ Uptake by [PhTt$_{tBu}$]Co(3,5-DBSQ) Monitored by Electronic Absorption Spectroscopy

A UV-vis cuvette charged with a stir bar was stored in an oven overnight and brought into the glovebox. A stock solution containing 2 mg of [PhTt$_{tBu}$]Co(3,5-DBSQ) in 3 mL of THF was prepared in the glovebox. The cuvette and a 20-mL scintillation vial containing 10 mL dry THF were sealed with rubber septa. The O$_2$ saturated THF solution was prepared by bubbling dry O$_2$ through THF for 15 min at room temperature. Then, the cuvette was flushed with dry O$_2$ for 5 min and 2 mL of O$_2$-saturated THF was transferred into the cuvette. First, a background absorption spectrum of the O$_2$-saturated THF was collected at -80 °C. Then, a 0.1 mL stock solution of [PhTt$_{tBu}$]Co(3,5-DBSQ) in an air-tight syringe was added slowly to the UV-vis cuvette at -80 °C. Absorption spectra were collected at one minute intervals for 1 h. These absorption data were plotted on the same coordinate with the absorption data of [PhTt$_{tBu}$]Co(3,5-DBSQ) in THF at the same concentration under Ar.

2.10.2 Study of the Products by $^1$H NMR, GC-MS and High Resolution Mass Spectroscopy

To a solution of [PhTt$_{tBu}$]Co(3,5-DBSQ) (50 mg, 0.074 mmol) in 15 mL of THF was bubbled dry O$_2$ for 3 min at room temperature. The solution was stirred for 16 hr, during which time the color of the solution changed from dark reddish brown to
orange. The solution was concentrated to 2-3 mL in vacuo and 1M HCl (1 mL, 1.0 mmol) or Na₂EDTA (82 mg, 0.22 mmol) in 10 mL H₂O was added to liberate 3,5-DBSQ derived products. After stirring the mixture for 5 min, 15 mL of H₂O was added and the products were extracted with ethyl ether (3 × 25 mL). The organic layers were combined and dried with anhydrous MgSO₄. The products were obtained after removing ethyl ether in vacuo. The production of 3,5-di-tert-butyl muconic anhydride (an intradiol cleaving product) and 4,6-di-tert-butyl-2-phenylbenzo[1,3,2]dioxaborole (a catechol derived phenylboronic ester) was confirmed by ¹H NMR, GC-MS (EI) and high resolution mass spectrometries. An authentic sample of 4,6-di-tert-butyl-2-phenylbenzo[1,3,2]dioxaborole was prepared following the literature procedure.⁶⁶ The products were quantified by ¹H NMR spectroscopy (methyl tert-butyl ether was the internal standard). 3,5-di-tert-butyl muconic anhydride (16%): ¹H NMR (CDCl₃) δ 6.43 (1H, d, J = 1.2 Hz, 4-H), 6.13 (1H, d, J = 1.2 Hz, 6-H), 1.26 (9H, s, tBu), 1.15 (9H, s, tBu). CI-MS: calcd. for C₁₄H₂₁O₃ (M + H)⁺ 237.1491 m/z, found (M + H)⁺ 237.1509 m/z. 4,6-di-tert-butyl-2-phenyl-benzo[1,3,2]dioxaborole (4%): ¹H NMR (CDCl₃) δ 8.11 (2H, dd J₁ = 8 Hz, J₂ = 1.2 Hz), 7.57 (1H, m), 7.49 (2H, m), 7.25 (1H, d, J = 2 Hz), 7.10 (1H, d, J = 2 Hz), 1.52 (9H, s), 1.37 (9H, s). EI-MS: m/z calcd. for C₂₀H₂₅O₂B (M)⁺ 308.1951, found (M)⁺ 308.1963.

2.11 Reaction of [PhTtBu]Ni(3,5-DBSQ) with O₂

A UV-vis cuvette charged with a stir bar was baked overnight. A stock solution containing 2 mg of [PhTtBu]Ni(3,5-DBSQ) in 6 mL of THF was prepared in the glovebox. The cuvette and a 20-mL scintillation vial containing 10 mL dry THF were sealed with rubber septa. The O₂-saturated THF solution was prepared by
bubbling dry O\textsubscript{2} through THF for 15 min at room temperature. Then, the cuvette was flushed with dry O\textsubscript{2} for 5 min and 2 mL of O\textsubscript{2}-saturated THF was transferred into the cuvette. First, a background absorption spectrum of the O\textsubscript{2}-saturated THF was collected at -80 °C. Then, a 0.1 mL stock solution of \([\text{PhTt}^{\text{Bu}}]\text{Ni}(3,5\text{-DBSQ})\) in an air-tight syringe added slowly to the UV-vis cuvette at -80 °C. The absorption spectra were collected at one min intervals for 30 min after addition of \([\text{PhTt}^{\text{Bu}}]\text{Ni}(3,5\text{-DBSQ})\). The solution was warmed to room temperature for 12 h and cooled back to -80 °C for data collection on the final products. These absorption data were plotted on the same coordinate with the absorption data of \([\text{PhTt}^{\text{Bu}}]\text{Ni}(3,5\text{-DBSQ})\) in THF at the same concentration under Ar.

2.12 X-ray Crystallography

2.12.1 X-ray Structural Solution and Refinement

Crystals were mounted using viscous oil onto plastic mesh and cooled to the data collection temperature under a stream of N\textsubscript{2} unless noted otherwise. Data were collected on a Bruker-AXS APEX II CCD diffractometer with graphite-monochromated Mo-K\textsubscript{α} radiation (\(\lambda=0.71073 \ \text{Å}\)). Unit cell parameters were obtained from 36 data frames, 0.3° \(\omega\), from three different sections of the Ewald sphere. The data-sets were treated with SADABS absorption corrections based on redundant multiscan data.\textsuperscript{67} The structures were solved using direct methods and refined with full-matrix, least-squares procedures on \(F^2\). All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions with geometrically calculated positions and with \(U_{iso}\) equal to 1.2, or 1.5
2.12.2 Crystallographic Data Collection and Structural Determination

2.12.2.1 \( \kappa^2\text{-PhTt}^{tBu}\text{Fe(AdNCHCHNAd)} \) (Ad = 1-adamantyl)

Crystal data collection and refinement parameters are given in Table 2.2. Yellow brown blocks of \( \kappa^2\text{-PhTt}^{tBu}\text{Fe(AdNCHCHNAd)} \) were grown by slow evaporation of concentrated pentane/diethyl ether solution (v: v = 1: 1). The systematic absences in the diffraction data are consistent with the triclinic space group, \( P\bar{1} \).

2.12.2.2 \( \kappa^2\text{-PhTt}^{tBu}\text{Fe(CyNCHCHNCy)} \) (Cy = cyclohexyl)

Crystal data collection and refinement parameters are given in Table 2.2. Yellow brown blocks of \( \kappa^2\text{-PhTt}^{tBu}\text{Fe(CyNCHCHNCy)} \) were grown by slow evaporation of concentrated diethyl ether solution. The systematic absences in the diffraction data are consistent with the monoclinic space group, \( P2_1/c \). The asymmetric unit contains two symmetry independent molecules.

2.12.2.3 \( \text{PhTt}^{tBu}\text{FeI} \)

Crystal data collection and refinement parameters are given in Table 2.3. Light green blocks of \( \text{PhTt}^{tBu}\text{FeI} \) were grown by slow evaporation of concentrated pentane
solution. The systematic absences in the diffraction data are consistent with the orthorhombic space group, \textit{Pbca}.
2.12.2.4 [PhTtBu]MnI

Crystal data collection and refinement parameters are given in Table 2.3. Colorless blocks of [PhTtBu]MnI were grown by slow evaporation of concentrated pentane/diethyl ether solution (v: v = 1: 1). The systematic absences in the diffraction data are consistent with the orthorhombic space group, \textit{Pbca}.

2.12.2.5 [PhTtBu]NiI

Crystal data collection and refinement parameters are given in Table 2.4. Dark orange plates of [PhTtBu]NiI were grown by slow evaporation of concentrated pentane solution. The systematic absences in the diffraction data are consistent with the orthorhombic space group, \textit{Pbca}.

2.12.2.6 [PhTtBu]CoI

Crystal data collection and refinement parameters are given in Table 2.4. Green blocks of [PhTtBu]CoI were grown by slow evaporation of concentrated pentane/diethyl ether solution (v: v = 1: 1). The systematic absences in the diffraction data are consistent with the monoclinic space group, \textit{P2}_1/c.

2.12.2.7 [PhTtBu]Co(3,5-DBCatH)

Crystal data collection and refinement parameters are given in Table 2.5. Brown/blue blocks of [PhTtBu]Co(3,5-DBCatH) were grown by cooling a saturated pentane/diethyl ether solution to -30 °C. The systematic absences in the diffraction
data are consistent with the triclinic space group, \( P\bar{1} \). The asymmetric unit includes one diethyl ether molecule.

2.12.2.8 \([\text{PhTt}^{\text{Bu}}]\text{Fe(PhenSQ)}\)

Crystal data collection and refinement parameters are given in Table 2.6. Dark brown blocks of \([\text{PhTt}^{\text{Bu}}]\text{Fe(PhenSQ)}\) were grown by cooling a saturated pentane/diethyl ether solution (v: v = 1: 1) to -30 °C. The systematic absences in the diffraction data are consistent with the triclinic space group, \( P\bar{1} \).

2.12.2.9 \([\text{PhTt}^{\text{Bu}}]\text{Mn(PhenSQ)}\)

Crystal data collection and refinement parameters are given in Table 2.6. Dark metallic green blocks of \([\text{PhTt}^{\text{Bu}}]\text{Mn(PhenSQ)}\) were grown by cooling a saturated pentane solution to -30 °C. The systematic absences in the diffraction data are consistent with the monoclinic space group, \( C2/c \).

2.12.2.10 \([\text{PhTt}^{\text{Bu}}]\text{Ni(PhenSQ)}\)

Crystal data collection and refinement parameters are given in Table 2.7. Dark purple blocks of \([\text{PhTt}^{\text{Bu}}]\text{Ni(PhenSQ)}\) were grown by slow evaporation of concentrated pentane/diethyl ether solution (v: v = 2: 1). The systematic absences in the diffraction data are consistent with the monoclinic space group, \( P2_1/n \).
2.12.2.11 [PhTt<sup>1Bu</sup>]Co(PhenSQ)

Crystal data collection and refinement parameters are given in Table 2.7 (200 K) and Table 2.8 (100 K and 295 K). Dark orange blocks of [PhTt<sup>1Bu</sup>]Co(PhenSQ) were grown by cooling a saturated pentane solution to -30 °C. The systematic absences in the diffraction data are consistent with the monoclinic space group, *P*<sub>2</sub><sub>/n</sub>.

2.12.2.12 [PhTt<sup>1Bu</sup>]Ni(3,5-DBSQ)

Crystal data collection and refinement parameters are given in Table 2.9. Dark red blocks of [PhTt<sup>1Bu</sup>]Ni(3,5-DBSQ) were grown by slow evaporation of concentrated pentane solution. The systematic absences in the diffraction data are consistent with the monoclinic space group, *C*<sub>2</sub>/<em>c</em>.

2.12.2.13 [PhTt<sup>1Bu</sup>]Co(3,5-DBSQ)

Crystal data collection and refinement parameters are given in Table 2.9. Dark brown blocks of [PhTt<sup>1Bu</sup>]Co(3,5-DBSQ) were grown by cooling a saturated pentane/toluene solution (v: v = 20: 1) to -30 °C. The systematic absences in the diffraction data are consistent with the triclinic space group, *P*<sup>†</sup>. The asymmetric unit contains one pentane molecule.
Table 2.2. Crystallographic data for \([\kappa^2\text{-PhTt}^{\text{tBu}}]\text{Fe(AdNCHCHNAd)}\) and \([\kappa^2\text{-PhTt}^{\text{tBu}}]\text{Fe(CyNCHCHNCy)}\).

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Table 2.3. Crystallographic data for [PhTt\textsuperscript{Bu}]FeI and [PhTt\textsuperscript{Bu}]MnI.

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Table 2.4. Crystallographic data for [PhTt\textsuperscript{Bu}]NiI and [PhTt\textsuperscript{Bu}]CoI.

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Table 2.5. Crystallographic data for [PhTtBu]Co(3,5-DBCatH)∙Et₂O.

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Table 2.6. Crystallographic data for [PhTt\textsuperscript{Bu}]Fe(phenSQ) and [PhTt\textsuperscript{Bu}]Mn(phenSQ).

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<td>C\textsubscript{2}/c</td>
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<td>Density, Mg/m\textsuperscript{3}</td>
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Table 2.7. Crystallographic data for [PhTtBuNi(phenSQ)] and [PhTtBuCo(phenSQ)] at 200 K.

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<td>C\textsubscript{35}H\textsubscript{46}BCoO\textsubscript{2}S\textsubscript{3}</td>
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<td>200(2)</td>
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<td>Wavelength, Å</td>
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<td>0.71073</td>
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<td>(P2_1/n)</td>
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<td>(\beta), deg</td>
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<td>(\gamma), deg</td>
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Table 2.8. Crystallographic data for [PhTt\textsuperscript{tBu}]Co(phenSQ) at 100 K and [PhTt\textsuperscript{tBu}]Co(phenSQ) at 295 K.

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<td>C\textsubscript{35}H\textsubscript{46}BCoO\textsubscript{2}S\textsubscript{3}</td>
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<td>Formula Weight</td>
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<td>Temperature, K</td>
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Table 2.9. Crystallographic data for [PhTt\textsuperscript{Bu}]Ni(3,5-DBSQ) and [PhTt\textsuperscript{Bu}]Co(3,5-DBSQ)·(C\textsubscript{5}H\textsubscript{12}).

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<td>R(F), Rw(F)</td>
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Chapter 3
SYNTHESIS, MOLECULAR and ELECTRONIC STRUCTURES, and REDOX PROPERTIES of MONONUCLEAR IRON(II) α-DIIMINATO π-RADICAL COMPLEXES SUPPORTED BY A TRIS(THIOETHER) LIGAND

3.1 Introduction

Our interest in the iron complexes of α-diimine ligands originates from a previous discovery by M. T. Mock during his doctoral studies in this laboratory. Mock successfully isolated from the reaction of a monovalent iron(I) precursor ([PhTt\textsuperscript{Bu}Fe(PMe\textsubscript{3})]) and adamantyl azide a dialkyltetraazadiene iron complex, namely [κ\textsuperscript{2}-PhTt\textsuperscript{Bu}]Fe(AdNNNAd).\textsuperscript{36} The molecular structure of this complex features a pseudo-tetrahedral geometry at the iron center composed of two thioether sulfur donors from the borate ligand and two nitrogen donors from the dialkyltetraazadiene ligand, Figure 3.1.\textsuperscript{36} As a potentially redox non-innocent ligand, the dialkyltetraazadiene ligand (AdNNNAd) can be described alternatively as a neutral ligand, a monoanionic π-radical, or a dianion. The X-ray crystallographic data revealed that the three N–N bonds within the AdNNNAd moiety have quite similar bond lengths, Figure 3.1, indicating a highly delocalized electronic structure within the FeN\textsubscript{4} chelate ring. While resonance structures containing neutral (Figure 3.2 A) and dianionic (Figure 3.2 C) forms of the AdNNNAd ligand are expected to display distinct N–N bond lengths within the N\textsubscript{4} ring, the monoanionic form (Figure 3.2 B) features electron delocalization throughout the N\textsubscript{4} π-system. Furthermore, [κ\textsuperscript{2}-PhTt\textsuperscript{Bu}]Fe(AdNNNAd) exhibited a weak electronic absorption band at 950 (112 M\textsuperscript{-1}
Similar absorptions in the near-IR region were found in Trogler’s CpCo(RNNNR) anionic complexes\(^{36}\) and Holland’s \(L^Me\text{Fe(AdNNNAd)}\) \((L^Me = HC[C(Me)N(2,6-iPr_2C_6H_3)]_2)\),\(^{59}\) in which the tetraazadiene ligands are described as their radical anions. Therefore, based on the metric parameters of the AdNNNAAd ligand and electronic spectrum of the complex, the best description of the complex is a tetraazadiene \(\pi\)-radical anion ligated iron(II) complex, Figure 3.2 B.\(^{36}\)

Figure 3.1. Molecular structure of [\(\kappa^2\text{-PhTt}^{\text{Bu}}\)Fe(AdNNNAAd)] (left) and the key bond lengths (right).
Figure 3.2. Three resonance structures of $[\kappa^2\text{-PhTt}^\text{Bu}]\text{Fe(AdNNNA}_{\text{d}}\text{Ad})$: high-spin iron(I) with $(\text{N}_4\text{Ad}_2)^0$ (A), high-spin iron(II) with an antiferromagnetically coupled $\text{N}_4\text{Ad}_2$ radical anion (B), and intermediate-spin iron(III) with $(\text{N}_4\text{Ad}_2)^{2-}$ (C).

Despite of the preliminary analysis supporting the AdNNNA_{d} π-radical anion description, the lack of additional spectroscopic evidence, e.g. Mössbauer data, due to the intrinsic instability of $[\kappa^2\text{-PhTt}^\text{Bu}]\text{Fe(AdNNNA}_{\text{d}}\text{Ad})$ hampered a more detailed examination of its electronic structure. Furthermore, recent examples shown by Neidig and Milstein provide a cautionary note: The redox state of a potentially redox non-innocent ligand might not be correctly assigned using a single physical/spectroscopic method, such as X-ray crystallography.\textsuperscript{2, 70} Thus, to provide a further insight into the electronic structure of $[\kappa^2\text{-PhTt}^\text{Bu}]\text{Fe(AdNNNA}_{\text{d}}\text{Ad})$, and also in a broader sense to study tris(thioether)-supported iron complexes with redox non-innocent ligands, the synthesis of $[\kappa^2\text{-PhTt}^\text{Bu}]\text{Fe(RNCHCHNR)}$ where RNCHCHNR represents α-diimine ligands that are isoelectronic to the tetraazadiene ligands was targeted. Compared with the tetraazadiene analogues, the α-diimines are much more stable, and therefore, provide greater stability for the metal complexes permitting for more detailed analyses.
Similar to the tetraazaadiene ligands, the α-diimine ligands can access three different redox states: neutral α-diimines, monoanionic π-radicals and dianionic diamides, Figure 3.3. While iron(II) complexes containing neutral α-diimine ligands are well-known as radical polymerization catalysts of α-olefins, their reduced products, i.e., the formally iron(I) or iron(0) species containing one or two α-diimine ligands often cause ambiguity in determining the physical oxidation state of metal centers. In pioneering work, Wieghardt and co-workers used a combination of structural and spectroscopic methods in conjunction with broken-symmetry (BS) density functional theory (DFT) calculations to determine unambiguously the electronic structures of these reduced species. For example, they examined a series of homoleptic bis(α-diimine)iron complexes discovering that these previously described iron(0) complexes with two neutral α-diimine ligands or intermediate-spin iron(II) complexes with a dianionic diamagnetic enediamide and a neutral diamagnetic α-diimine are best described as high-spin iron(II) with two monoanionic α-diiminato π-radical ligands antiferromagnetically coupled to the metal center, Figure 3.3. Surprisingly, although a number of reduced mono(α-diimine)iron complexes with redox innocent ligands were reported in the literature, very few were interrogated using this multitechnique approach to understand their detailed electronic structures. As demonstrated by the recent work of Krüger and co-workers, these reduced mono(α-diimine)iron complexes may have interesting features such as spin-crossover property. Thus, it is worth efforts to synthesize reduced mono(α-diimine)iron complexes with tris(thioether)borate ligand and fully understand their electronic structures.
In this Chapter, the synthesis and molecular structures of two mono(α-diimine)iron complexes, namely \([\kappa^2\text{-PhTt}^{\text{Bu}}\text{Fe(AdNCHCHNAd)}\text{ (Ad = Adamantyl) and } [\kappa^2\text{-PhTt}^{\text{Bu}}\text{Fe(CyNCHCHNCy)}\text{ (Cy = Cyclohexyl) are described. Both complexes were characterized by single crystal X-ray diffraction, high-resolution LIFDI mass spectroscopy, }^1\text{H NMR spectroscopy, solution magnetic moment measurement (Evans Method), electronic absorption spectroscopy, cyclic voltammetry (CV) and differential pulse voltammetry (DPV). As a closer analogue of } [\kappa^2\text{-PhTt}^{\text{Bu}}\text{Fe(AdNNNNAd)}, [\kappa^2\text{-PhTt}^{\text{Bu}}\text{Fe(AdNCHCHNAd)}\text{ was characterized by Mössbauer spectroscopy. Single-point DFT calculations on the molecular structure of } [\kappa^2\text{-PhTt}^{\text{Bu}}\text{Fe(AdNCHCHNAd)}\text{ derived from X-ray diffraction studies using the broken-symmetry approach was conducted to gain further insights into its electronic structure. Structural and spectroscopic features of } [\kappa^2\text{-PhTt}^{\text{Bu}}\text{Fe(AdNCHCHNAd)}\text{ were compared to those of } [\kappa^2\text{-PhTt}^{\text{Bu}}\text{Fe(AdNNNNAd)}\text{ to further elucidate the electronic structures of both complexes.}

![Chemical structures](image)

Figure 3.3. Three redox forms of α-diimine ligands (top) and bis(α-diiminato) iron(II) complexes (bottom).
3.2 \([\kappa^2-\text{PhTT}^\text{Bu}]\text{Fe(RNCHCHNR)}\) (R = Adamantyl or Cyclohexyl)

3.2.1 Synthesis

\([\kappa^2-\text{PhTT}^\text{Bu}]\text{Fe(RNCHCHNR)}\) (R = Adamantyl or Cyclohexyl) were prepared by addition of 1 equiv. potassium graphite (KC\(_8\)) to a 1:1 mixture of \([\text{PhTT}^\text{Bu}]\text{FeCl}\) and \(\alpha\)-diimines in THF/diethyl ether, Scheme 3.1. Slow addition of \(\alpha\)-diimine AdN-CH=CH-NAd or CyN-CH=CH-NCy to the THF/diethyl ether solution of \([\text{PhTT}^\text{Bu}]\text{FeCl}\) caused a color change from pale yellow to purple (R = Ad) or blue (R = Cy). The color change indicated coordination of \(\alpha\)-diimines to the iron center. Subsequent reduction of the mixture by 1 equiv. of KC\(_8\) caused the color to change from purple (or blue) to orange brown. After removing the solvent under vacuum, a brown residue was obtained. This brown residue was washed with a small amount of pentane to remove bis(\(\alpha\)-diimine)iron by-products. The molecular structure of \((\text{CyNCHCHNCy})_2\text{Fe}\) is shown in Figure 3.4. The remainder of the residue was dissolved in benzene and passed through a plug of APTS-coated silica gel to remove impurities. Removing benzene under vacuum afforded \([\kappa^2-\text{PhTT}^\text{Bu}]\text{Fe(AdNCHCHNAd)}\) in 36% yield or \([\kappa^2-\text{PhTT}^\text{Bu}]\text{Fe(CyNCHCHNCy)}\) in 45% yield as yellow brown solids.

![Scheme 3.1. Synthesis of \([\kappa^2-\text{PhTT}^\text{Bu}]\text{Fe(RNCHCHNR)}\) complexes (R = Adamantyl or Cyclohexyl).](image-url)
3.2.2 Molecular Structures of $[\kappa^2$-PhTt\textsuperscript{Bu}]Fe(AdNCHCHNAd) and $[\kappa^2$-
PhTt\textsuperscript{Bu}]Fe(CyNCHCHNCy)

Thermal ellipsoid plots of the molecular structures of $[\kappa^2$
PhTt\textsuperscript{Bu}]Fe(AdNCHCHNAd) and $[\kappa^2$-
PhTt\textsuperscript{Bu}]Fe(CyNCHCHNCy) are shown in Figure
3.5 and Figure 3.6, respectively. Selected metric parameters of
$[\kappa^2$
PhTt\textsuperscript{Bu}]Fe(AdNCHCHNAd) and $[\kappa^2$-
PhTt\textsuperscript{Bu}]Fe(CyNCHCHNCy) are given in Table
3.1 and Table 3.2, respectively. Both complexes contain a pseudotetrahedral iron
center coordinated by two thioether sulfur donors from the $\kappa^2$-borate ligand and two
nitrogen donors from the $\alpha$-diimine ligands. The two planes, $\text{S1} \text{–Fe} \text{–S2}$ and
$\text{N1} \text{–Fe} \text{–N2}$ form a dihedral angle of 92.2° for $[\kappa^2$-
PhTt\textsuperscript{Bu}]Fe(AdNCHCHNAd) and 89.7° for $[\kappa^2$-
PhTt\textsuperscript{Bu}]Fe(CyNCHCHNCy). Notably, the tetraazadiene complex $[\kappa^2$
PhTt\textsuperscript{Bu}]Fe(AdNNNNAd) also adopts such coordination mode The average bond
distances of Fe–S1 and Fe–S2 for $[\kappa^2$-
PhTt\textsuperscript{Bu}]Fe(AdNCHCHNAd) and $[\kappa^2$
-PhTt\textsuperscript{Bu}]Fe(CyNCHCHNCy) are 2.325(1) Å and 2.327(1) Å, respectively. These
indistinguishable distances suggest that the electron densities on the iron centers are very similar. The S1–Fe–S2 bond angles for \([\kappa^2\text{-PhTt}^{\text{Bu}}]\text{Fe(AdNCHCHNAd)}\) and \([\kappa^2\text{-PhTt}^{\text{Bu}}]\text{Fe(CyNCHCHNCy)}\) are 93.84(2)° and 94.70(3)°, respectively, which are also very similar and consistent with the bite angle of the PhTt\text{Bu} ligand. The two nitrogen atoms and two carbon atoms from the \(\alpha\)-diimine ligands together with the iron center form a planar, 5-membered ring. The planarity of the ring is evident by the sum of the five dihedral angles, 539.8 (2)° for \([\kappa^2\text{-PhTt}^{\text{Bu}}]\text{Fe(AdNCHCHNAd)}\) and 539.5(2)° for \([\kappa^2\text{-PhTt}^{\text{Bu}}]\text{Fe(CyNCHCHNCy)}\). The average Fe–N bond distances are 1.974(2) Å for \([\kappa^2\text{-PhTt}^{\text{Bu}}]\text{Fe(AdNCHCHNAd)}\) and 1.970(3) Å for \([\kappa^2\text{-PhTt}^{\text{Bu}}]\text{Fe(CyNCHCHNCy)}\). The average Fe–N bond distance of 1.979(1) Å was found in Chirik’s iron-iron dimer \([\text{ArNC(Me)C(Me)NAr}]\text{Fe}\_2(\mu-\text{Cl})_2\) (Ar = 2,6-diisopropylphenyl),\(^{76}\) which was later described by Wieghardt as a high-spin diferrous complex coordinated by two \(\alpha\)-diiminato \(\pi\)-radicals.\(^{31}\) Similar Fe–N bond distances of all three complexes suggest that the iron centers in \([\kappa^2\text{-PhTt}^{\text{Bu}}]\text{Fe(AdNCHCHNAd)}\) and \([\kappa^2\text{-PhTt}^{\text{Bu}}]\text{Fe(CyNCHCHNCy)}\) are in the high-spin ferrous state and the \(\alpha\)-diimine ligands are in the monoanionic \(\pi\)-radical states.

The metric parameters that are most indicative of the redox state assignment of the \(\alpha\)-diimine ligands are the C–N and C–C bond distances within the \(\alpha\)-diimine moiety.\(^{31}\) In general, as summarized by Wieghardt, the three redox states of the \(\alpha\)-diimine ligands have distinct C–N and C–C bond distances as shown in Figure 3.5.\(^{31}\)
Figure 3.5. Typical C–N and C–C bond distances labeled in red (Å) for α-diimine ligands at three different redox states. A: neutral α-diimines; B: monoanionic π-radicals; C: dianionic diamides.

Taking these values as benchmarks, the average C–N bond lengths of 1.334(2) Å for [κ²-PhTtBu]Fe(AdNCHCHNAd) and 1.341(4) Å for [κ²-PhTtBu]Fe(CyNCHCHNCy) are consistent with α-diiminato π-radical monoanion description. Analogously, the C–C bond lengths of 1.395(3) Å for [κ²-PhTtBu]Fe(AdNCHCHNAd) and 1.395(4) Å for [κ²-PhTtBu]Fe(CyNCHCHNCy) also support this assignment. Overall, the metric parameters suggest that both compounds are mononuclear iron(II) complexes with α-diiminato π-radical ligands.

Finally, the structural parameters of [κ²-PhTtBu]Fe(AdNCHCHNAd) were compared to those of its isoelectronic analogue [κ²-PhTtBu]Fe(AdNNNNAd)³⁶ to gain insight into the electronic structures. The structure of [κ²-PhTtBu]Fe(AdNNNNAd) was compared to Holland’s tetraazadiene iron(II) complex L⁵⁶Fe(AdNNNNAd) (L⁵⁶ = HC[C(Me)N(2,6-iPr₂C₆H₃)]₂),⁶⁹ which was published the year after Mock et al. reported [κ²-PhTtBu]Fe(AdNNNNAd). Key comparative metric parameters are listed in Table 3.3. The average Fe–S bond lengths of [κ²-PhTtBu]Fe(AdNCHCHNAd) (2.325(1) Å) and [κ²-PhTtBu]Fe(AdNNNNAd) (2.299(1) Å) only differ by ca. 0.03 Å.
The average Fe–N bond lengths of \([\kappa^2\text{-PhTt}^{\text{Bu}}\text{Fe(AdNCHCHNAd)}]\) and \([\kappa^2\text{-PhTt}^{\text{Bu}}\text{Fe(AdNNNNAd)}]\) are also quite similar at 1.974(2) Å and 1.945(3) Å, respectively. These similarities among the metric parameters suggest that they have similar electronic structures, i.e. \([\kappa^2\text{-PhTt}^{\text{Bu}}\text{Fe(AdNNNNAd)}]\) is indeed best described as a tetraazadiene π-radical ligated iron(II) complex. The slightly shorter Fe–S and Fe–N bond lengths for \([\kappa^2\text{-PhTt}^{\text{Bu}}\text{Fe(AdNNNNAd)}]\) than those for \([\kappa^2\text{-PhTt}^{\text{Bu}}\text{Fe(RNCHCHNR)}\ (R = \text{Ad or Cy})]\) reflect the more electron-deficient FeII in \([\kappa^2\text{-PhTt}^{\text{Bu}}\text{Fe(AdNNNNAd)}]\). This is likely caused by the back-donation from FeII to AdNNNNAd π-radical which is greater in magnitude than the back-donation from FeII to RNCHCHNR π-radical. By comparing the three N–N bond lengths of \([\kappa^2\text{-PhTt}^{\text{Bu}}\text{Fe(AdNNNNAd)}]\) to those of Holland’s complex \(L^\text{Me}\text{Fe(AdNNNNAd)}\), which contains a well-characterized tetraazadiene π-radical ligated iron(II) complex, it was concluded that \([\kappa^2\text{-PhTt}^{\text{Bu}}\text{Fe(AdNNNNAd)}]\) contains a tetraazadiene π-radical anion.
Figure 3.6. Molecular structure of [κ²-PhTlBu]Fe(AdNCHCHNA)] with atom labeling. Thermal ellipsoids are drawn to 30% probability. Hydrogen atoms have been omitted for clarity.
Figure 3.7. Molecular structure of $[\kappa^2\text{-PhTt}^{\text{Bu}}]\text{Fe(CyNCHCHNCy)}$ with atom labeling. Thermal ellipsoids are drawn to 30% probability. Hydrogen atoms have been omitted for clarity.

Table 3.1. Selected bond lengths (Å) and bond angles (°) for $[\kappa^2\text{-PhTt}^{\text{Bu}}]\text{Fe(AdNCHCHNAAd)}$.

<table>
<thead>
<tr>
<th></th>
<th>Length (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe–S1</td>
<td>2.316(1)</td>
<td>S1–Fe–S2</td>
</tr>
<tr>
<td>Fe–S2</td>
<td>2.334(1)</td>
<td>N1–Fe–N2</td>
</tr>
<tr>
<td>Fe–N1</td>
<td>1.971(2)</td>
<td>N1–Fe–S1</td>
</tr>
<tr>
<td>Fe–N2</td>
<td>1.976(2)</td>
<td>N2–Fe–S1</td>
</tr>
<tr>
<td>N1–C11</td>
<td>1.336(2)</td>
<td>N1–Fe–S2</td>
</tr>
<tr>
<td>N2–C12</td>
<td>1.332(2)</td>
<td>N2–Fe–S2</td>
</tr>
<tr>
<td>C11–C12</td>
<td>1.395(3)</td>
<td>N1–C11–C12–N2</td>
</tr>
</tbody>
</table>
Table 3.2. Selected bond lengths (Å) and bond angles (°) for [κ²-PhTt(Bu)]Fe(CyNCHCHNCy).

<table>
<thead>
<tr>
<th></th>
<th>Length (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe–S1</td>
<td>2.327(1)</td>
<td>S1–Fe1–S2 94.70(3)</td>
</tr>
<tr>
<td>Fe–S2</td>
<td>2.327(1)</td>
<td>N2–Fe1–N1 85.29(11)</td>
</tr>
<tr>
<td>Fe–N1</td>
<td>1.970(3)</td>
<td>N1–Fe1–S1 125.45(8)</td>
</tr>
<tr>
<td>Fe–N2</td>
<td>1.969(2)</td>
<td>N2–Fe1–S1 117.94(8)</td>
</tr>
<tr>
<td>N1–C28</td>
<td>1.343(4)</td>
<td>N1–Fe1–S2 121.16(8)</td>
</tr>
<tr>
<td>N2–C29</td>
<td>1.339(4)</td>
<td>N2–Fe1–S2 114.23(8)</td>
</tr>
<tr>
<td>C28–C29</td>
<td>1.395(4)</td>
<td>N1–C28–C29–N2 -1.0(5)</td>
</tr>
</tbody>
</table>

Table 3.3. Selected bond lengths (Å) for [κ²-PhTt(Bu)]Fe(AdNCHCHNAd), [κ²-PhTt(Bu)]Fe(AdNNNNAd) and L^MeFe(AdNNNNAd).

<table>
<thead>
<tr>
<th></th>
<th>Selected Bond Lengths (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe–S</td>
</tr>
<tr>
<td>[κ²-PhTt(Bu)]Fe(AdNCHCHNAd)</td>
<td>2.316(1) 1.971(2)</td>
</tr>
<tr>
<td></td>
<td>2.334(1) 1.943(3)</td>
</tr>
<tr>
<td>[κ²-PhTt(Bu)]Fe(AdNNNNAd)</td>
<td>2.300(1) 1.971(2)</td>
</tr>
<tr>
<td></td>
<td>2.298(1) 1.943(3)</td>
</tr>
<tr>
<td>L^MeFe(AdNNNNAd)</td>
<td>N. A.</td>
</tr>
<tr>
<td></td>
<td>2.042(2)</td>
</tr>
</tbody>
</table>

3.2.3 Proton NMR Spectroscopy of [κ²-PhTt(Bu)]Fe(AdNCHCHNAd) and [κ²-PhTt(Bu)]Fe(CyNCHCHNCy)

The proton NMR spectra of both α-diiminato iron complexes exhibit broad, but well resolved paramagnetically-shifted resonances. Table 3.4 contains the proton NMR spectral data for [κ²-PhTt(Bu)]Fe(AdNCHCHNAd), [κ²-PhTt(Bu)]Fe(CyNCHCHNCy) and [κ²-PhTt(Bu)]Fe(AdNNNNAd) for comparative purposes. The tert-butyl groups of the ligated thioether arms from [κ²-PhTt(Bu)]Fe(AdNCHCHNAd), [κ²-PhTt(Bu)]Fe(CyNCHCHNCy) and [κ²-PhTt(Bu)]Fe(AdNNNNAd) shift the resonance to lower frequencies compared to the corresponding monometallic complexes.
PhTt\textsuperscript{tBu}Fe(AdNNNNAd) are located at δ 8.8, 8.9 and 10.6, respectively. The tert-butyl groups of the unligated thioether arms are located at δ 3.2 for [κ\textsuperscript{2}-PhTt\textsuperscript{tBu}]Fe(AdNCHCHNAd), δ 2.6 for [κ\textsuperscript{2}-PhTt\textsuperscript{tBu}]Fe(CyNCHCHNCy) and δ 1.2 for [κ\textsuperscript{2}-PhTt\textsuperscript{tBu}]Fe(AdNNNNAd). The phenyl protons of [κ\textsuperscript{2}-PhTt\textsuperscript{tBu}]Fe(AdNCHCHNAd) are assigned to the features at δ 7.8 and 6.9. The phenyl protons of [κ\textsuperscript{2}-PhTt\textsuperscript{tBu}]Fe(CyNCHCHNCy) are assigned to the features at δ 7.9 and 6.8. These resonances have similar δ as those of the phenyl protons of [κ\textsuperscript{2}-PhTt\textsuperscript{tBu}]Fe(AdNNNNAd), Table 3.4. Broad features at δ -1.3, -1.1 and -1.0 are assigned to the methylene protons of the PhTt\textsuperscript{tBu} ligands from [κ\textsuperscript{2}-PhTt\textsuperscript{tBu}]Fe(AdNCHCHNAd), [κ\textsuperscript{2}-PhTt\textsuperscript{tBu}]Fe(CyNCHCHNCy) and [κ\textsuperscript{2}-PhTt\textsuperscript{tBu}]Fe(AdNNNNAd), respectively. Similar chemical shift patterns were observed for the rest of the protons from AdNCHCHNAd, CyNCHCHNCy and AdNNNNAd ligands as well. Thus, the proton NMR spectroscopy suggests that all three complexes have similar electronic structures.
Table 3.4. Proton NMR spectral data for LFe(AdNCHNAAd), LFe(CyNCHNChNCy) and LFe(AdNNNNAd) ($L = \kappa^2$-PhTt${_{tBu}}$).

<table>
<thead>
<tr>
<th></th>
<th>Chemical Shift ($\delta$) in ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(t-butyl)S1,2</td>
</tr>
<tr>
<td>LFe(AdNCHNAAd)</td>
<td>8.8</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>LFe(CyNCHNChNCy)</td>
<td>8.9</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>LFe(AdNNNNAd)</td>
<td>10.6</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a *tert*-butyl groups of the ligated thioether arms.
b *tert*-butyl groups of the unligated thioether arms.
c The third proton signal from the phenyl group could not be clearly observed.

3.2.4 Mössbauer Spectroscopy of $[\kappa^2$-PhTt$^{tBu}]$Fe(AdNCHNAAd)

While the C–N and C–C bond lengths afford information about the redox states of the α-diimine ligands, $^{57}$Fe Mössbauer spectroscopy provides insight into the oxidation state of the iron center. As a closer isoelectronic analogue of $[\kappa^2$-PhTt$^{tBu}]$Fe(AdNNNNAd), $[\kappa^2$-PhTt$^{tBu}]$Fe(AdNCHNAAd) was subjected to the examination by $^{57}$Fe Mössbauer spectroscopy. Figure 3.8 shows the Mössbauer spectrum of $[\kappa^2$-PhTt$^{tBu}]$Fe(AdNCHNAAd) at 80 K in a magnetic field of 0.04 T. Table 3.5 contains the Mössbauer parameters for $[\kappa^2$-PhTt$^{tBu}]$Fe(AdNCHNAAd) and several relevant iron complexes for comparison.

$[\kappa^2$-PhTt$^{tBu}]$Fe(AdNCHNAAd) exhibited an isomer shift $\delta = 0.60$ mm/s and quadrupole splitting $\Delta E_Q = -4.03$ mm/s. The isomer shift is much larger than those of
the all S and N,S ligated iron(III) compounds in the literature (one example is given in Table 3.5). Thus, the possibility of an iron(III) oxidation state is ruled out. The high-spin iron(II) dimer \([\text{[PhTt}^{\text{Bu}}\text{FeCl}]_2\) \((S = 2)\) has an isomer shift \(\delta = 0.96(3)\) mm/s and quadrupole splitting \(\Delta E_Q = 3.45(5)\).\(^{36}\) whereas high-spin iron(I) complexes \((S = 3/2)\) \([\text{[PhTt}^{\text{Bu}}\text{Fe(PMe}_3)\text{]}\) and \([\text{[PhTt}^{\text{Bu}}\text{Fe(PhCCPh)}\text{]}\) have isomer shifts of \(\delta = 0.76(2)\) mm/s and \(\delta = 0.62(1)\) mm/s, respectively and quadrupole splittings \(\Delta E_Q = 1.88(2)\) mm/s and \(\Delta E_Q = 1.65(1)\) mm/s, respectively.\(^{36}\) An N,N bidentate ligand supported diferrous \([2\text{Fe}-2S]\) cluster has \(\delta = 0.79\) mm/s and \(\Delta E_Q = 2.67\) mm/s.\(^{81}\) Therefore, based on the Mössbauer data alone, the high-spin iron(II) and high-spin iron(I) scenarios for \([\kappa^2\text{-PhTt}^{\text{Bu}}\text{Fe(AdNCHCHNAd)}\]) cannot be distinguished.

![Mössbauer spectrum](image)

Figure 3.8. Mössbauer spectrum of a solid microcrystalline sample of \([\kappa^2\text{-PhTt}^{\text{Bu}}\text{Fe(AdNCHCHNAd)}\]) in nujol at 80 K in a magnetic field of 0.04 T. The hashed lines represent the raw data and the solid line is a result of the least-squares fit of the data.
Table 3.5. Mössbauer parameters for \([\kappa^2-\text{PhTt}^{(\text{Bu})}]\text{Fe(AdNCHCHNAd)}\) and some relevant sulfur-ligated iron complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\delta) (mm/s)</th>
<th>(\Delta Q) (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\kappa^2-\text{PhTt}^{(\text{Bu})}]\text{Fe(AdNCHCHNAd)})</td>
<td>0.60</td>
<td>-4.03</td>
</tr>
<tr>
<td>([\text{PhTt}^{(\text{Bu})}]\text{FeCl})</td>
<td>0.96(3)</td>
<td>3.45(5)</td>
</tr>
<tr>
<td>([\text{PhTt}^{(\text{Bu})}]\text{Fe(PMe}_3\text{)})</td>
<td>0.76(2)</td>
<td>1.88(2)</td>
</tr>
<tr>
<td>([\text{PhTt}^{(\text{Bu})}]\text{Fe(PhCCPh)})</td>
<td>0.62(1)</td>
<td>1.65(1)</td>
</tr>
<tr>
<td>{N,N}(^a) ligated diferrous [2Fe-2S]</td>
<td>0.79</td>
<td>2.67</td>
</tr>
<tr>
<td>{N,N}(^a) ligated diferric [2Fe-2S]</td>
<td>0.24</td>
<td>0.87</td>
</tr>
</tbody>
</table>

\(^a\)\{N,N\} = bidentate bis(benzimidazolato).

3.2.5 Magnetic Properties of \([\kappa^2-\text{PhTt}^{(\text{Bu})}]\text{Fe(AdNCHCHNAd)}\) and \([\kappa^2-\text{PhTt}^{(\text{Bu})}]\text{Fe(CyNCHCHNCy)}\)

Solution magnetic moments of \([\kappa^2-\text{PhTt}^{(\text{Bu})}]\text{Fe(AdNCHCHNAd)}\) and \([\kappa^2-\text{PhTt}^{(\text{Bu})}]\text{Fe(CyNCHCHNCy)}\) were measured by the Evans Method. Both complexes exhibit \(\mu_{\text{eff}}\) (C\(_6\)D\(_6\)) = 3.9(1) \(\mu\text{B}\). This value is that of the spin-only value (3.87 \(\mu\text{B}\)) for \(S = 3/2\), \(g = 2.0\) system, suggesting strong antiferromagnetic coupling between the high-spin Fe\(^{II}\) ion and the \(\alpha\)-diiminato \(\pi\)-radical.

3.2.6 Single-Point DFT Calculations of \([\kappa^2-\text{PhTt}^{(\text{Bu})}]\text{Fe(AdNCHCHNAd)}\)

In order to gain further insights into the electronic structure of \([\kappa^2-\text{PhTt}^{(\text{Bu})}]\text{Fe(AdNCHCHNAd)}\), single-point DFT calculations on the crystal structure geometry of \([\kappa^2-\text{PhTt}^{(\text{Bu})}]\text{Fe(AdNCHCHNAd)}\) were performed with the ORCA program package using the broken-symmetry approach, TPSSh functional, TZVP basis set for iron and iron-bound nitrogen and sulfur atoms and SVP basis set for all other atoms. The Mössbauer parameters were predicted based on the solution and compared to the experimental ones to evaluate the accuracy of the computation. As shown in Table 3.6, the calculated isomer shift (\(\delta = 0.45\) mm/s) and quadrupole
splitting ($\Delta E_Q = -3.11$ mm/s) match reasonably well with the experimental values ($\delta = 0.60$ mm/s, $\Delta E_Q = -4.03$ mm/s), indicating that the DFT model is effective in describing the electronic structure of $[\kappa^2$-PhTt$^{\text{tBu}}]$Fe(AdNCHCHNAd).

Table 3.6. Experimental and DFT calculated Mössbauer parameters for $[\kappa^2$-PhTt$^{\text{tBu}}]$Fe(AdNCHCHNAd).

<table>
<thead>
<tr>
<th></th>
<th>$\delta$ (mm/s)</th>
<th>$\Delta E_Q$ (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>0.45</td>
<td>-3.11</td>
</tr>
<tr>
<td>Experimental</td>
<td>0.60</td>
<td>-4.03</td>
</tr>
</tbody>
</table>

The qualitative molecular orbital (MO) diagram derived from the current model is shown in Figure 3.9. It shows that there are four unpaired spin-up electrons and one electron pair localized on the iron-based MOs, in accord with the high-spin ($S = 2$) ferrous assignment. There is also one unpaired spin-down electron on the $\pi^*$ orbital of the $\alpha$-diimine ligand. The spin-down electron interacts with one of the spin-up electrons on the iron-based MO (mostly composed of $d_{xy}$ orbital), with overlap $S = 0.57$ (the range of $S$ is 0–1), leading to strong antiferromagnetic coupling ($J = -788$ cm$^{-1}$) between the high-spin iron(II) and the $\alpha$-diiminato $\pi$-radical and an overall $S = 3/2$ ground state.
Figure 3.9. Qualitative MO diagram of the spectroscopically-validated DFT model with a broken-symmetry BS(4, 1) solution.
3.2.7 Electronic Absorption Spectroscopy of $[\kappa^2$-PhTt$^{tBu}$]Fe(AdNCHCHNAd) and $[\kappa^2$-PhTt$^{tBu}$]Fe(CyNCHCHNCy)

While the previously discussed spectroscopic methods such as NMR, EPR and Mössbauer spectrosopies interrogate the electronic ground state, electronic absorption spectroscopy probes the electronic excited states. Figure 3.10 contains the electronic absorption spectra of $[\kappa^2$-PhTt$^{tBu}$]Fe(AdNCHCHNAd) (blue) and $[\kappa^2$-PhTt$^{tBu}$]Fe(CyNCHCHNCy) (red).

![Electronic absorption spectra of $[\kappa^2$-PhTt$^{tBu}$]Fe(AdNCHCHNAd) (blue) and $[\kappa^2$-PhTt$^{tBu}$]Fe(CyNCHCHNCy) (red) in THF.](image)

Both complexes exhibit multiple electronic absorption features. The energies of the transitions for $[\kappa^2$-PhTt$^{tBu}$]Fe(AdNCHCHNAd) overlap extremely well with those for $[\kappa^2$-PhTt$^{tBu}$]Fe(CyNCHCHNCy), indicating that they have electronic excited
states whose energies are close to one another. High-energy absorption features at 289 (9748 M⁻¹ cm⁻¹) nm for [κ²-PhTt²Bu]Fe(AdNCHCHNAd) and 294 (8400) nm for [κ²-PhTt²Bu]Fe(CyNCHCHNCy) are assigned to Fe←Sthioether LMCT bands. These assignments are based on the fact that [κ²-PhTt²Bu]Fe(AdNNNNAd) exhibited similar absorption feature at 280 (5900 M⁻¹ cm⁻¹) nm that was assigned to Fe←Sthioether LMCT band. The absorption features at 402 (7983 M⁻¹ cm⁻¹) nm and 456 (sh) nm for [κ²-PhTt²Bu]Fe(AdNCHCHNAd) as well as 401 (6816) and 458 (sh) nm for [κ²-PhTt²Bu]Fe(CyNCHCHNCy) are likely associated with charge transfer transitions within the (α-diiminato)Fe moiety. Similar absorption features were also observed for a bis(α-diiminato)iron(II) complex [iPrNC(Ph)CHNiPr]₂Fe at 441 nm (6000 M⁻¹ cm⁻¹) and 515 nm (2000). Notably, the analogous iron(II) complex [iPrNC(Ph)CHNiPr]FeCl₂ with a neutral α-diimine ligand lacks these intense charge transfer bands, suggesting that these CT transitions are characteristic of the α-diiminato π-radical ligands. Again, similar absorption features are observed for [κ²-PhTt²Bu]Fe(AdNNNNAd) at 367 nm (4280 M⁻¹ cm⁻¹) and 413 nm (2200), consistent with the presence of a tetraazadiene π-radical. Finally, the low intensity features at 1007 (188 M⁻¹ cm⁻¹) nm for [κ²-PhTt²Bu]Fe(AdNCHCHNAd), 984 (195 M⁻¹ cm⁻¹) nm for [κ²-PhTt²Bu]Fe(CyNCHCHNCy), and 950 (112 M⁻¹ cm⁻¹) nm for [κ²-PhTt²Bu]Fe(AdNNNNAd) are evidences for the presence of ligand based π-radicals as well. Similar characteristic bands were also observed in bis(α-diiminato)iron(II) complexes.
3.2.8 Cyclic voltammetry and differential pulse voltammetry of \([\kappa^2-PhTt^{Bu}]Fe(AdNCHCHNAd)\) and \([\kappa^2-PhTt^{Bu}]Fe(CyNCHCHNCy)\)

The redox properties of \([\kappa^2-PhTt^{Bu}]Fe(AdNCHCHNAd)\) and \([\kappa^2-PhTt^{Bu}]Fe(CyNCHCHNCy)\) were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Figure 3.11 and Figure 3.12 contain the DPVs and CVs, respectively. Table 3.7 contains the values of the redox potentials.

![Figure 3.11. Differential pulse voltammograms of \([\kappa^2-PhTt^{Bu}]Fe(AdNCHCHNAd)\) (left) and \([\kappa^2-PhTt^{Bu}]Fe(CyNCHCHNCy)\) (right) complexes. The potentials are referenced to the Fe^+/Fc couple.](image)

Table 3.7. Reduction and oxidation potentials (V) of \([\kappa^2-PhTt^{Bu}]Fe(AdNCHCHNAd)\) and \([\kappa^2-PhTt^{Bu}]Fe(CyNCHCHNCy)\) measured by differential pulse voltammetry.

<table>
<thead>
<tr>
<th></th>
<th>Reduction potential (V)</th>
<th>Oxidation potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\kappa^2-PhTt^{Bu}]Fe(AdNCHCHNAd))</td>
<td>-2.16</td>
<td>-0.61, -0.10</td>
</tr>
<tr>
<td>([\kappa^2-PhTt^{Bu}]Fe(CyNCHCHNCy))</td>
<td>-2.09</td>
<td>-0.63, -0.09</td>
</tr>
</tbody>
</table>

The DPV reduction events occurred at -2.16 V and -2.09 V for \([\kappa^2-PhTt^{Bu}]Fe(AdNCHCHNAd)\) and \([\kappa^2-PhTt^{Bu}]Fe(CyNCHCHNCy)\), respectively. These
events are manifested in the CV traces as reversible redox couples at $E_{1/2} = -2.19$ V for $[\kappa^2$-PhTt$_{Bu}$]Fe(AdNCHCHNA) and $E_{1/2} = -2.14$ V for $[\kappa^2$-PhTt$_{Bu}$]Fe(CyNCHCHNCy). The DPV traces also show two consecutive oxidation events for each complex. The first oxidations at -0.61 V for $[\kappa^2$-PhTt$_{Bu}$]Fe(AdNCHCHNA) and -0.63 for $[\kappa^2$-PhTt$_{Bu}$]Fe(CyNCHCHNCy) are assigned to the neutral α-diimine/monoanionic α-diiminato radical redox couples. These assignments are based on the thermodynamic considerations of the fact that formally tetrahedral mononuclear (α-diimine)iron(II) complexes exist as (neutral α-diimine)iron(II) instead of (monoanionic α-diiminato)iron(III). The second oxidations at -0.10 V for $[\kappa^2$-PhTt$_{Bu}$]Fe(AdNCHCHNA) and -0.09 V for $[\kappa^2$-PhTt$_{Bu}$]Fe(CyNCHCHNCy) are assigned to the iron(III)/iron(II) redox couples. Both the first and second oxidation events for $[\kappa^2$-PhTt$_{Bu}$]Fe(AdNCHCHNA) and $[\kappa^2$-PhTt$_{Bu}$]Fe(CyNCHCHNCy) are irreversible, as shown by their CV traces.
Figure 3.12. Cyclic voltammograms of LFe(AdNCHCHNAd) (blue) and LFe(CyNCHCHNCy) (red) complexes (L = [κ²-PhTt^Bu]). The potentials are referenced to Fe⁺/Fc couple.

3.3 Conclusions

Tris(thioether)-supported α-diiminato-iron complexes [κ²-PhTt^Bu]Fe(AdNCHCHNAd) (Ad = Adamantyl) and [κ²-PhTt^Bu]Fe(CyNCHCHNCy) (Cy = Cyclohexyl) were prepared through reduction of [PhTt^Bu]FeCl in the presence of AdNCHCHNAd and CyNCHCHNCy, respectively. Both complexes were characterized by LIFDI mass spectroscopy, single crystal X-ray diffraction, ¹H NMR spectroscopy, solution magnetic moment measurements (Evans Method), electronic spectroscopy, cyclic voltammetry (CV) and differential pulse voltammetry (DPV). In addition, [κ²-PhTt^Bu]Fe(AdNCHCHNAd) was also characterized by Mössbauer...
spectroscopy. The combined spectroscopic and magnetic evidence suggests $[\kappa^2$-PhTt$^{\text{Bu}}]$Fe(RNCHCHNR) (R = Ad or Cy) being high-spin ferrous complexes with an antiferromagnetically coupled α-diiminato π-radical. This assignment is further corroborated by single-point DFT calculations on the structure of $[\kappa^2$-PhTt$^{\text{Bu}}]$Fe(AdNCHCHNAd) using the broken-symmetry (BS) approach. The structural and spectroscopic features of $[\kappa^2$-PhTt$^{\text{Bu}}]$Fe(AdNCHCHNAd) were compared to those of its isoelectronic analogue, $[\kappa^2$-PhTt$^{\text{Bu}}]$Fe(AdNNNNAd), the latter of which was prepared by M. T. Mock. Such comparison led to the same conclusion that was drawn by M. T. Mock et al.: $[\kappa^2$-PhTt$^{\text{Bu}}]$Fe(AdNNNNAd) contains a high-spin ferrous center that is antiferromagnetically coupled to the dialkyltetraazadiene π-radical anion.
Chapter 4
SYNTHESIS, CHARACTERIZATION AND SOME REACTIVITY of [PhTt\textsuperscript{tBu}] LIGAND SUPPORTED IRON, MANGANESE, NICKEL and COBALT IODIDE COMPLEXES

4.1 Introduction

Transition metal halide and pseudo-halide complexes of the form LMX (L = ancillary ligand, X = halides or pseudo-halides) are effective precursors for other coordination and organometallic complexes, such as LMR (R = heteroatom or carbon nucleophiles) type of complexes. Ever since the bulky anionic tris(thioether) ligand, i.e. [PhTt\textsuperscript{tBu}] ligand, was reported by Riordan and coworkers in 1998, [PhTt\textsuperscript{tBu}]MX complexes has been used to generate a variety of coordination and organometallic compounds with the tripodal S\textsubscript{3} donor set. The most frequently prepared and used [PhTt\textsuperscript{tBu}]MX complexes are the chloride analogues, [PhTt\textsuperscript{tBu}]MCl (M = Ni, Co, Fe, Cd), which are generated from the metathesis reaction of [PhTt\textsuperscript{tBu}]Tl with MCl\textsubscript{2} (M = Ni, Co, Cd) or FeCl\textsubscript{2}(THF)\textsubscript{1.5}. A number of organonickel, organocobalt and organoiron complexes, for example, have been prepared commencing with [PhTt\textsuperscript{tBu}]MCl (M = Ni, Co, Fe) precursors through metathesis reactions with Grignard or MgR\textsubscript{2} reagents. Moreover, monovalent iron, cobalt and nickel complexes have been generated from the reduction of [PhTt\textsuperscript{tBu}]MCl (M = Ni, Co, Fe) in the presence of suitable trapping ligands such as phosphines and CO.

Despite of the apparent success of [PhTt\textsuperscript{tBu}]MCl in generating divalent organometallic complexes and monovalent complexes, these metal chlorides are
sluggish precursors in other reactions. For example, when [PhTt$^{tBu}$]MCl ($M = \text{Fe, Co}$) and oxygen nucleophiles were combined, the reactions required excess nucleophile and extended reaction times, presumably due to the poor leaving group ability of the chloride.\(^{87}\) Under these circumstances, a more efficient and practical synthetic route to [PhTt$^{tBu}$]MOR complexes was sought. Furthermore, we are very interested in synthesizing $M(II)$-semiquinonate complexes supported by [PhTt$^{tBu}$] ligand, namely [PhTt$^{tBu}$]$M(II)$SQ ($SQ = \text{semiquinonate}$), which we envision can be prepared through nucleophilic substitution reactions of proper [PhTt$^{tBu}$]MX precursors with semiquinonate salts.

Motivated by the preparation of [PhTt$^{tBu}$] ligand supported transition metal complexes with oxygen-donor ligands, we disclose in this chapter the synthesis and characterizations of a series of metal iodide complexes [PhTt$^{tBu}$]MI ($M = \text{Mn, Fe, Co, Ni}$) as effective precursors to the target complexes. In two representative cases, [PhTt$^{tBu}$]MI ($M = \text{Co, Fe}$) turned out to be more effective compared to [PhTt$^{tBu}$]MCl ($M = \text{Co, Fe}$). These cases will be discussed in this chapter. A more extensive use of [PhTt$^{tBu}$]MI as the starting materials for the preparation of [PhTt$^{tBu}$]$M(II)$SQ will be discussed in the Chapter 5.

4.2 [PhTt$^{tBu}$]NiI

4.2.1 Synthesis of [PhTt$^{tBu}$]NiI

The preparation of [PhTt$^{tBu}$]NiI is analogous to the preparation of [PhTt$^{tBu}$]NiCl. However, considering the low solubility of NiI\(_2\) in polar organic solvents such as THF, NiI\(_2\) crystals were ground into fine powder and stirred in THF
for 6 hr to reach equilibrium. One half equivalent of \([\text{PhTt}^{\text{Bu}}]\text{Tl}\) was then added to the \(\text{NiI}_2\) suspension in THF over 10 min. The reason why only half equivalent of the ligand was added is to suppress the formation of \([\kappa^2-\text{PhTt}^{\text{Bu}}]\text{Ni(\eta^2-CH}_2\text{SC(CH}_3)_3\text{)}\) due to the presence of excess \([\text{PhTt}^{\text{Bu}}]\text{Tl}\) to provide \(\text{CH}_2\text{SC(CH}_3)_3\) as nucleophile. Upon the addition of \([\text{PhTt}^{\text{Bu}}]\text{Tl}\), the color of the solution turned red and yellow precipitate (TII) formed. The reaction mixture was stirred for 16 hr and filtered through a pad of Celite to remove TII. The solvent was then removed in vacuo to afford \([\text{PhTt}^{\text{Bu}}]\text{NiI}\) as a brown powder in 69% yield.

### 4.2.2 Molecule Structure of \([\text{PhTt}^{\text{Bu}}]\text{NiI}\)

The thermal ellipsoid plot of the molecular structure of \([\text{PhTt}^{\text{Bu}}]\text{NiI}\) is shown in Figure 4.1. Selected metric parameters of \([\text{PhTt}^{\text{Bu}}]\text{NiI}\) is given in Table 4.1. Table 4.2 contains the average Ni–S bond distances for \([\text{PhTt}^{\text{Bu}}]\text{NiI}\), \([\text{PhTt}^{\text{Bu}}]\text{NiCl}\), and \([\text{Tm}^{\text{Ph}}]\text{NiI}\) \((\text{Tm}^{\text{Ph}} = \text{phenyl derivative of hydrotris(mercaptoimidazolyl)borates})\). \([\text{Tm}^{\text{Ph}}]\text{NiI}\) features the same type of donor sets around Ni as \([\text{PhTt}^{\text{Bu}}]\text{NiI}\) does. Table 4.3 contains the Ni–I bond distances for \([\text{PhTt}^{\text{Bu}}]\text{NiI}\), \([\text{Tm}^{\text{Ph}}]\text{NiI}\), and \([\text{Tp}^{\text{Ph,Me}}]\text{NiI}\) \((\text{Tp}^{\text{Ph,Me}} = \text{hydrotris(3-phenyl-5-methyl-1-pyrazolyl)borate})\). Analogous to the structure of \([\text{PhTt}^{\text{Bu}}]\text{NiCl}\), \([\text{PhTt}^{\text{Bu}}]\text{NiI}\) possesses pseudo-\(C_3\) symmetry generated by the tris(thioether) ligand. The average Ni–S bond distance for \([\text{PhTt}^{\text{Bu}}]\text{NiI}\) (2.284(1) Å) is very close to the average Ni–S bond distances for \([\text{PhTt}^{\text{Bu}}]\text{NiCl}\) (2.279(3) Å) and \([\text{Tm}^{\text{Ph}}]\text{NiI}\) (2.278(1) Å), Table 4.2. The tert-butyl groups in \([\text{PhTt}^{\text{Bu}}]\text{NiI}\) are all tilting in the same direction around the nickel center generating a pinwheel-like structure. The iodide resides in the pocket created by the tert-butyl groups of the ligand. The Ni–I bond distance for \([\text{PhTt}^{\text{Bu}}]\text{NiI}\) (2.4835(5) Å) is shorter than the Ni–I bond distances for \([\text{Tm}^{\text{Ph}}]\text{NiI}\) (2.545(1) Å) and \([\text{Tp}^{\text{Ph,Me}}]\text{NiI}\) (2.4945(4) Å). A similar
trend was observed that the M–I (M = Co, Mn, Fe) bond distances in [PhTtBu] supported metal complexes are shorter than the corresponding M–I (M = Co, Mn, Fe) bond distances in [TmR] supported metal complexes. This observation is rationalized for Mn via analysis of the MO diagram, vide infra, and this explanation is presumed to be operative for the other metal complexes.

Figure 4.1. Molecular structure of [PhTtBu]NiI with atom labeling. Thermal ellipsoids are drawn to 30% probability. Hydrogen atoms have been omitted for clarity.
Table 4.1. Selected bond lengths (Å) and bond angles (°) for [PhTt^Bu]NiI.

<table>
<thead>
<tr>
<th></th>
<th>Length (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni1–S1</td>
<td>2.2804(6)</td>
<td>S1–Ni1–S2 94.15(2)</td>
</tr>
<tr>
<td>Ni1–S2</td>
<td>2.2890(6)</td>
<td>S1–Ni1–S3 95.11(2)</td>
</tr>
<tr>
<td>Ni1–S3</td>
<td>2.2842(6)</td>
<td>S2–Ni1–S3 94.67(2)</td>
</tr>
<tr>
<td>Ni1–I1</td>
<td>2.4835(5)</td>
<td>S1–Ni1–I1 123.44(5)</td>
</tr>
</tbody>
</table>

Table 4.2. Average Ni–S Bond Distance (Å) for [PhTt^Bu]NiI, [PhTt^Bu]NiCl and [Tm^Ph]NiI (Tm^Ph = phenyl derivative of hydrotris(mercaptopimidazolyl)borates).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Average Ni–S Bond Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[PhTt^Bu]NiI</td>
<td>2.284(1)</td>
</tr>
<tr>
<td>[PhTt^Bu]NiCl</td>
<td>2.279(3)</td>
</tr>
<tr>
<td>[Tm^Ph]NiI</td>
<td>2.278(1)</td>
</tr>
</tbody>
</table>

Table 4.3. Ni–I bond distances for [PhTt^Bu]NiI, [Tm^Ph]NiI and [Tp^Ph,Me]NiI (Tp^Ph,Me = hydrotris(3-phenyl-5-methyl-1-pyrazolyl)borate).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ni–I Bond Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[PhTt^Bu]NiI</td>
<td>2.4835(5)</td>
</tr>
<tr>
<td>[Tm^Ph]NiI</td>
<td>2.545(1)</td>
</tr>
<tr>
<td>[Tp^Ph,Me]NiI</td>
<td>2.4945(4)</td>
</tr>
</tbody>
</table>
4.2.3 Spectroscopic Characteristics of [PhTtBu]NiI

Table 4.4 contains the $^1$H NMR spectral data of [PhTtBu]NiI and [PhTtBu]NiCl for comparison. The chemical shift pattern of [PhTtBu]NiI is similar to that of [PhTtBu]NiCl. The tert-butyl groups in [PhTtBu]NiI are located at $\delta$ 15.2. The resonance at $\delta$ 11.1 is assigned to the meta-proton of the phenyl group on boron, whereas the resonances at $\delta$ 8.5 and $\delta$ 8.3 are assigned to the ortho- and para-protons, respectively. The methylene groups adjacent to the sulfur atoms are not observable in the spectrum due to the paramagnetic broadening effect.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Shift ($\delta$) in ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(t-butyl)S</td>
</tr>
<tr>
<td>[PhTtBu]NiI</td>
<td>15.2</td>
</tr>
<tr>
<td>[PhTtBu]NiCl</td>
<td>19.1</td>
</tr>
</tbody>
</table>

<sup>a</sup>in C<sub>6</sub>D<sub>6</sub>.  
<sup>b</sup>in CDCl<sub>3</sub>.  
<sup>c</sup>The meta-protons are not observed.

The electronic spectrum of [PhTtBu]NiI is shown in Figure 4.2. The energies and molar absorptivities of the absorption features of [PhTtBu]NiI, [PhTtBu]NiCl, [Tm<sup>Ph</sup>]NiI, [Tp<sup>Ph,Me</sup>]NiI<sup>89</sup> and [Tp<sup>Me,Me</sup>]NiI<sup>90</sup> are given in Table 4.5. The absorption feature at 452 nm (6036 M<sup>-1</sup> cm<sup>-1</sup>) for [PhTtBu]NiI is assigned to Ni dπ* ← S<sub>thioether</sub> LMCT band, as similar features were also present for Ni complexes containing sulfur ligands such as [PhTtBu]NiCl (425 nm (3300 M<sup>-1</sup> cm<sup>-1</sup>) and [Tm<sup>Ph</sup>]NiI (411 nm (4800)), but absent for [Tp<sup>Ph,Me</sup>]NiI and [Tp<sup>Me,Me</sup>]NiI. It was reported that the Ni dπ* ← I π<sub>π</sub> LMCT band was split into two for [Tp<sup>Ph,Me</sup>]NiI at 378 (1010 M<sup>-1</sup> cm<sup>-1</sup>), 425
(840 M$^{-1}$ cm$^{-1}$) nm and for [Tp$^{Me,Me}$]NiI at 367 (3120 M$^{-1}$ cm$^{-1}$), 388 (3130 M$^{-1}$ cm$^{-1}$) nm, respectively. Therefore, the absorption features at 375 (sh, 2579 M$^{-1}$ cm$^{-1}$), 413 (sh, 4190 M$^{-1}$ cm$^{-1}$) nm for [PhTt$^{Bu}$]NiI are likely Ni dπ*$\leftrightarrow$I π LMCT bands. [PhTt$^{Bu}$]NiI also displays ligand-field transitions at 567 (972 M$^{-1}$ cm$^{-1}$), 841 (427 M$^{-1}$ cm$^{-1}$), and 903 (432 M$^{-1}$ cm$^{-1}$) nm, consistent with high-spin Ni(II) ($S = 1$) in a $C_3$ symmetry. Similar ligand-field transitions were also reported for [PhTt$^{Bu}$]NiCl (534 (280 M$^{-1}$ cm$^{-1}$), 836 (220 M$^{-1}$ cm$^{-1}$) nm), [Tp$^{Ph,Me}$]NiI (523 (500 M$^{-1}$ cm$^{-1}$), 851 (90 M$^{-1}$ cm$^{-1}$), 950 (140 M$^{-1}$ cm$^{-1}$) nm), and [Tp$^{Me,Me}$]NiI (521 (700 M$^{-1}$ cm$^{-1}$), 826 (150 M$^{-1}$ cm$^{-1}$), 907 (123 M$^{-1}$ cm$^{-1}$) nm).

Figure 4.2. Electronic absorption spectrum of [PhTt$^{Bu}$]NiI in toluene.
Table 4.5. Electronic absorption spectral data of [PhTt\textsuperscript{Bu}]NiI, [PhTt\textsuperscript{Bu}]NiCl, [Tm\textsuperscript{Ph}]NiI, [Tp\textsuperscript{Ph,Me}]NiI and [Tp\textsuperscript{Me,Me}]NiI.

<table>
<thead>
<tr>
<th>Compound</th>
<th>λ\textsubscript{max}, nm (ε, M\textsuperscript{-1} cm\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>[PhTt\textsuperscript{Bu}]NiI\textsuperscript{a}</td>
<td>311 (1518), 375 (sh, 2579), 413 (sh, 4190), 452 (6036), 567 (972), 841 (427), 903 (432)</td>
</tr>
<tr>
<td>[PhTt\textsuperscript{Bu}]NiCl\textsuperscript{b}</td>
<td>282 (4600), 298 (2900), 388 (3900), 425 (3300), 534 (280), 836 (220)</td>
</tr>
<tr>
<td>[Tm\textsuperscript{Ph}]NiI\textsuperscript{b}</td>
<td>411 (4800), 699 (450), 784 (350)</td>
</tr>
<tr>
<td>[Tp\textsuperscript{Ph,Me}]NiI\textsuperscript{b}</td>
<td>378 (1010), 425 (840), 523 (500), 602(sh, 160), 851 (90), 950 (140)</td>
</tr>
<tr>
<td>[Tp\textsuperscript{Me,Me}]NiI\textsuperscript{c}</td>
<td>367 (3120), 388 (3130), 518 (1140), 592 (sh, 190), 835 (250), 918 (220)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}in toluene.
\textsuperscript{b}in CH\textsubscript{2}Cl\textsubscript{2}.
\textsuperscript{c}in CCl\textsubscript{4} and units were converted from cm\textsuperscript{-1} in the original paper to nm.

4.3 \textbf{[PhTt\textsuperscript{Bu}]CoI}

4.3.1 \textbf{Synthesis of [PhTt\textsuperscript{Bu}]CoI}

[PhTt\textsuperscript{Bu}]CoI\textsuperscript{91} was first prepared by Peter J. Schebler while a doctoral student in the Riordan Lab. One equivalent of [PhTt\textsuperscript{Bu}]Tl was added as a powder to the CoI\textsubscript{2} solution in THF over 10 min. Upon the addition of [PhTt\textsuperscript{Bu}]Tl, the color of the solution turned from blue to green and yellow precipitate (TlI) formed. The reaction mixture was stirred for 6 hr and filtered through a pad of Celite to remove TlI. The solvent was then removed in vacuo affording [PhTt\textsuperscript{Bu}]CoI as a green powder in 86% yield.

4.3.2 \textbf{Molecular Structure of [PhTt\textsuperscript{Bu}]CoI}

The thermal ellipsoid plot of [PhTt\textsuperscript{Bu}]CoI is shown in Figure 4.3.\textsuperscript{91} Selected metric parameters are summarized in Table 4.6. Table 4.7 contains the average Co–S bond distances for [PhTt\textsuperscript{Bu}]CoI,\textsuperscript{91} [PhTt\textsuperscript{Bu}]CoCl,\textsuperscript{34} [Tm\textsuperscript{Ph}]CoI,\textsuperscript{88} and [Tm\textsuperscript{Bu}]CoI\textsuperscript{92}
(Tm$^{\text{Bu}}$ = tert-butyl derivative of hydrotris(mercaptoimidazolyl)borates). Table 4.8 contains the Co–I bond distances for [PhTt$^{\text{Bu}}$]CoI, [Tm$^{\text{Ph}}$]CoI, [Tm$^{\text{Bu}}$]CoI, and [Tp$^{\text{Pr,Me}}$]CoI$^{93}$ (Tp$^{\text{Pr,Me}}$ = hydrotris(3-isopropyl-5-methyl-1-pyrazolyl)borate). Similar to [PhTt$^{\text{Bu}}$]CoCl, the molecular structure of [PhTt$^{\text{Bu}}$]CoI possesses pseudo-C$_3$ symmetry generated by the tris(thioether) ligand. The average Co–S bond distance for [PhTt$^{\text{Bu}}$]CoI (2.320(1) Å) is experimentally indistinguishable from the average Co–S bond distance for [PhTt$^{\text{Bu}}$]CoCl (2.322(4) Å), but slightly longer than those for [Tm$^{\text{Ph}}$]CoI (2.3071(9) Å) and [Tm$^{\text{Bu}}$]CoI (2.310(1) Å), consistent with the tris(thioether) ligand being a weaker σ donor. The tert-butyl groups in [PhTt$^{\text{Bu}}$]CoI cant in the same direction around the cobalt center. The Co–I bond distance for [PhTt$^{\text{Bu}}$]CoI (2.5361(4) Å) is shorter than the Co–I bond distances for [Tm$^{\text{Ph}}$]CoI (2.5789(9) Å) and [Tm$^{\text{Bu}}$]CoI (2.5769(7) Å), but similar to the Co–I bond distance for [Tp$^{\text{Pr,Me}}$]CoI (2.538(2) Å).
Figure 4.3. Molecular structure of [PhTt^{Bu}]CoI with atom labeling. Thermal ellipsoids are drawn to 30% probability. Hydrogen atoms have been omitted for clarity.

Table 4.6. Selected bond lengths (Å) and bond angles (°) for [PhTt^{Bu}]CoI.

<table>
<thead>
<tr>
<th></th>
<th>Length (Å)</th>
<th>Angle (°)</th>
</tr>
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<tbody>
<tr>
<td>Co1-S1</td>
<td>2.3184(7)</td>
<td>S1- Co1-S2</td>
</tr>
<tr>
<td>Co1-S2</td>
<td>2.3257(7)</td>
<td>S1- Co1-S3</td>
</tr>
<tr>
<td>Co1-S3</td>
<td>2.3153(7)</td>
<td>S2- Co1-S3</td>
</tr>
<tr>
<td>Co1-II</td>
<td>2.5361(4)</td>
<td>S1- Co1-II</td>
</tr>
</tbody>
</table>
Table 4.7. Average Co–S Bond Distance (Å) for [PhTt<sup>Bu</sup>]CoI, [PhTt<sup>Bu</sup>]CoCl, [Tm<sup>Ph</sup>]CoI and [Tm<sup>Bu</sup>]CoI.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Average Co–S Bond Distance (Å)</th>
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<tbody>
<tr>
<td>[PhTt&lt;sup&gt;Bu&lt;/sup&gt;]CoI</td>
<td>2.320(1)</td>
</tr>
<tr>
<td>[PhTt&lt;sup&gt;Bu&lt;/sup&gt;]CoCl</td>
<td>2.322(4)</td>
</tr>
<tr>
<td>[Tm&lt;sup&gt;Ph&lt;/sup&gt;]CoI</td>
<td>2.3071(9)</td>
</tr>
<tr>
<td>[Tm&lt;sup&gt;Bu&lt;/sup&gt;]CoI</td>
<td>2.310(1)</td>
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</table>

Table 4.8. Co–I bond distances for [PhTt<sup>Bu</sup>]CoI, [Tm<sup>Ph</sup>]CoI, [Tm<sup>Bu</sup>]CoI and [Tp<sup>Pr,Me</sup>]CoI.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Co-I Bond Distance (Å)</th>
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<tbody>
<tr>
<td>[PhTt&lt;sup&gt;Bu&lt;/sup&gt;]CoI</td>
<td>2.5361(4)</td>
</tr>
<tr>
<td>[Tm&lt;sup&gt;Ph&lt;/sup&gt;]CoI</td>
<td>2.5789(9)</td>
</tr>
<tr>
<td>[Tm&lt;sup&gt;Bu&lt;/sup&gt;]CoI</td>
<td>2.5769(7)</td>
</tr>
<tr>
<td>[Tp&lt;sup&gt;Pr,Me&lt;/sup&gt;]CoI</td>
<td>2.538(2)</td>
</tr>
</tbody>
</table>
4.3.3 Spectroscopic Characteristics and Magnetism of [PhTt\textsuperscript{Bu}]CoI

[PhTt\textsuperscript{Bu}]CoI was studied by \textsuperscript{1}H NMR and electronic absorption spectroscopies.\textsuperscript{91} Table 4.9 contains the \textsuperscript{1}H NMR spectral data of [PhTt\textsuperscript{Bu}]CoI and [PhTt\textsuperscript{Bu}]CoCl\textsuperscript{34} for comparison. Expectedly, the chemical shift pattern of [PhTt\textsuperscript{Bu}]CoI is somewhat similar to that of [PhTt\textsuperscript{Bu}]CoCl. The tert-butyl groups in [PhTt\textsuperscript{Bu}]CoI are located at δ 14.1. The resonance at δ 9.0 is assigned to the para-proton of the phenyl group on the boron due to its integration, whereas the resonance at δ 7.4 is assigned to either the ortho- or the meta-protons. The other two protons on the phenyl group are not observed due to paramagnetism. The methylene groups adjacent to the sulfur atoms were not observed as well.

Table 4.9. \textsuperscript{1}H NMR spectral data for [PhTt\textsuperscript{Bu}]CoI and [PhTt\textsuperscript{Bu}]CoCl.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Shift (δ) in ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(tert-butyl)S</td>
</tr>
<tr>
<td>[PhTt\textsuperscript{Bu}]CoI\textsuperscript{a}</td>
<td>14.1</td>
</tr>
<tr>
<td>[PhTt\textsuperscript{Bu}]CoCl\textsuperscript{a}</td>
<td>16.5</td>
</tr>
</tbody>
</table>

\textsuperscript{a}in C\textsubscript{6}D\textsubscript{6}.

\textsuperscript{b}two protons on the phenyl group are not observable.

The electronic absorption spectrum of [PhTt\textsuperscript{Bu}]CoI is shown in Figure 4.4. The data for [PhTt\textsuperscript{Bu}]CoI, [PhTt\textsuperscript{Bu}]CoCl\textsuperscript{34}, [Tm\textsuperscript{Ph}]Co\textsuperscript{88}, [Tm\textsuperscript{Bu}]Co\textsuperscript{92} and [Tp\textsuperscript{iPr,Me}]CoI\textsuperscript{93} are summarized in Table 4.10. The electronic absorption spectrum of [PhTt\textsuperscript{Bu}]CoI is in analogy with the rest of the tetrahedral d\textsuperscript{7} Co(II) complexes listed in Table 4.10. According to the ligand-field transition assignments for [PhTt\textsuperscript{Bu}]CoCl and [Tp\textsuperscript{iPr,Me}]CoI, the ligand-field transitions for [PhTt\textsuperscript{Bu}]CoI at 665 (sh, 934 M\textsuperscript{1} cm\textsuperscript{-1}) and 712 (1410 M\textsuperscript{-1} cm\textsuperscript{-1}) nm are assigned to the \textsuperscript{4}A\textsubscript{2}(F)→\textsuperscript{4}T\textsubscript{1}(P) transition, whereas the transition at 986 (412 M\textsuperscript{-1} cm\textsuperscript{-1}) nm is assigned to \textsuperscript{4}A\textsubscript{2}(F)→\textsuperscript{4}T\textsubscript{1}(F) transition. These
three transitions are characteristic of high-spin Co$^{II}$ ($S = 3/2$) in a tetrahedral ligand field.

![PhTtCol](image)

**Figure 4.4.** Electronic absorption spectrum of [PhTt$^{Bu}$]Co in THF.

**Table 4.10.** Electronic absorption spectral data of [PhTt$^{Bu}$]CoI, [PhTt$^{Bu}$]CoCl, [Tm$^{Ph}$]CoI, [Tm$^{Bu}$]CoI and [Tp$^{Ph,Me}$]CoI.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{max}$, nm ($\varepsilon$, M$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[PhTt$^{Bu}$]CoI$^a$</td>
<td>314 (3600), 369 (4070), 665 (sh, 934), 712 (1410), 986 (412)</td>
</tr>
<tr>
<td>[PhTt$^{Bu}$]CoCl$^b$</td>
<td>245 (4300), 298 (2800), 360 (sh, 1300), 664 (880), 695 (740), 932 (130)</td>
</tr>
<tr>
<td>[Tm$^{Ph}$]CoI$^b$</td>
<td>393 (2500, sh), 694 (650), 730 (860), 761 (1000)</td>
</tr>
<tr>
<td>[Tm$^{Bu}$]CoI$^b$</td>
<td>393 (2500, sh), 695 (780), 740 (910, sh), 758 (980)</td>
</tr>
<tr>
<td>[Tp$^{Ph,Me}$]CoI$^c$</td>
<td>273 (3200), 310 (2800), 605 (620), 645 (780), 905 (180)</td>
</tr>
</tbody>
</table>

$^a$ in THF.

$^b$ in CH$_2$Cl$_2$.

$^c$ in CH$_2$Cl$_2$/CH$_3$CN (9/1).
The electronic structure of [PhTt\textsuperscript{tBu}]CoI was further probed by magnetic measurements both in solution and in solid state. The solution magnetic moment of [PhTt\textsuperscript{tBu}]CoI at room temperature is 4.58(3) $\mu_B$, consistent with $S = 3/2$ spin state for high-spin Co\textsuperscript{II} ion.\textsuperscript{91} This moment is significantly higher than the spin-only value of 3.87 $\mu_B$ for $S = 3/2$ system, indicating a large spin-orbital coupling, which is often observed for high-spin Co\textsuperscript{II} complexes. The temperature-dependent magnetic susceptibility of the solid sample was measured by SQUID magnetometry, Figure 4.5. Consistent with the magnetic moment in solution, the room temperature $\chi_T$ (2.46 cm\textsuperscript{3}.K.mol\textsuperscript{-1}) is significantly higher than the spin only value for an $S = 3/2$ center (1.837 cm\textsuperscript{3}.K.mol\textsuperscript{-1}), which is attributed to a significant orbital contribution to the magnetic moment. Upon decreasing temperature, the $\chi_T$ value decreases slowly until 10K and then quickly decreases to a minimum of 1.4 cm\textsuperscript{3}.K.mol\textsuperscript{-1} at 2K. The sharp decrease at low temperature corresponds to the spin depopulation from the $Ms = \pm 3/2$ spin state to $Ms = \pm 1/2$ spin state and indicates the anisotropic nature of the cobalt center. This assumption is further supported by the lack of saturation in the magnetization versus field data even at 7 T, Figure 4.6. The field-dependent magnetization data for [PhTt\textsuperscript{tBu}]CoI at temperatures between 1.8 and 4.5 K, Figure 4.7 exhibit a non-superposition of the iso-field lines, which further supports the presence of significant zero-field splitting. Attempts to determine zero-field splitting parameters by fitting the field-dependent magnetization data using \textit{ANISOFIT2.0} resulted in a $D$ value of -24.75 cm\textsuperscript{-1} with $E = 0.73$. The large negative D value in 1 implies very large energy gaps between the $\pm 3/2$ and $\pm 1/2$ Ms levels with substantial predicted energy barriers for spin reversal.
Figure 4.5. Temperature dependence of the $\chi T$ versus $T$ plot (blue circles) and $\chi$ versus $T$ plot (red diamonds) for [PhTtBu]CoI at 2-300 K.

Figure 4.6. Field dependent magnetization data for [PhTtBu]CoI. The red circles and red line represent the experimental data. The blue line represent $S = 3/2$ situation without zero-field splitting or intermolecular interaction.
Figure 4.7. Reduced magnetization data for \([\text{PhTt}^{t\text{Bu}}]\text{CoI}\) at 1.8-4.5 K. The red lines represent the best fits produced by theory.

4.4 \([\text{PhTt}^{t\text{Bu}}]\text{MnI}\)

4.4.1 Synthesis of \([\text{PhTt}^{t\text{Bu}}]\text{MnI}\)

The coordination chemistry of Mn\(^{II}\) with \([\text{PhTt}^{t\text{Bu}}]\) ligand was previously explored by Professor Louise Liable-Sands, Widener University, during a sabbatical in the Riordan laboratory. Professor Liable-Sands deduced that THF is not an ideal solvent for the preparation of \([\text{PhTt}^{t\text{Bu}}]\text{MnX}\) complexes (X = Cl, Br, I), likely due to the low solubility of MnX\(_2\) precursors in THF. Later, it was found by the author of this dissertation that when acetonitrile was used as solvent, all the MnI\(_2\) dissolved generating a colorless solution. The high solubility of MnI\(_2\) in acetonitrile is likely due
to the formation of a soluble MnI$_2$(CH$_3$CN)$_n$ adduct. One equivalent of [PhTt$^{18}$Bu]Tl was then slowly added to the MnI$_2$ solution in acetonitrile. No color change was observed upon the addition of [PhTt$^{18}$Bu]Tl. However, the formation of a yellow precipitate (TII) indicated the reaction proceeded. The reaction mixture was stirred for 2 hr and filtered through a pad of Celite to remove TII. The solvent was then removed in vacuo affording a colorless gel. Pentane/diethyl ether (5/1) was added so as to extract the product into the solution. The solution was filtered through a Celite pad and the solvent was removed in vacuo affording a white solid in 86% yield. High resolution LIFDI mass spectroscopy, Figure 4.8, confirmed the composition of the white solid as [PhTt$^{18}$Bu]MnI.$^{91}$
4.4.2 Molecular Structure of [PhTt\textsuperscript{Bu}]MnI

The thermal ellipsoid plot of [PhTt\textsuperscript{Bu}]MnI is shown in Figure 4.9.\textsuperscript{91} Selected metric parameters of [PhTt\textsuperscript{Bu}]MnI is summarized in Table 4.11. Table 4.12 contains the average Mn–S bond distance and Mn–I bond distance for [PhTt\textsuperscript{Bu}]MnI and [Tm\textsuperscript{Ph}]MnI\textsuperscript{88}. 

---

Figure 4.8. Calculated (top) and experimental (bottom) high resolution LIFDI mass spectra of [PhTt\textsuperscript{Bu}]MnI.
Figure 4.9. Molecular structure of [PhTt^{th}]MnI with atom labeling. Thermal ellipsoids are drawn to 30% probability. Hydrogen atoms have been omitted for clarity.
Table 4.11. Selected bond lengths (Å) and bond angles (°) for [PhTtBu]MnI.

<table>
<thead>
<tr>
<th></th>
<th>Length (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn1–S1</td>
<td>2.4566(11)</td>
<td>S1–Mn1–S2 94.66(4)</td>
</tr>
<tr>
<td>Mn1–S2</td>
<td>2.4635(12)</td>
<td>S1–Mn1–S3 92.73(4)</td>
</tr>
<tr>
<td>Mn1–S3</td>
<td>2.4586(11)</td>
<td>S2–Mn1–S3 93.52(3)</td>
</tr>
<tr>
<td>Mn1–I1</td>
<td>2.5849(7)</td>
<td>S1–Mn1–I1 120.73(3)</td>
</tr>
</tbody>
</table>

Table 4.12. Average Mn–S Distance and Mn–I Bond Distance (Å) for [PhTtBu]MnI and [TmPh]MnI.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Average Mn–S Bond Distance (Å)</th>
<th>Mn–I Bond Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[PhTtBu]MnI</td>
<td>2.460(1)</td>
<td>2.585(1)</td>
</tr>
<tr>
<td>[TmPh]MnI</td>
<td>2.437(2)</td>
<td>2.626(2)</td>
</tr>
</tbody>
</table>

The molecular structure of [PhTtBu]MnI possesses pseudo-$C_3$ symmetry generated by the tris(thioether) ligand. The average Mn–S bond distance for [PhTtBu]MnI (2.460(1) Å) is slightly longer than the average Mn–S bond distance for [TmPh]MnI (2.437(2) Å), due to the tris(thioether) ligand serving as a weaker σ donor. The Mn–I bond distance for [PhTtBu]MnI (2.585(1) Å) is shorter than that for [TmPh]MnI (2.626(2) Å) as a consequence of weaker σ interactions between thioether sulfurs with the $d_{xz}$ and $d_{yz}$ orbitals on the Mn$^{II}$ center, which in turn lowers their energy levels and affords a better orbital overlap with the pπ orbitals on the iodide forming a stronger Mn–I bond. One such dπ-pπ interaction is illustrated in Figure 4.10.
Figure 4.10. Bonding interaction of d_{xz} orbital of Mn with p_{x} orbital of iodide.

4.4.3 Spectroscopic Characteristics and Magnetism of [PhTt\textsuperscript{tBu}]MnI

The solution magnetic moment of [PhTt\textsuperscript{tBu}]MnI at room temperature is $\mu_{\text{eff}} (C_6D_6) = 5.9(1) \, \mu_B$ consistent with the presence of 5 unpaired electrons of a high-spin Mn(II) center.\textsuperscript{91} Consequently, the $^1H$ NMR spectrum of [PhTt\textsuperscript{tBu}]MnI exhibited broad and paramagnetically-shifted resonances.\textsuperscript{91} The resonance at $\delta 22.5$ is assigned to the tert-butyl groups in [PhTt\textsuperscript{tBu}]MnI. The resonance at $\delta 10.0$ is assigned to the ortho- or the meta-protons of the phenyl group on the boron. The resonance at $\delta 7.5$ is assigned to the para-proton and $\delta 6.6$ is assigned to the meta- or ortho-protons of the phenyl group on the boron.
4.5 [PhTt\textit{\text{^\text{Bu}}} FeI

4.5.1 Synthesis of [PhTt\textit{\text{^\text{Bu}}} FeI

Previous efforts by M. T. Mock from this laboratory did not lead to a successful preparation of [PhTt\textit{\text{^\text{Bu}}} FeI. It was suspected that the choice of the solvent played a key role, similar to what was learned from the preparation of [PhTt\textit{\text{^\text{Bu}}} MnI. Thus, one equivalent of [PhTt\textit{\text{^\text{Bu}}} Tl was slowly added to the FeI$_2$ solution in acetonitrile, instead of THF. The color of the solution changed from nearly black to yellow brown and yellow precipitate (TlI) formed. The reaction mixture was stirred for 2 hr and filtered through a pad of Celite to remove TlI. The solvent was then removed in vacuo affording a light brown gel. Pentane/diethyl ether (10/1) was added to extract the product into the solution. The solution was filtered through a Celite pad and the solvent was removed in vacuo to afford a pale green solid. Recrystallization by slow evaporation of the pentane solution afforded light green crystals in 22% yield. High resolution LIFDI mass spectroscopy, Figure 4.1, confirmed the composition of the light green crystals as [PhTt\textit{\text{^\text{Bu}}} FeI.$^{91}$
Figure 4.11. Calculated (top) and experimental (bottom) high resolution LIFDI mass spectra of [PhTl^{Bu}]FeI.
4.5.2 Molecular Structure of [PhTt\textsuperscript{tBu}]FeI

The molecular structure of [PhTt\textsuperscript{tBu}]FeI was studied by single-crystal X-ray diffraction analysis. The thermal ellipsoid plot is shown in Figure 4.12, which establishes that [PhTt\textsuperscript{tBu}]FeI is a monomer in the solid state in contrast to dimeric \{[PhTt\textsuperscript{tBu}]FeCl\}_2. Selected metric parameters of [PhTt\textsuperscript{tBu}]FeI are summarized in Table 4.13. Table 4.14 contains the average Fe–S bond distances for [PhTt\textsuperscript{tBu}]FeI, [PhTt\textsuperscript{tBu}]FeCl\textsuperscript{36}, and [Tm\textsuperscript{tBu}]FeI\textsuperscript{88}. The average Fe–S bond length for [PhTt\textsuperscript{tBu}]FeI (2.388(1) Å) is shorter than that for [PhTt\textsuperscript{tBu}]FeCl, largely due to the higher coordination number of the latter complex. The slightly longer average Fe–S bond length for [PhTt\textsuperscript{tBu}]FeI compared to that for [Tm\textsuperscript{tBu}]FeI (2.370(1) Å) is consistent with previous observations for the Ni, Co and Mn analogues.\textsuperscript{88,92} Table 4.15 contains the Fe–I bond distances for [PhTt\textsuperscript{tBu}]FeI, [Tm\textsuperscript{tBu}]FeI\textsuperscript{88} and [Tp\textsuperscript{tBu,Me}]FeI\textsuperscript{83} (Tp\textsuperscript{tBu,Me} = hydrotris(3-tert-butyl-5-methyl-1-pyrazolyl)borate). The Fe–I bond lengths follow the trend [Tp\textsuperscript{tBu,Me}]FeI > [Tm\textsuperscript{tBu}]FeI > [PhTt\textsuperscript{tBu}]FeI.
Figure 4.12. Molecular structure of $[\text{PhTt}^{\text{Bu}}]\text{FeI}$ with atom labeling. Thermal ellipsoids are drawn to 30% probability. Hydrogen atoms have been omitted for clarity.

Table 4.13. Selected bond lengths (Å) and bond angles (°) for $[\text{PhTt}^{\text{Bu}}]\text{FeI}$.

<table>
<thead>
<tr>
<th></th>
<th>Length (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe1–S1</td>
<td>2.3918(8)</td>
<td>S1–Fe1–S2</td>
</tr>
<tr>
<td>Fe1–S2</td>
<td>2.3894(8)</td>
<td>S1–Fe1–S3</td>
</tr>
<tr>
<td>Fe1–S3</td>
<td>2.3823(8)</td>
<td>S2–Fe1–S3</td>
</tr>
<tr>
<td>Fe1–I1</td>
<td>2.5426(5)</td>
<td>S1–Fe1–I1</td>
</tr>
</tbody>
</table>
Table 4.14. Average Fe–S Distance (Å) for [PhTtBu]FeI, [PhTtBu]FeCl and [TmBu]FeI.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Average Fe–S Bond Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[PhTtBu]FeI</td>
<td>2.388(1)</td>
</tr>
<tr>
<td>[PhTtBu]FeCl</td>
<td>2.451(2)</td>
</tr>
<tr>
<td>[TmBu]FeI</td>
<td>2.370(1)</td>
</tr>
</tbody>
</table>

Table 4.15. Fe–I bond distances for [PhTtBu]FeI, [TmBu]FeI and [TpBu,Me]FeI.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Fe–I Bond Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[PhTtBu]FeI</td>
<td>2.5426(5)</td>
</tr>
<tr>
<td>[TmBu]FeI</td>
<td>2.573(1)</td>
</tr>
<tr>
<td>[TpBu,Me]FeI</td>
<td>2.5964(12)</td>
</tr>
</tbody>
</table>
4.5.3 Spectroscopic Characteristics and Magnetism of [PhTt\textsuperscript{tBu}]FeI

The solution magnetic moment of [PhTt\textsuperscript{tBu}]FeI at room temperature is $\mu_{\text{eff}}$ (C\textsubscript{6}D\textsubscript{6}) = 5.35(3) $\mu_B$ consistent with the presence of 4 unpaired electrons of a high-spin Fe\textsuperscript{II} center.\textsuperscript{91} Consequently, the $^1$H NMR spectrum of [PhTt\textsuperscript{tBu}]FeI exhibited well resolved paramagnetically-shifted resonances.\textsuperscript{91} The resonance at $\delta$ 14.6 is assigned to the tert-butyl groups of [PhTt\textsuperscript{tBu}] ligand. The resonance at $\delta$ 14.2 is assigned to the ortho- or the meta-protons of the phenyl group on the boron. The resonance at $\delta$ 9.1 is assigned to the para-proton and $\delta$ 8.2 is assigned to the meta- or ortho-protons of the phenyl group on the boron.

The electronic spectrum of [PhTt\textsuperscript{tBu}]FeI is contained in Figure 4.13.\textsuperscript{91} The data for [PhTt\textsuperscript{tBu}]FeI and [Tm\textsuperscript{tBu}]Fe\textsuperscript{88} are summarized in Table 4.16. No discernible ligand-field transitions were observed for [PhTt\textsuperscript{tBu}]FeI in the 400-1000 nm region, consistent with the pseudotetrahedral high-spin Fe\textsuperscript{II} ($S = 2$) center whose ligand-field transitions are in the IR region.\textsuperscript{94}

![Figure 4.13. Electronic absorption spectrum of [PhTt\textsuperscript{tBu}]FeI in THF.](image)
Table 4.16. Electronic absorptions of \([\text{PhTt}^{t\text{Bu}}]\text{FeI}\) and \([\text{Tm}^{t\text{Bu}}]\text{FeI}\).

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\lambda_{\text{max}}, \text{nm (}\epsilon, \text{M}^{-1} \text{cm}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{PhTt}^{t\text{Bu}}]\text{FeI})^a</td>
<td>264 (3620), 315 (3140), 368 (sh, 1730)</td>
</tr>
<tr>
<td>([\text{Tm}^{t\text{Bu}}]\text{FeI})^b</td>
<td>286 (29500), 361 (10700)</td>
</tr>
</tbody>
</table>

^a in THF.  
^b in \(\text{CH}_2\text{Cl}_2\).

4.6 \([\text{PhTt}^{t\text{Bu}}]\text{Co(3,5-DBCatH)}\)

4.6.1 Comparison of the Two Synthetic Routes Leading to \([\text{PhTt}^{t\text{Bu}}]\text{Co(3,5-DBCatH)}\)

An example that \([\text{PhTt}^{t\text{Bu}}]\text{MI}\) (M = Co, Fe) complexes are better synthetic precursors compared to \([\text{PhTt}^{t\text{Bu}}]\text{MCl}\) (M = Co, Fe) complexes, is the reaction of \([\text{PhTt}^{t\text{Bu}}]\text{CoX}\) (X = Cl, I) with mono-deprotonated catecholate salts generating \([\text{PhTt}^{t\text{Bu}}]\text{Co(3,5-DBCatH)}\), Scheme 4.1. The reaction of \([\text{PhTt}^{t\text{Bu}}]\text{CoCl}\) with K(3,5-DBCatH) required 1.3 equiv of K(3,5-DBCatH) and 22 hr before furnishing a product/starting material ratio of 94.5/5.5. Alternatively, \([\text{PhTt}^{t\text{Bu}}]\text{Co(3,5-DBCatH)}\) was prepared from the reaction of \([\text{PhTt}^{t\text{Bu}}]\text{CoI}\) with Tl(3,5-DBCatH), which only required 1.1 equiv of Tl(3,5-DBCatH) and 6 hr before yielding a product/starting material ratio of 96.0/4.0. Furthermore, based on the \(^1\text{H}\) NMR spectra of the crude products, Figure 4.14, the second route provided fewer impurities.
Scheme 4.1. Preparation of [PhTt\(^{Bu}\)]Co(3,5-DBCatH). Top: Using [PhTt\(^{Bu}\)]CoCl and K(3,5-DBCatH); Bottom: Using [PhTt\(^{Bu}\)]CoI and Tl(3,5-DBCatH).

Figure 4.14. \(^1\)H NMR spectra of [PhTt\(^{Bu}\)]Co(3,5-DBCatH) from [PhTt\(^{Bu}\)]CoCl (top) and [PhTt\(^{Bu}\)]CoI (bottom).
4.6.2 Molecular Structure of [PhTt^{Bu}]Co(3,5-DBCatH)

Figure 4.15. Molecular structure of [PhTt^{Bu}]Co(3,5-DBCatH) with atom labeling. Thermal ellipsoids are drawn to 30% probability. Hydrogen atoms have been omitted for clarity.
The thermal ellipsoid plot of [PhTtBu]Co(3,5-DBCatH) is shown in Figure 4.15 with selected metric parameters summarized in Table 4.17. The cobalt center is coordinated by three sulfur atoms from the tris(thioether) ligand and one oxygen atom (O1) from the mono-deprotonated catecholate ligand. The O1 atom is in the ortho position relative to both tert-butyl groups of the catecholate ligand. The other oxygen atom (O2) from the catecholate ligand is protonated and not bound to the metal. Distinct from [PhTtBu]CoI, which has a distorted tetrahedral geometry ($\tau_4^{95} = 0.24$), the geometry of [PhTtBu]Co(3,5-DBCatH) lies between tetrahedral and trigonal pyramidal with $\tau_4^{95} = 0.42$. This latter geometry is manifested by the deviation of the O1 atom from the 3-fold axis defined by the B---Co vector (B---Co--O1 = 167.46°). The average Co–S bond distance for [PhTtBu]Co(3,5-DBCatH) (2.328(1) Å) is very close to the average Co–S bond distance for [PhTtBu]CoI (2.320(1) Å). The average S–Co–S angle for [PhTtBu]Co(3,5-DBCatH) (99.57(2)°) is also very close to the average S–Co–S angle for [PhTtBu]CoI (99.84(2)°). These similarities indicate that the pocket created by [PhTtBu] ligand is large enough to accommodate the catecholate ligand coordinated in a monodentate fashion without causing much steric strain.

<table>
<thead>
<tr>
<th></th>
<th>Length (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co–S1</td>
<td>2.3334(5)</td>
<td>S1–Co–S2</td>
</tr>
<tr>
<td>Co–S2</td>
<td>2.3381(6)</td>
<td>S1–Co–S3</td>
</tr>
<tr>
<td>Co–S3</td>
<td>2.3136(5)</td>
<td>S2–Co–S3</td>
</tr>
<tr>
<td>Co–O1</td>
<td>1.8670(13)</td>
<td>O1–Co--B</td>
</tr>
<tr>
<td>O1–C27</td>
<td>1.345(2)</td>
<td>Co–O1–C27</td>
</tr>
</tbody>
</table>

Table 4.17. Selected bond lengths (Å) and bond angles (°) for [PhTtBu]Co(3,5-DBCatH).
A search of the Cambridge Structural Database revealed a single structure containing the Co(3,5-DBCatH) moiety, namely Co(Hdmg)$_2$(Ph$_3$P)(3,5-DBCatH)$_6$ (Hdmg = dimethylglyoximate). This complex, Figure 4.16, contains Co$^{III}$ instead of Co$^{II}$. The Co$^{III}$ is six-coordinate and the mono-deprotonated catecholate ligand coordinates in a monodentate fashion as well. Counterintuitively, the Co$^{III}$–O bond distance for Co(Hdmg)$_2$(Ph$_3$P)(3,5-DBCatH) (1.969(3) Å) is significantly longer than the Co$^{II}$–O bond distance for [PhTt$_{tBu}$]Co(3,5-DBCatH) (1.8670(13) Å). This is a consequence of the trans influence of the Ph$_3$P ligand as well as the higher coordination number of the Co$^{III}$ complex.

Figure 4.16. Molecular structure of Co(Hdmg)$_2$(Ph$_3$P)(3,5-DBCatH) with atom labeling. Hydrogen atoms have been omitted for clarity.
4.6.3 Spectroscopic Characteristics of $[\text{PhTt}^{t\text{Bu}}]\text{Co}(3,5-\text{DBCatH})$

The $^1\text{H}$ NMR spectrum of $[\text{PhTt}^{t\text{Bu}}]\text{Co}(3,5-\text{DBCatH})$ exhibited well resolved paramagnetically-shifted resonances, Figure 4.14. The resonance at $\delta$ 10.5 is assigned to the tert-butyl groups of $[\text{PhTt}^{t\text{Bu}}]$ ligand. The resonance at $\delta$ 15.7 is assigned to the ortho- or meta-protons of the phenyl group on the boron. The resonance at $\delta$ 9.7 is assigned to the para-proton and $\delta$ 8.5 is assigned to the meta- or ortho-protons of the phenyl group on the boron. The two tert-butyl groups of the catecholate ligand reside at $\delta$ 4.8 and -2.1, respectively. There is also one resonance at $\delta$ -43.6 that is tentatively assigned to the aromatic proton on the catecholate ring. The general pattern of the $^1\text{H}$ NMR spectrum of $[\text{PhTt}^{t\text{Bu}}]\text{Co}(3,5-\text{DBCatH})$ is analogous to those of other $[\text{PhTt}^{t\text{Bu}}]\text{CoX}$ ($X = \text{Cl, I}$), indicating that they all have similar electronic structures.

![Electronic absorption spectrum of $[\text{PhTt}^{t\text{Bu}}]\text{Co}(3,5-\text{DBCatH})$ in THF.](image)

Figure 4.17. Electronic absorption spectrum of $[\text{PhTt}^{t\text{Bu}}]\text{Co}(3,5-\text{DBCatH})$ in THF.
The electronic spectrum of [PhTt^{tBu}]Co(3,5-DBCatH) is shown in Figure 4.17. The intense absorption features at 287 (8444 M\(^{-1}\) cm\(^{-1}\)), 336 (sh, 2437) and 427 (2069) nm are assigned as charge transfer (CT) bands. The ligand-field transitions at 664 (430 M\(^{-1}\) cm\(^{-1}\)), 718 (426 M\(^{-1}\) cm\(^{-1}\)) and 792 (364 M\(^{-1}\) cm\(^{-1}\)) nm are characteristic of tetrahedral high-spin Co\(^{II}\) (\(S = 3/2\)) complexes.

### 4.7 Comparison of the Two Synthetic Routes Leading to [PhTt^{tBu}]Fe(CO)\(_2\)

The second example showing that [PhTt^{tBu}]MI (M = Co, Fe) are superior over [PhTt^{tBu}]MCl (M = Co, Fe) is the preparation of [PhTt^{tBu}]Fe(CO)\(_2\), which was reported previously by M. T. Mock\(^{36}\) using the ligand substitution reaction of [PhTt^{tBu}]Fe(PMe\(_3\)) with CO. To obtain [PhTt^{tBu}]Fe(PMe\(_3\)), [PhTt^{tBu}]FeCl is reduced by potassium graphite (KC\(_8\)) in the presence of PMe\(_3\); the yield of this step is moderate. Attempts to prepare [PhTt^{tBu}]Fe(CO)\(_2\) by adding CO to [PhTt^{tBu}]FeCl in the presence of KC\(_8\) proved to be unsuccessful. Notably, direct preparation of [PhTt^{tBu}]Fe(CO)\(_2\) was achieved by adding 1 atm of CO to [PhTt^{tBu}]FeI in the presence of KC\(_8\), Scheme 4.2. The \(^1\)H NMR spectrum of [PhTt^{tBu}]Fe(CO)\(_2\) prepared through the new route is depicted in Figure 4.18. At low temperature (-78 °C), CO binds to [PhTt^{tBu}]FeI in diethyl ether solution causing a color change from green to red. This phenomenon is not observed with [PhTt^{tBu}]FeCl. Thus, the difference in CO affinity between [PhTt^{tBu}]FeI and [PhTt^{tBu}]FeCl explains the course of these reactions. Beside proceeding in fewer steps, another advantage of using [PhTt^{tBu}]FeI to prepare [PhTt^{tBu}]Fe(CO)\(_2\) is that it avoids the generation of (PMe\(_3\))\(_2\)Fe(CO)\(_3\), a byproduct which is difficult to separate from [PhTt^{tBu}]Fe(CO)\(_2\).
Scheme 4.2. Comparison of the two synthetic routes leading to $[\text{PhTt}^{\text{Bu}}]\text{Fe(CO)}_2$.

Figure 4.18. $^1\text{H NMR}$ spectrum of $[\text{PhTt}^{\text{Bu}}]\text{Fe(CO)}_2$ from the reaction of $[\text{PhTt}^{\text{Bu}}]\text{FeI} + \text{KC}_8 + \text{CO}$. 
4.8 Conclusion

A series of tris(thioether)-supported metal iodide complexes [PhTt\textsubscript{Bu}]MI (M = Mn, Fe, Co, Ni) were prepared and characterized by LIFDI mass spectroscopy, X-ray crystallography, \textsuperscript{1}H NMR spectroscopy, magnetic measurements and electronic absorption spectroscopy. These complexes were compared structurally and spectroscopically to other metal iodide complexes supported by scorpionate ligands such as Tp and Tm. [PhTt\textsubscript{Bu}]MI (M = Mn, Fe, Co, Ni) all feature pseudotetrahedral coordination and contain high-spin metal centers. [PhTt\textsubscript{Bu}]CoI features a large spin-orbit coupling and a significant zero-field splitting (zfs), as discovered by the SQUID magnetometry. Preliminary reactivity studies show that in some cases the iodide complexes are better synthetic precursors than the corresponding chloride analogues.

In one case, [PhTt\textsubscript{Bu}]CoI proved to be a more effective starting material than [PhTt\textsubscript{Bu}]CoCl in generating [PhTt\textsubscript{Bu}]Co(3,5-DBCatH). This is likely due to the iodide being a better leaving group. In a second example, [PhTt\textsubscript{Bu}]FeI reacted with CO in the presence of KC\textsubscript{8} affording [PhTt\textsubscript{Bu}]Fe(CO)\textsubscript{2}. Notably, [PhTt\textsubscript{Bu}]FeCl did not react with CO in the presence of KC\textsubscript{8}. This is likely due to the iodide being a weaker electron-withdrawing group, which makes the ferrous center more electron-rich and thus, a better acceptor for CO ligands.
Chapter 5

FIVE-COORDINATE M(II)-SEMIQUINONATE COMPLEXES (M = Fe, Mn, Ni, Co) SUPPORTED by [PhTt^tBu] LIGAND: SYNTHESIS, MOLECULAR and ELECTRONIC STRUCTURES, MAGNETIC and REDOX PROPERTIES, and O₂ REACTIVITY

5.1 Introduction

Transition metal dioxolene complexes, in which the dioxolene ligand can exist in three redox states— [catecholate]²⁻, [semiquinonate]¹⁻ and [quinone]⁰ — have attracted much attention in the last several decades. The study of the electronic and magnetic properties of transition metal-dioxolene complexes, with particular attention to valence tautomerism⁹⁷-⁹⁹ and spin-crossover,¹⁰⁰-¹⁰⁵ is an area of such interest. Additionally, biomimetic and bioinspired transition metal-dioxolene chemistry, in which metal-dioxolene complexes serve as structural and/or functional models for the catechol dioxygenases, is another subject that has been intensively studied.¹²-¹⁶, ¹十八, ²², ²⁴, ¹⁰⁶-¹¹⁷ Related to this subject, transition metal-dioxolene complexes also serve as functional models for catechol oxidases¹¹⁸, ¹¹⁹ and as catalysts for other substrate oxidation reactions with dioxygen.²³

Among many transition metal-dioxolene complexes, the 1:1 transition metal-dioxolene complexes supported by ancillary ligands are simple and elegant. By varying the ancillary ligands, geometric and electronic structures as well as magnetic properties of the metal-dioxolene complexes can be tuned. This strategy has resulted in a number of transition metal-dioxolene complexes including 1:1 Mn-dioxolene¹¹⁷ and 1:1 Co-dioxolene complexes¹²⁰-¹²³ exhibiting valence tautomeric interconversion
between $\text{M}^{\text{II}}$-semiquinonate and $\text{M}^{\text{III}}$-catecholate ($\text{M} = \text{Mn}$ and $\text{Co}$) states. In addition, the valence tautomers of the Ni-dioxolene species, i.e. Ni$^{\text{II}}$-semiquinonate and Ni$^{\text{III}}$-catecholate species, were isolated and characterized through simple modification of the ancillary ligand.$^{124, 125}$ Although rare, 1:1 Fe-dioxolene$^{100-103}$ and Co-dioxolene$^{104, 105}$ complexes exhibiting spin-crossover properties were also reported.

In biology, five-coordinate 1:1 Fe$^{\text{III}}$-catecholate species in a N2O ligand environment are found in the active sites of the intradiol catechol dioxygenases, non-heme iron(III) enzymes that catalyze the oxidative cleavage of the C1–C2 bond of catechols.$^8$ In spite of the implication that the valence tautomeric state of such 1:1 Fe$^{\text{III}}$-catecholate species, namely an Fe$^{\text{II}}$-semiquinonate state, may be the active form for $\text{O}_2$ activation in the intradiol catechol dioxygenases and their model complexes,$^{14-16, 18, 103}$ no 1:1 Fe$^{\text{II}}$-semiquinonate species have been isolated and characterized prior to this study.$^91$ Given the importance of 1:1 Fe$^{\text{II}}$-semiquinonate species for understanding the $\text{O}_2$ activating mechanism for the intradiol dioxygenase catalysis, it is highly desirable to prepare such a species, understand its electronic structure, and probe its $\text{O}_2$ reactivity.

It is also of interest to explore the intradiol cleavage reactivity of other M$^{\text{II}}$-semiquinonate complexes. Such interest originates from the work of Lipsomb and coworkers$^{25-28}$ on the extradiol catechol dioxygenases, a class of non-heme iron(II) or manganese(II) enzyme catalyzing the oxidative cleavage of C2–C3 bond of catechols.$^8, 10$ They have shown that substituting the iron(II) ion in the active site of the native enzyme with manganese(II) or cobalt(II) yields comparable extradiol cleavage activities. These results are striking given the difference in redox potentials among the metal sites. Further, these results support the intermediacy of a proposed superoxo-
M$^\text{II}$-semiquinonate species (M = Fe, Mn, Co) in the catalytic cycles. Analogously, by studying the O$_2$ reactivity of other M$^\text{II}$-semiquinonate complexes additional knowledge of the catalytic mechanism for the intradiol catechol dioxygenases will be gained.

In this Chapter, the synthesis, molecular and electronic structures, magnetic and redox properties, and O$_2$ reactivity of a series of M$^\text{II}$-semiquinonate complexes (M = Fe, Mn, Ni, Co) supported by [PhTt$_{\text{tBu}}$] ligand are reported. Two types of semiquinone ligands were used in this study: phenanthrenesemiquinone (phenSQ) and 3,5-di-tert-butyl-o-benzosemiquinone (3,5-DBSQ). The study of these complexes led to the following key contributions:

1) full characterization of the first mononuclear Fe$^\text{II}$-semiquinonate species and its demonstrated intradiol cleavage reactivity.

2) demonstration of the first intradiol cleavage reactivity exhibited by a well-characterized Co$^\text{II}$-semiquinonate species.

3) disclosure of the first five-coordinate Co$^\text{II}$-semiquinonate complex exhibiting spin crossover instead of valence tautomerization behavior.

5.2 Synthesis and Characterizations of [PhTt$_{\text{tBu}}$]M(PhenSQ) (M = Fe, Mn, Ni, Co)

5.2.1 Synthesis of [PhTt$_{\text{tBu}}$]M(PhenSQ) (M = Fe, Mn, Ni, Co)

[PhTt$_{\text{tBu}}$]M(phenSQ) (M = Fe$^{91}$, Mn$^{91}$, Ni$^{126}$, Co$^{91}$) complexes were synthesized using two complementary preparative routes, Scheme 5.1. Metathesis of [PhTt$_{\text{tBu}}$]MI (M = Fe, Mn, Co, Ni) with Ti(phenSQ) yielded [PhTt$_{\text{tBu}}$]M(phenSQ) in excellent yields (89–95%). [PhTt$_{\text{tBu}}$Fe](phenSQ) and [PhTt$_{\text{tBu}}$Co](phenSQ) were also prepared by reacting the appropriate Fe(I) and Co(I) sources with phenanthrenequinone (phenQ), respectively. High resolution LIFDI mass spectroscopy
data combined with $^1$H NMR spectral analysis confirmed the composition and purity of [PhTt$^{tBu}$]M(phenSQ) complexes.

5.2.2 Molecular Structures of [PhTt$^{tBu}$]M(phenSQ) (M = Fe, Mn, Ni, Co)

[PhTt$^{tBu}$]M(phenSQ) (M = Fe, Mn, Ni, Co) complexes were characterized by X-ray crystallography and their thermal ellipsoid plots at 200 K are contained in Figures 5.1 and 5.2. Selected metric parameters of [PhTt$^{tBu}$]M(phenSQ) are summarized in Table 5.1. The C–O bond distances of the dioxolene moieties of all the complexes fall into the semiquinonate (SQ) regime (typical C–O bond lengths for SQ are 1.27-1.30 Å). Therefore, the best description of the electronic structures for these complexes when considering the metric parameters is M$^{II}$-semiquinonate complexes.
Figure 5.1. Molecular structures of [PhTtBu]Fe(phenSQ) (top) and [PhTtBu]Mn(phenSQ) (bottom) with atom labeling. Thermal ellipsoids are drawn to 30% probability. Hydrogen atoms have been omitted for clarity.
Figure 5.2. Molecular structures of $[\text{PhTt}^{\text{Bu}}]\text{Ni(phenSQ)}$ (top) and $[\text{PhTt}^{\text{Bu}}]\text{Co(phenSQ)}$ (bottom) with atom labeling. Thermal ellipsoids are drawn to 30% probability. Hydrogen atoms have been omitted for clarity.
Table 5.1. Selected bond lengths (Å) and $\tau_5$-values of [PhTt^{tBu}]M(phenSQ) at 200 K.

<table>
<thead>
<tr>
<th>M</th>
<th>Fe</th>
<th>Mn</th>
<th>Co</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>M–S2ax</td>
<td>2.388(1)</td>
<td>2.587(1)</td>
<td>2.309(1)</td>
<td>2.303(1)</td>
</tr>
<tr>
<td>M–S1eq</td>
<td>2.456(1)</td>
<td>2.502(1)</td>
<td>2.297(1)</td>
<td>2.381(1)</td>
</tr>
<tr>
<td>M–S3eq</td>
<td>2.506(1)</td>
<td>2.497(1)</td>
<td>2.279(1)</td>
<td>2.358(1)</td>
</tr>
<tr>
<td>M–O1</td>
<td>2.064(2)</td>
<td>2.109(2)</td>
<td>1.922(1)</td>
<td>2.015(2)</td>
</tr>
<tr>
<td>M–O2</td>
<td>2.015(2)</td>
<td>2.080(2)</td>
<td>1.912(1)</td>
<td>1.986(2)</td>
</tr>
<tr>
<td>O1–C22</td>
<td>1.285(2)</td>
<td>1.282(4)</td>
<td>1.301(2)</td>
<td>1.280(3)</td>
</tr>
<tr>
<td>O2–C35</td>
<td>1.435(3)</td>
<td>1.436(5)</td>
<td>1.411(2)</td>
<td>1.433(3)</td>
</tr>
<tr>
<td>$\tau_5$-values</td>
<td>0.14</td>
<td>0.58</td>
<td>0.01</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Table 5.2 contains the Fe–O/N bond distances for [PhTt^{tBu}]Fe(phenSQ)$_{91}$, [Tp^{Ph,Ph}]Fe(ISQ$_{tBu2}^{Bu}$)$_{21}$ (ISQ = iminobenzosemiquinonate), and [Tp^{Bu,iPr}]Fe(3,5-DBC)$_{22}$ reported by Fiedler and coworkers is a well characterized iron(II)-ISQ complex in which the high-spin iron(II) center ($S = 2$) is antiferromagnetically coupled to the ISQ radical ($S = 1/2$) yielding an overall $S = 3/2$ ground state.$^{21}$ In contrast, [Tp^{Bu,iPr}]Fe(3,5-DBC) reported by Hikichi and coworkers is best described as an iron(III)-catecholate complex.$^{22}$ The Fe–O bond distances for [PhTt^{tBu}]Fe(phenSQ) are 2.064(2) and 2.015(2) Å. These bond lengths are very close to the Fe–O bond length for [Tp^{Ph,Ph}]Fe(ISQ$_{tBu2}^{Bu}$), but much longer than the Fe–O bond lengths for [Tp^{Bu,iPr}]Fe(3,5-DBC) (1.94(1) and 1.93(1) Å), consistent with the presence of an iron(II) center in [PhTt^{tBu}]Fe(phenSQ).

Table 5.2. Fe–O/N Bond Distances (Å) for [PhTt^{tBu}]Fe(phenSQ), [Tp^{Ph,Ph}]Fe(ISQ$_{tBu2}^{Bu}$) and [Tp^{Bu,iPr}]Fe(3,5-DBC).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Fe–O/N Bond Distances (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[PhTt^{tBu}]Fe(phenSQ)</td>
<td>2.064(2), 2.015(2)</td>
</tr>
<tr>
<td>[Tp^{Ph,Ph}]Fe(ISQ$_{tBu2}^{Bu}$)</td>
<td>2.095(2) (Fe-O), 1.982(2) (Fe-N)</td>
</tr>
<tr>
<td>[Tp^{Bu,iPr}]Fe(3,5-DBC)</td>
<td>1.94(1), 1.93(1)</td>
</tr>
</tbody>
</table>
Table 5.3 contains the Mn–O bond distances for [PhTtBu]Mn(phenSQ), [TpCum,Me]Mn (NN-SQ), [TpCum,Me]Mn (NN-SQ), [TpCum,Me]Mn (NN-SQ) reported by Schultz and coworkers is a five-coordinate complex containing a high-spin MnII center antiferromagnetically coupled to the NN-SQ diradical. [TpIPr2]Mn(3,5-DBSQ) was reported by Hikichi and coworkers and [TPA]Mn(3,5-DBSQ) was reported by Funabiki and coworkers. Both of these latter six-coordinate complexes are MnII-SQ. The similarity in the Mn–O bond lengths for [PhTtBu]Mn(phenSQ) compared with the other three complexes clearly shows that [PhTtBu]Mn(phenSQ) is a MnII-SQ complex.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mn–O Bond Distances (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[PhTtBu]Mn(phenSQ)</td>
<td>2.109(2), 2.080(2)</td>
</tr>
<tr>
<td>[TpCum,Me]Mn(NN-SQ)</td>
<td>2.172(4), 2.058(5)</td>
</tr>
<tr>
<td>[TpIPr2]Mn(3,5-DBSQ)(CH3CN)</td>
<td>2.1113(19), 2.1739(16)</td>
</tr>
<tr>
<td>[TPA]Mn(3,5-DBSQ)</td>
<td>2.121(2), 2.138(2)</td>
</tr>
</tbody>
</table>

Table 5.4 contains the Ni–O bond distances for [PhTtBu]Ni(phenSQ), [PCP]Ni(3,6-DBSQ), [PCP]Ni(3,6-DBSQ) reported by Schultz and coworkers is a five-coordinate NiII-SQ complex. It contains a high-spin NiII center (S = 1) antiferromagnetically coupled to the NN-SQ diradical (S = 1).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ni–O Bond Distances (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[PhTtBu]Ni(phenSQ)</td>
<td>2.109(2), 2.080(2)</td>
</tr>
<tr>
<td>[PCP]Ni(3,6-DBSQ)</td>
<td>2.1113(19), 2.1739(16)</td>
</tr>
</tbody>
</table>
= 1) affording a \( S = 0 \) ground state. \([\text{PCP}]\mathrm{Ni}(3,6-\text{DBSQ})\) reported by Bubnov and coworkers is a five-coordinate \( \text{Ni}^{\text{II}} \)-SQ complex supported by a PCP pincer ligand. \([\text{Ni}(\text{PyBz}_2)(3,5-\text{DBSQ})]\text{PF}_6\) reported by Tanaka and coworkers is a four-coordinate square-planar \( \text{Ni}^{\text{II}} \)-SQ complex supported by a \([\text{N(pyridine)},\text{N(amine)}]\) bidentate ligand. The last two complexes contain low-spin \( \text{Ni}^{\text{II}} \) centers (\( S = 0 \)). The average \( \text{Ni}–\text{O} \) bond length for \([\text{PhTt}^\text{Bu}]\mathrm{Ni}(\text{phenSQ})\) (2.001(2) Å) is almost identical to the average \( \text{Ni}–\text{O} \) bond length for \([\text{Tp}^\text{Cum,Me}]\mathrm{Ni}(\text{NN-SQ})\) (2.002(1) Å), although \([\text{Tp}^\text{Cum,Me}]\mathrm{Ni}(\text{NN-SQ})\) features greater asymmetry between the \( \text{Ni}–\text{O} \) bonds. The two low-spin \( \text{Ni}^{\text{II}} \)-SQ complexes have shorter \( \text{Ni}–\text{O} \) bonds compared to \([\text{PhTt}^\text{Bu}]\mathrm{Ni}(\text{phenSQ})\). Thus, the \( \text{Ni}^{\text{II}} \) ion in \([\text{PhTt}^\text{Bu}]\mathrm{Ni}(\text{phenSQ})\) is likely high-spin.

Table 5.4. \( \text{Ni}–\text{O} \) bond distances for \([\text{PhTt}^\text{Bu}]\mathrm{Ni}(\text{phenSQ})\), \([\text{Tp}^\text{Cum,Me}]\mathrm{Ni}(\text{NN-SQ})\), \([\text{PCP}]\mathrm{Ni}(3,6-\text{DBSQ})\) and \([\text{Ni}(\text{PyBz}_2)(3,5-\text{DBSQ})]\text{PF}_6\).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ni–O Bond Distances (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{PhTt}^\text{Bu}]\mathrm{Ni}(\text{phenSQ}))</td>
<td>2.015(2), 1.986(2)</td>
</tr>
<tr>
<td>([\text{Tp}^\text{Cum,Me}]\mathrm{Ni}(\text{NN-SQ}))</td>
<td>2.046(1), 1.957(1)</td>
</tr>
<tr>
<td>([\text{PCP}]\mathrm{Ni}(3,6-\text{DBSQ}))</td>
<td>1.9238(10), 2.0595(10)</td>
</tr>
<tr>
<td>([\text{Ni}(\text{PyBz}_2)(3,5-\text{DBSQ})]\text{PF}_6)</td>
<td>1.860(3), 1.843(3)</td>
</tr>
</tbody>
</table>

Interestingly, the average M–O distance at 200 K follows the trend Mn–O > Fe–O > Ni–O > Co–O, whereas the covalent radii are in the order of Mn > Fe > Co > Ni. The short Co–O distances are in harmony with longer C–O (1.301(2) and 1.297(2) Å) and shorter C–C (1.411(2) Å) distances for \([\text{PhTt}^\text{Bu}]\mathrm{Co}(\text{phenSQ})\) compared to its Fe, Mn and Ni analogues. Stronger back-donation from the cobalt to the semiquinonate moiety provides a rationale for these observations. The novel metric parameters for \([\text{PhTt}^\text{Bu}]\mathrm{Co}(\text{phenSQ})\) suggest a different electronic structure from
those of \([\text{PhTt}^{\text{Bu}}]\text{M(phenSQ)}\) (M = Fe, Mn, Ni). Similar short Co–O bond lengths (Co1–O1 1.856(2) Å, Co1–O2 1.865(2) Å) were observed in the six-coordinate low-spin Co(II)-SQ complex, \([\text{Co}(\text{L-N}_4\text{Bu}_2)(3,5-\text{DBSQ})](\text{B}(p-\text{C}_6\text{H}_4\text{Cl})_4)\) \((\text{L-N}_4\text{Bu}_2 = \text{N, N-di-}t\text{-butyl-2,11-diaza}[3.3](2,6)\text{pyridinophane})\), reported by Krüger and coworkers.\(^{104}\)

Structural analysis indicated that \([\text{PhTt}^{\text{Bu}}]\text{Co(phenSQ)}\) at 200 K could be a low-spin Co(II)-SQ complex, and yet the room temperature electronic spectrum was indicative of a high-spin site, \textit{vide infra}. Thus, the crystallographic data at lower (100 K) and higher (295 K) temperatures were collected, with the resulting metric parameters contained in Table 5.5. Comparison of the metric data for \([\text{PhTt}^{\text{Bu}}]\text{Co(phenSQ)}\) collected at 100 K and 295 K reveals dramatic differences in the bond lengths. The results are summarized as follows:

1) Going from 100 K to 295 K, the Co–S1 and Co–S3 bonds in the basal plane elongated by about 0.12-0.15 Å, the Co–S2 bond in the axial position lengthened by about 0.05 Å. The net result is that the basal Co–S bonds are much longer than the axial Co–S bond at 295 K. As depicted in Figure 5.3, this structural change lowers the energy of the highest occupied molecular orbital \((d_{x^2-y^2})\) much more than it lowers the energy of the second highest occupied molecular orbital \((d_z^2)\). Thus, the energy gap between \(d_{x^2-y^2}\) and \(d_z^2\) is reduced, which makes the high-spin configuration more favorable.
Figure 5.3. Qualitative energy diagram for $d_{x^2-y^2}$ and $d_{z^2}$ orbitals of [PhTt[Bu]Co(phenSQ) in the high-spin and low-spin configurations.

2) The Co–O bonds elongated by 0.08-0.09 Å when comparing the structure recorded at 100 K to the one at 295 K. Such elongation also lowers the energy of $d_{x^2-y^2}$ orbital and makes the high-spin configuration more favorable. Also noticed is that at 295 K the average Co–O bond length is very close to the average Ni–O bond length, so that the trend of M–O bond lengths is now Mn–O > Fe–O > Co–O ≈ Ni–O. This trend is more consistent with the valence radii order of Mn > Fe > Co > Ni, indicating that the spin state of Co$^{II}$ at 295 K is likely high-spin as found in the other metal complexes.
3) At 100 K, the average C–O distance is 1.303(3) Å. At 295 K, the average C–O distance is 1.283(3) Å. These C–O distances are consistent with the semiquinonate rather than the catecholate form.

Table 5.5. Selected bond lengths (Å) of [PhTt{Bu}Co(phenSQ) at 100 K and 295 K.

<table>
<thead>
<tr>
<th>Bond</th>
<th>100 K</th>
<th>295 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co–S1</td>
<td>2.258(1)</td>
<td>2.405(1)</td>
</tr>
<tr>
<td>Co–S3</td>
<td>2.246(1)</td>
<td>2.372(1)</td>
</tr>
<tr>
<td>Co–S2</td>
<td>2.294(1)</td>
<td>2.342(1)</td>
</tr>
<tr>
<td>Co–O1</td>
<td>1.900(2)</td>
<td>1.993(2)</td>
</tr>
<tr>
<td>Co–O2</td>
<td>1.893(2)</td>
<td>1.973(2)</td>
</tr>
<tr>
<td>O1–C22</td>
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<td>1.286(3)</td>
</tr>
<tr>
<td>O2–C35</td>
<td>1.300(3)</td>
<td>1.279(3)</td>
</tr>
<tr>
<td>C35–C22</td>
<td>1.406(3)</td>
<td>1.422(4)</td>
</tr>
</tbody>
</table>

In short, the temperature-dependent crystallographic data are consistent with the assignment that at 295 K the Co in [PhTt{Bu}Co(phenSQ) is in a high-spin configuration, whereas at 100 K the Co is in a low-spin configuration. This temperature-dependent spin-state behavior is supported further by variable temperature spectroscopic and magnetic data, vide infra.

5.2.3 Electronic Absorption Spectra of [PhTt{Bu}]M(PhenSQ) (M = Fe, Mn, Ni, Co)

The electronic spectra of [PhTt{Bu}]M(phenSQ) (M = Fe, Mn, Ni, Co) in THF are displayed in Figure 5.4. [PhTt{Bu}]Fe(phenSQ) showed two features of low intensity at 600 (868 M⁻¹ cm⁻¹) and 935 (539) nm, the latter being consistent with a typical ligand-field transition for five-coordinate, high-spin Fe¹¹ complexes. No
ligand field transitions were observed for [PhTtBu|Mn(phenSQ)], indicating a high-spin MnII center. [PhTtBu]Ni(phenSQ) showed ligand-field transitions at 846 (710 M⁻¹ cm⁻¹) and 966 (sh, 282) nm. These transitions are in accord with the high-spin NiII (S = 1) configuration. Indeed, ligand-field transitions of previously reported five-coordinate NiII complexes supported by the tris(thioether)borate ligands occur at similar energies, 866 (54 M⁻¹ cm⁻¹) nm for [PhTtBu]Ni(NO₃) and 845 (350) nm for [PhTtAd]Ni(O₂), both complexes contain high-spin nickel(II) centers. More detailed assignments of the absorption features for [PhTtBu]Ni(phenSQ) and [PhTtBu]Fe(phenSQ) are discussed in the computational section, vide infra.

Figure 5.4. Electronic absorption spectra of [PhTtBu|M(PhenSQ)] (M = Fe, Mn, Ni, Co) in THF at room temperature. The insert highlights the ligand-field transitions between 550-1000 nm.
At room temperature, [PhTt(Bu)]Co(phenSQ) exhibits two features at 683 (1310 M⁻¹ cm⁻¹) and 803 (1290) nm in THF, Figure 5.4, which are consistent with the ligand-field transitions for five-coordinate, high-spin Co³⁺ complexes. As discussed in the previous section, [PhTt(Bu)]Co(phenSQ) exhibits temperature-dependent structural changes, which likely result from a spin state change. The variable temperature electronic spectra further support this assertion. Figure 5.5 shows the electronic spectral changes for [PhTt(Bu)]Co(phenSQ) in toluene as the temperature is reduced from 20 to -80 °C (top) and raised from -80 to 20 °C (bottom).
Figure 5.5. Electronic absorption spectral changes for [PhTt^tBu]Co(phenSQ) in toluene as the temperature varies: 20 to -80 °C (top); -80 to 20 °C (bottom).
The low intensity bands at 708 nm and 806 nm, which are indicative of a five-coordinate high-spin CoII, were replaced by a much more intense CT band at 823 nm (7361 M⁻¹ cm⁻¹) as the temperature decreased from 20 to -80 °C. The 823 nm band resembles the CT band of Krüger’s low-spin Co(II)-SQ complex [Co(L-N₄tBu₂)(3,5-DBSQ)](B(p-C₆H₄Cl)₄) (1075 (7640 M⁻¹ cm⁻¹) and 1042 (6890) nm), consistent with the high-spin to low-spin transition as the temperature decreases. The temperature-dependent spin transition is reversible, as shown by the return of the ligand field bands as the temperature was raised from -80 to 20 °C, Figure 5.5, bottom.

5.2.4 Magnetic Properties of [PhTtBu]M(PhenSQ) (M = Fe, Mn, Ni, Co)

5.2.4.1 Magnetic Properties of [PhTtBu]Fe(PhenSQ)

The effective magnetic moment for [PhTtBu]Fe(PhenSQ) in solution was measured by the Evans method. [PhTtBu]Fe(phenSQ) displayed μₑffective = 4.65(2) μB in benzene-d₆ at room temperature, consistent with an S = 3/2 spin state. The origin of the difference between the experimental μₑffective value compared to the spin-only value of 3.87 μB for S = 3/2, g = 2.0 system was investigated by SQUID magnetometry.

The temperature-dependent magnetic properties of [PhTtBu]Fe(phenSQ) in the solid state were probed by SQUID magnetometry. As shown in Figure 5.6, The χT value of 2.58 cm³.K.mol⁻¹ at 300 K comports with the solution magnetic moment at room temperature and is indicative of an S = 3/2 ground state. As the temperature is lowered from 300 to 50 K, the χT value slowly drops to 2.19 cm³.K.mol⁻¹, which is still higher than the spin-only value of 1.88 cm³.K.mol⁻¹. The decrease in χT is due to the thermal depopulation of the S = 5/2 excited state and is indicative of
antiferromagnetic coupling between the high-spin iron(II) center and the phenSQ radical. Interestingly, Fiedler’s mononuclear five-coordinate Fe$^{II}$-$p$-semiquinonate complex shows ferromagnetic coupling between the high-spin Fe$^{II}$ and the $p$-semiquinonate radical, as supported by their EPR data and DFT calculations.$^{19}$ The ferromagnetic exchange interaction in Fe$^{II}$-$p$-semiquinonate complex is likely due to the small overlap of its magnetic orbitals.

Below 50 K, the $\chi T$ value drops sharply, which could be attributed to zero field splitting (ZFS) and/or intermolecular interactions. The field dependent magnetization data collected at 1.8 K, Figure 5.7, slowly increased at lower fields, which is indicative of antiferromagnetic intermolecular interactions. At field above 5 T, it approaches saturation to 2.1 $\mu_B$, well below the expected value, which is also indicative of ZFS and/or intermolecular interactions. The susceptibility data were fitted to the Heisenberg Hamiltonian $H = -2J(S_1\cdot S_2)$ using PHI$^\circledR$ software.$^{134}$ The $\chi T$ values in the high temperature regime (300-50 K) were used to calculate a coupling constant of $J = -127$ cm$^{-1}$ ($H = -2J(S_1\cdot S_2)$) with $g = 2.22$. Fits of the low temperature data were used to estimate ZFS parameters of the Fe center ($D$) and intermolecular interactions ($zj$). Best fits were obtained for $D = 14.5$ cm$^{-1}$, $E = 0.001$ cm$^{-1}$ and $zj = -0.23$ cm$^{-1}$. No satisfactory fits were obtained without including intermolecular interactions. The field dependent magnetization data between 1.8 and 4.5K, Figure 5.8, are non-superimposable indicating the presence of ZFS in the molecule. Fits of the data using ANISOFIT$^{135}$ resulted in molecular ZFS parameters $D = 3.77$ cm$^{-1}$, $E = 0.003$ cm$^{-1}$ and $g = 1.73$. 


Figure 5.6. Temperature dependence of $\chi T$ versus $T$ plots (blue circles) for [PhTtBu]Fe(phenSQ). The susceptibility data were fitted (black and green lines) to Heisenberg Hamiltonian $H = -2J(S_1 \cdot S_2)$ using PHI® software yielding $J = -127 \text{ cm}^{-1}$ ($g = 2.22$), $D = 14.5 \text{ cm}^{-1}$, $E = 0.001 \text{ cm}^{-1}$ and $zj = -0.23 \text{ cm}^{-1}$.

Figure 5.7. Saturation magnetization data for [PhTtBu]Fe(phenSQ) at 1.8 K.
Figure 5.8. Reduced magnetization data for [PhTt\textsuperscript{tBu}]Fe(phenSQ) at 1.8-4.5 K. The red lines represent the best fits produced by theory.

### 5.2.4.2 Magnetic Properties of [PhTt\textsuperscript{tBu}]Mn(PhenSQ)

[PhTt\textsuperscript{tBu}]Mn(phenSQ) displays $\mu_{\text{eff}} = 5.01(6) \ \mu_B$ in benzene-$d_6$, which is very close to the spin-only value for an $S = 2$ system (4.90 $\mu_B$). Thus, the electronic structure of [PhTt\textsuperscript{tBu}]Mn(PhenSQ) can be described as having a high-spin Mn(II) ($S = 5/2$) antiferromagnetically coupled to the phenSQ radical giving an overall $S = 2$ ground state.\textsuperscript{91}
5.2.4.3 Magnetic Property of [PhTt^{Bu}]Ni(PhenSQ)

The room temperature effective magnetic moment $\mu_{\text{eff}}$ for [PhTt^{Bu}]Ni(PhenSQ) in benzene-$d_6$ is 2.20 $\mu_B$, which is indicative of an $S = 1/2$ ground state. The origin of a higher $\mu_{\text{eff}}$ value (2.20 $\mu_B$) compared to the spin-only value (1.73 $\mu_B$) for $S = 1/2$, $g = 2.0$ system was studied by SQUID magnetometry.

The temperature-dependent magnetic properties of [PhTt^{Bu}]Ni(PhenSQ) were probed using SQUID magnetometry. As shown in Figure 5.9, the $\chi_T$ value is 0.497 cm$^3$.K.mol$^{-1}$ at 300 K, corresponding to $\mu_{\text{eff}} = 1.99$ $\mu_B$, which is somewhat similar to the solution $\mu_{\text{eff}}$ value (2.20 $\mu_B$). Again, this $\mu_{\text{eff}}$ value is slightly higher than the spin-only value of 1.73 $\mu_B$, but much lower than that for an uncoupled system ($\mu_{\text{eff}} = 3.32$ $\mu_B$), suggesting strong antiferromagnetic coupling between the high-spin Ni$^{\text{II}}$ center ($S = 1$) and phenSQ radical ($S = 1/2$). The calculated $g$ value is 2.30 based on the magnetic data at 300 K, reflecting the anisotropic nature of the Ni center. Above 300 K, $\chi_T$ gradually increases due to the thermal population of an $S = 3/2$ exited state. Below 15K, the $\chi_T$ value drops sharply due to intermolecular interactions. The field dependent magnetization data collected at 1.8 K, Figure 5.10, increase slowly at lower fields indicative of antiferromagnetic intermolecular interactions. At fields above 5T, the magnetization data approaches saturation for the $S = 1/2$ ground state. The susceptibility data were fitted to Heisenberg Hamiltonian $H = -2J(S_1 \cdot S_2)$ using PHI® software. A large exchange coupling constant of $J = -318$ cm$^{-1}$ ($g = 2.22$, assuming $J \gg D$) with intermolecular dipole coupling $\zeta j = -0.57$ cm$^{-1}$ was obtained.

Notably, a triazamacrocyle supported five-coordinate Ni(II)-SQ complex reported by Dei and coworkers exhibited strong antiferromagnetic coupling between high-spin Ni$^{\text{II}}$ and SQ radical with $\mu_{\text{eff}} = 1.89$ $\mu_B$. The absolute value of the coupling
constant of this complex was estimated to be greater than 300 cm\(^{-1}\), due to the lack of populating excited states even up to 300 K.\(^{136}\) Similarly, in Shultz’s [Tp\(^{\text{Cum,Me}}\)Ni(NN-SQ) complex, the calculated \(J_{\text{Ni-SQ}}\) is between -244 cm\(^{-1}\) and -525 cm\(^{-1}\).\(^{127}\) To the best of our knowledge, the results provided herein include the first accurate coupling constant measured between a five-coordinate, high-spin Ni\(^{II}\) center (\(S = 1\)) antiferromagnetically coupled to a semiquinonate ligand (\(S = 1/2\)).

![Figure 5.9](image.png)

Figure 5.9. Temperature dependence of \(\chi T\) versus \(T\) plots (blue circles) for [PhTt\(^{\text{tBu}}\)Ni(phenSQ)]. The susceptibility data were fitted (black line) to Heisenberg Hamiltonian \(H = -2J(S_1 \cdot S_2)\) using PHI\(^{\text{®}}\) software yielding \(J = -320\) cm\(^{-1}\) (\(g = 2.22\)) and \(\zeta J = -0.57\) cm\(^{-1}\).
Figure 5.10. Field dependent magnetization data for [PhTt^Bu]Ni(phenSQ) at 1.8 K. The red circles and red line represent the experimental data. The black line represent $S = 1/2$ situation without intermolecular interaction.

5.2.4.4 Magnetic Properties of [PhTt^Bu]Co(PhenSQ)

As discussed earlier in the Chapter, the temperature-dependent structural and the electronic spectral data for PhTt^Bu]Co(phenSQ) can be explained by a temperature-dependent spin state change. At low temperatures, [PhTt^Bu]Co(phenSQ) is best described as a low-spin Co$^{II}$-SQ complex; at high temperatures, it is appropriately assigned as a AF-coupled high-spin Co$^{II}$-SQ complex.

The temperature-dependent magnetic properties of [PhTt^Bu]Co(phenSQ) were probed by SQUID magnetometry to further interrogate this molecule. As shown in Figure 5.11, between 2 K and 100 K the $\chi T$ value remains effectively unchanged (0.096 cm$^3$.K.mol$^{-1}$ at 2 K). For low-spin Co$^{II}$ ($S = 1/2$) with an antiferromagnetically
coupled SQ radical ($S = 1/2$), the ground state is diamagnetic ($S = 0$, $\chi T = 0$). The residual $\chi T$ value even at 2 K is likely due to a large spin-orbit coupling. Upon increasing the temperature above 150 K, the $\chi T$ value increases gradually to 1.17 cm$^3$.K.mol$^{-1}$ ($\mu_{\text{eff}} = 3.06 \mu_B$) at 300 K, indicating a spin transition to a high-spin Co$^{II}$ species with an antiferromagnetically coupled SQ radical. The solution magnetic moment at room temperature is 3.43(3) $\mu_B$, consistent with the solid state value. The spin transition is not complete at 300 K, yet the $\chi T$ value at 300 K is already greater than the spin-only value of 1.00 cm$^3$.K.mol$^{-1}$ for $S = 1$, $g = 2.0$ ground state. This is likely due to a large spin-orbit coupling or thermal population of the excited states or a combination of both. The compound is unstable above 310K, which precluded the ability to measure magnetic properties at higher temperatures. No hysteresis was observed in the $\chi T$ plot.
5.2.5 Mössbauer Studies of [PhTt\textsuperscript{tBu}]Fe(PhenSQ)

The solid state Mössbauer spectra of [PhTt\textsuperscript{tBu}]Fe(PhenSQ) were collected in an applied field of 0.04 T and at variable temperatures. The zero field spectrum recorded at 100 K is displayed in Figure 5.12. The spectra at 6 K–100K consist of a single sharp quadrupole doublet, with an isomer shift of 0.92 mm/s and a quadrupole splitting of 2.29 mm/s, which are consistent with a high-spin Fe\textsuperscript{II} complex.\textsuperscript{79} Temperatures up to 200 K did not affect the quadrupole splitting significantly. A five-coordinate high-spin ferrous complex, \{[PhTt\textsuperscript{dBu}]FeCl\}_2, was previously characterized in our laboratories, for which the isomer shift and quadrupole splitting values were 0.96 mm/s and 3.45 mm/s, respectively.\textsuperscript{36} Recently, Fiedler and Popescu et al. have explored the oxidation of Fe\textsuperscript{II}-catecholate complexes with Mössbauer spectroscopy,
showing that metal based oxidation leads to a significantly lower isomer shift (0.5 mm/s) as expected for an iron-centered oxidation.\textsuperscript{137}

![Zero-field Mössbauer spectrum of [PhTt\textsuperscript{Bu}]Fe(phenSQ) at 100 K. The solid red line is a least-square fit obtained with the parameters shown.](image)

Figure 5.12. Zero-field Mössbauer spectrum of [PhTt\textsuperscript{Bu}]Fe(phenSQ) at 100 K. The solid red line is a least-square fit obtained with the parameters shown.

5.3 Synthesis and Characterizations of [PhTt\textsuperscript{Bu}]M(3,5-DBSQ) (M = Mn, Ni, Co)

5.3.1 Synthesis of [PhTt\textsuperscript{Bu}]M(3,5-DBSQ) (M = Mn, Ni, Co)

Analogous to the synthetic route applied to [PhTt\textsuperscript{Bu}]M(phenSQ), [PhTt\textsuperscript{Bu}]M(3,5-DBSQ) (M = Mn, Ni, Co\textsuperscript{91}) was prepared in good to excellent yields through metathesis of [PhTt\textsuperscript{Bu}]MI (M = Mn, Co, Ni) with Tl(3,5-DBSQ), Scheme 5.3. Interestingly, exposure of [PhTt\textsuperscript{Bu}]Co(3,5-DBCatH) to O\textsubscript{2} generated [PhTt\textsuperscript{Bu}]Co(3,5-DBSQ), Scheme 5.2. High resolution LIFDI mass spectroscopy data combined with \textsuperscript{1}H NMR spectral analysis confirmed the composition and purity of [PhTt\textsuperscript{Bu}]Ni(3,5-DBSQ) and [PhTt\textsuperscript{Bu}]Co(3,5-DBSQ). [PhTt\textsuperscript{Bu}]Mn(3,5-DBSQ) is thermally unstable in
solution and thus, difficult to purify. Nonetheless, its formation was confirmed by $^1$H NMR and LIFDI spectroscopies.

Scheme 5.2 Synthetic routes to [PhTtBu]$^N$M(3,5-DBSQ) (M = Mn, Ni, Co).
5.3.2 Molecular Structures of [PhTtBu]M(3,5-DBSQ) (M = Ni, Co)

[PhTtBu]Ni(3,5-DBSQ) and [PhTtBu]Co(3,5-DBSQ) were characterized by X-ray crystallography. Their thermal ellipsoid plots at 200 K are shown in Figure 5.13 with selected metric parameters summarized in Table 5.6. Similar to the phenSQ analogues, [PhTtBu]Ni(3,5-DBSQ) and [PhTtBu]Co(3,5-DBSQ) are five-coordinate with 3,5-DBSQ binding in a bidentate fashion. The geometry of [PhTtBu]Ni(3,5-DBSQ) is distorted square pyramidal (τ5 = 0.34). The O1, O2 atoms of the semiquinonate ligands and the S1, S3 atoms of the [PhTtBu] ligand define the equatorial plane. The average C–O distance for [PhTtBu]Ni(3,5-DBSQ) is 1.285(2) Å, which agrees with the semiquinonate description (C–O bond lengths for semiquinonates: 1.27-1.31 Å). The average Ni–O distance for [PhTtBu]Ni(3,5-DBSQ) (1.999(1) Å) is experimentally indistinguishable from those for [PhTtBu]Ni(phenSQ) (2.001(2) Å) and TpCuMeNi(NN-SQ)127 (2.002(1) Å), indicating [PhTtBu]Ni(3,5-DBSQ) also contains a high-spin Ni(II) ion.

The geometry of [PhTtBu]Co(3,5-DBSQ) is also a distorted square pyramidal (τ5 = 0.17). The average C–O distance for [PhTtBu]Co(3,5-DBSQ) (1.314(2) Å) is a bit long compared to those for the semiquinonate ligands coordinated to high-spin metal centers, but is very close to those values reported for [Co(L-N4tBu2)(3,5-DBSQ)](B(p-C6H4Cl)4)104 (1.313(2) Å) and [Ni(PyBz2)(3,5-DBSQ)]PF6124 (1.300(5) Å) in which the metal centers are low-spin. The average Co–O distance for [PhTtBu]Co(3,5-DBSQ) (1.884(1) Å) is close to that for [Co(L-N4tBu2)(3,5-DBSQ)](B(p-C6H4Cl)4) (1.890(2) Å), but longer than that for (triphos)Co(3,5-DBCat)BPh4138 (triphos = MeC(CH2PPh2)) (1.86 (1) Å), a five-coordinate CoIII-catecholate complex reported by Bianchini and coworkers. These comparisons suggest that [PhTtBu]Co(3,5-DBSQ) is indeed best described as a low-spin CoII-SQ complex.
Figure 5.13. Molecular structures of [PhTt\(^{iBu}\)]Ni(3,5-DBSQ) (top) and [PhTt\(^{iBu}\)]Co(3,5-DBSQ) (bottom) with atom labeling. Thermal ellipsoids are drawn to 30% probability. Hydrogen atoms have been omitted for clarity.
Table 5.6. Selected bond lengths (Å) and $\tau_5$ values for [PhTtBu]Ni(3,5-DBSQ) and [PhTtBu]Co(3,5-DBSQ) at 200 K.

<table>
<thead>
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<th>Co(3,5-DBSQ)</th>
</tr>
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<td>2.270(1)</td>
</tr>
<tr>
<td>M–S(basal)</td>
<td>2.382(1)</td>
<td>2.253(1)</td>
</tr>
<tr>
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</tr>
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</tr>
<tr>
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</tr>
<tr>
<td>$\tau$-value</td>
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<td>0.17</td>
</tr>
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</table>

5.3.3 $^1$H NMR and LIFDI Mass Spectroscopies of [PhTtBu]Mn(3,5-DBSQ)

At room temperature, [PhTtBu]Mn(3,5-DBSQ) decomposes slowly in diethyl ether over the course of 24 hours and immediately in THF. This intrinsic instability has thus far hampered the ability to prepared single crystals suitable for X-ray diffraction analysis. The crude product likely contains impurities as suggested by the LIFDI mass spectrum. Nevertheless, the formation and composition of [PhTtBu]Mn(3,5-DBSQ) was confirmed by high resolution LIFDI mass spectroscopy, Figure 5.14. Due to the similarity in the $^1$H NMR spectra between [PhTtBu]Mn(phenSQ) and [PhTtBu]Mn(3,5-DBSQ), Figure 5.15, [PhTtBu]Mn(3,5-DBSQ) is assigned as a Mn(II)-SQ complex.
Figure 5.14. High resolution LIFDI mass spectra of [PhTt\textsuperscript{tBu}]Mn(3,5-DBSQ).

Figure 5.15. Comparison of the $^1$H NMR spectra of [PhTt\textsuperscript{tBu}]Mn(3,5-DBSQ) (top) and [PhTt\textsuperscript{tBu}]Mn(phenSQ) (bottom).
5.3.4 Electronic Absorption Spectra of [PhTtBu]M(3,5-DBSQ) (M = Ni, Co)

The electronic absorption spectrum of [PhTtBu]Ni(3,5-DBSQ) in toluene is shown in Figure 5.16. Two ligand field transitions at 842 (823 M⁻¹ cm⁻¹) and 966 (sh, 365) nm were observed. These transitions are in close analogy to those at 846 (710) and 966 (sh, 282) nm for [PhTtBu]Ni(phenSQ), suggesting that [PhTtBu]Ni(3,5-DBSQ) also contains a high-spin NiII center.

The electronic absorption spectrum of [PhTtBu]Co(3,5-DBSQ) at room temperature together with [PhTtBu]Co(phenSQ) at -80 °C are shown in Figure 5.17. At room temperature, [PhTtBu]Co(3,5-DBSQ) showed three intense features at 784 (5466 M⁻¹ cm⁻¹), 495 (4123) and 298 (9936) nm, which are similar to those at 823 (7361), 514 (5223) and 340 (11078) nm for [PhTtBu]Co(phenSQ) at -80 °C. Such congruity indicates that the electronic structure of [PhTtBu]Co(3,5-DBSQ) at room temperature is similar to that of [PhTtBu]Co(phenSQ) at -80 °C, the latter possessing a low-spin CoII AF-coupled to a SQ radical. Thus, [PhTtBu]Co(3,5-DBSQ) at room temperature is best described as a low-spin (or mostly low-spin) CoII-SQ complex. This assignment also agrees with the conclusion drawn from the crystallographic data.
Figure 5.16. The electronic absorption spectrum of [PhTt\textsuperscript{Bu}]Ni(3,5-DBSQ) in toluene. The insert highlights the ligand field transitions.

Figure 5.17. Comparison of the electronic absorption spectra of [PhTt\textsuperscript{Bu}]Ni(3,5-DBSQ) in THF at room temperature and [PhTt\textsuperscript{Bu}]Co(phenSQ) at -80 °C in toluene.
5.3.5 Magnetic Properties of [PhTt^tBu]M(3,5-DBSQ) (M = Ni, Co)

The temperature dependent magnetic properties of [PhTt^tBu]Ni(3,5-DBSQ) were probed using SQUID magnetometry, Figure 5.18. The $\chi_T$ value is 0.52 cm$^3$.K.mol$^{-1}$ at 300 K, corresponding to $\mu_{\text{eff}} = 2.03 \mu_B$ which is consistent with the solution $\mu_{\text{eff}}$ of 2.25 $\mu_B$ at room temperature. The $\chi_T$ value at 300 K was slightly higher than the spin-only value of 0.375 cm$^3$.K.mol$^{-1}$ (1.73 $\mu_B$) expected for an $S = 1/2$, $g = 2.0$ ground state, but much lower than that for uncoupled system ($\mu_{\text{eff}} = 3.32 \mu_B$), suggesting strong antiferromagnetic coupling between the high-spin Ni$^{II}$ ($S = 1$) and 3,5-DBSQ radical ($S = 1/2$). The calculated $g$-value is 2.35 based on the magnetic data at 300 K, reflecting the anisotropic nature of the Ni center. The $\chi_T$ value was effectively constant over the temperature range 2-300 K, which further supports the presence of very strong antiferromagnetic coupling leading to the population of $S = 1/2$ state. Beyond 300 K, $\chi_T$ gradually increased due to thermal population of the $S = 3/2$ exited state. The field dependent magnetization data collected at 1.8K approached saturation to the $S = 1/2$ ground state at fields above 5T, Figure 5.19. The susceptibility data were fitted to Heisenberg Hamiltonian $H = -2J(S_1\cdot S_2)$ using PHI® software. The absence of any deviations in the $\chi_T$ values at low temperature also suggests negligible ZFS parameters and the absence of intermolecular interactions in the system. A large value of $J$, -382 cm$^{-1}$ ($g = 2.236$) was obtained.
Figure 5.18. Temperature dependence of $\chi_T$ versus T plots (blue circles) for [PhTt$^{tBu}$]Ni(3,5-DBSQ). The susceptibility data were fitted (black line) to Heisenberg Hamiltonian $H = -2J(S_1 \cdot S_2)$ using PHI® software yielding $J = -380 \text{ cm}^{-1}$ ($g = 2.236$).

Figure 5.19. Field dependent magnetization data for [PhTt$^{tBu}$]Ni(3,5-DBSQ) at 1.8 K. The red circles and red line represent the experimental data. The black line represent $S = 1/2$ situation without intermolecular interaction.
The temperature dependent magnetic properties of [PhTtBu]Co(3,5-DBSQ) were probed using SQUID magnetometry, Figure 5.20. The χT value at 300 K was 1.13 cm³.K.mol⁻¹, corresponding to μeff = 3.01 μB, consistent with the solution μeff of 2.91(2) μB at room temperature. The χT value decreased gradually to ca. 0.6 cm³.K.mol⁻¹ as the temperature dropped to 200 K, indicative of a spin transition. At 200 K, most of the molecules of [PhTtBu]Co(3,5-DBSQ) are low-spin CoII-SQ. Above 200 K, the high-spin CoII-SQ state starts to be populated. However, the spin-transition is far from complete at 300 K. Therefore, the electronic spectrum at room temperature reflects the low-spin CoII-SQ character. Below 200 K, the χT value decreased very slowly to ca. 0.5 cm³.K.mol⁻¹ at 50 K. This residual χT is likely due to a large spin-orbit coupling or thermal population of the excited states of an antiferromagnetic coupled low-spin CoII-SQ (S = 0).

Figure 5.20. Temperature dependence of χT versus T plot (blue circles) and χ versus T plot (red diamonds) for [PhTtBu]Co(3,5-DBSQ).
5.4 Attempts to Synthesize [PhTt^{Bu}]Fe^{II}(3,5-DBSQ) or [PhTt^{Bu}]Fe^{III}(3,5-DBC)

3,5-DBSQ has a higher reduction potential than that of phenSQ. In other words, 3,5-DBSQ is more readily reduced to 3,5-di-tert-butyl-catecholate (3,5-DBC). Thus, stabilization of the Fe^{II}-semiquinonate species is much more challenging with 3,5-DBSQ. This is reflected by the fact that only Fe^{III}(3,5-DBC) complexes were made with various supporting ligands and by our inability to prepare either Fe^{II}(3,5-DBSQ) or Fe^{III}(3,5-DBC) with the [PhTt^{Bu}]Fe fragment, Scheme 5.3.

![Scheme 5.3. Unsuccessful synthesis of [PhTt^{Bu}]Fe^{II}(3,5-DBSQ) or [PhTt^{Bu}]Fe^{III}(3,5-DBC).](image)

As shown in Scheme 5.3 and confirmed by the HR-LIFDI mass spectroscopy, Figure 5.21, neither route affords the target complex. The color of the crude product(s) is dark blue/black and it is NMR silent, which are indicative of the formation of Fe(III) complex(es). The HR-LIFDI mass spectrum showed a $m/z = 776.39$ peak envelope, which agrees with the calculated $m/z = 776.36$ for [PhTt^{Bu}]Fe^{III}(3,5-DBC) +
CH₂S(tBu), Figure 5.21. The formation of this adduct is proposed to entail the initial formation of [PhTtBu]Fe³⁺(3,5-DBC) instead of [PhTtBu]Fe²⁺(3,5-DBSQ). As Fe(III) is more Lewis acidic than Fe(II), one thioether arm migrates from the boron to iron as a strong σ-donor ligand to support the Fe(III). The thioether arm migration was observed previously in some cases for nickel complexes. Due to the higher oxidation potentials of Mn²⁺, Ni²⁺ and Co²⁺, the formations of M³⁺(3,5-DBC) complexes (M = Mn, Ni, Co) was largely inhibited (a small amount of the thioether adduct of Mn³⁺-3,5-DBC was observed in the HR-LIFDI mass spectrum) and therefore, little driving force for the migration of the thioether arm is apparent.

Figure 5.21. HR-LIFDI mass spectra of the crude product of [PhTtBu]Fe⁺ + Tl(3,5-DBSQ) (shown as experimental). The calculated spectra of spectulated products are shown above it.
5.5 DFT and TD-DFT Studies of [PhTt\textsuperscript{tBu}]Fe(PhenSQ), [PhTt\textsuperscript{tBu}]Ni(PhenSQ) and [PhTt\textsuperscript{tBu}]Ni(3,5-DBSQ)

5.5.1 DFT and TD-DFT Studies of [PhTt\textsuperscript{tBu}]Fe(PhenSQ)

To provide a detailed description of the electronic structure of [PhTt\textsuperscript{tBu}]Fe(phenSQ), DFT calculations were performed using the broken symmetry approach. Starting from the molecular structure of [PhTt\textsuperscript{tBu}]Fe(phenSQ) deduced by X-ray diffraction, initial geometry optimizations were performed using BP86 and B3LYP functionals on the $S = 3/2$ spin state. Then, single-point DFT calculations were conducted on the optimized geometry to obtain electronic structure information. The metric parameters and electronic structure descriptions obtained from both experimental data and DFT calculations are provided in Table 5.7. In the X-ray structure, the Fe–S2 (axial) bond is shorter than the Fe–S1 (equatorial) and Fe–S3 (equatorial) bonds by about 0.07 Å and 0.12 Å, respectively. In the DFT model, Fe(phenSQ)1 obtained using B3LYP, the Fe–S2 bond (axial) is longer than the other two Fe–S bonds (equatorial) by about 0.15 Å. Therefore, the electronic structure derived from this model does not agree with the experimental structural data. When the BP86 functional was applied for geometry optimization, the optimized structure agreed well with the structure determined by X-ray diffraction. The calculated electronic structure of the resulting model Fe(phenSQ)2 was also consistent with the experimental data. Unfortunately, the calculated electronic absorption spectrum using single-point TD-DFT methods agrees poorly with the experimental data, calling for a better model. Satisfyingly, when the B3LYP functional was applied to FephenSQ2 model for a further geometry optimization, the metric parameters of the new model FephenSQ3 is in good agreement with the X-ray diffraction data. More importantly, the calculated electronic structure of FephenSQ3 is consistent with the experimental...
data and the TD-DFT calculated electronic spectrum agrees reasonably well with the experimental spectrum, *vide infra*. Thus, FphenSQ3 was deemed the most appropriate model.

The TD-DFT calculated electronic spectrum using the Fe(phenSQ)3 model together with the experimental electronic spectrum is displayed in Figure 5.22. Characteristic transitions for the calculated spectrum are assigned according to the electron density difference maps (EDDMs). Regions with a gain and a loss in electron density are depicted in blue and white, respectively. The two intense features at 384 (16736 M\(^{-1}\) cm\(^{-1}\)) and 412 (14784) nm in the calculated spectrum clearly show ligand-
to-metal (SQ to Fe) charge transfer (LMCT) character. These features match with the transition at 401 (5230 M⁻¹ cm⁻¹) nm in the experimental spectrum, which therefore, is assigned to this LMCT transition. There are also two features in the calculated spectrum at 571 (3575 M⁻¹ cm⁻¹) and 592 (3693) nm that show both metal-to-ligand (Fe to SQ) charge transfer and ligand-to-ligand ([PhTtBu] to SQ) charge transfer (LLCT) characters. These features match with the experimental transition at 600 (868 M⁻¹ cm⁻¹) nm. Finally, a dₓz/dᵧz→dₓ²−ᵧ² transition appeared in the calculated spectrum at 874 (4 M⁻¹ cm⁻¹) nm.
Figure 5.22. Comparison of the experimental electronic spectrum and TD-DFT calculated spectrum, the latter based on the Fe(phenSQ)3 model.
To further gauge the accuracy of the Fe(phenSQ)3 model for the electronic structure description, Mössbauer parameters were derived for FephenSQ3 from DFT calculations, which yielded an isomer shift $\delta = 0.791$ mm/s and quadrupole splitting $\Delta E_Q = 2.486$ mm/s. These values are in excellent agreement with the experimental isomer shift $\delta = 0.92$ mm/s and quadrupole splitting $\Delta E_Q = 2.29$ mm/s, Table 5.8.

Table 5.8. Experimental and DFT-calculated Mössbauer parameters based on the Fe(phenSQ)3 model.

<table>
<thead>
<tr>
<th></th>
<th>$\delta$ (mm/s)</th>
<th>$\Delta E_Q$ (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>0.92</td>
<td>2.29</td>
</tr>
<tr>
<td>Calculated</td>
<td>0.791</td>
<td>2.486</td>
</tr>
</tbody>
</table>

Knowing that the Fe(phenSQ)3 model is competent in describing the electronic structure of [PhTtBu]Fe(phenSQ), a qualitative MO diagram derived from the Fe(phenSQ)3 model was obtained by single-point DFT calculations. As shown in Figure 5.23, the Fe(II) is high-spin ($S = 2$), with four unpaired spin-up electrons occupying four Fe(d)-based MOs and one electron-pair occupying a Fe(d$_{xy}$)-based MO. The spin-up electron in the e(d$_{xz}$)-based MO is coupled to the spin-down electron in the phenSQ $\pi^*$ based MO with a modest spatial overlap of $S = 0.28$, giving rise to the antiferromagnetic coupling between the high-spin Fe(II) and the phenSQ radical observed by SQUID magnetometry.
Figure 5.23. Qualitative MO diagram of Fe(phenSQ)3 model.
5.5.2 DFT and TD-DFT Studies of [PhTt\textsuperscript{Bu}]Ni(PhenSQ) and [PhTt\textsuperscript{Bu}]Ni(3,5-DBSQ)

Analogous to the approach applied to [PhTt\textsuperscript{Bu}]Fe(phenSQ), broken symmetry DFT calculations were performed on [PhTt\textsuperscript{Bu}]Ni(phenSQ) and [PhTt\textsuperscript{Bu}]Ni(3,5-DBSQ) in order to provide a detailed description of the electronic structures and to correlate the electronic structures with the magnetic properties. Initial geometry optimizations based on the molecular structures deduced by X-ray diffraction studies were performed using BP86 and B3LYP functionals under $S = 1/2$ spin state, followed by single-point DFT calculations on the optimized geometries to obtain the electronic structure information. When the B3LYP functional was used, the calculated geometric and electronic structures of [PhTt\textsuperscript{Bu}]Ni(phenSQ) and [PhTt\textsuperscript{Bu}]Ni(3,5-DBSQ) did not agree with the experimental data, Table 5.9, Ni(phenSQ)\textsubscript{1} and Ni(3,5-DBSQ)\textsubscript{1}. Although structural models obtained using the BP86 functional agree nicely with the experimental molecular structures and are predicted to have the correct electronic structures, Table 5.9, Ni(phenSQ)\textsubscript{2} and Ni(3,5-DBSQ)\textsubscript{2}, the TD-DFT calculated electronic spectra are not consistent with the experimental data. Satisfyingly, when the B3LYP functional was applied to Ni(phenSQ)\textsubscript{2} and Ni(3,5-DBSQ)\textsubscript{2} models for further geometry optimizations, the new models Ni(phenSQ)\textsubscript{3} and Ni(3,5-DBSQ)\textsubscript{3} afforded geometric and electronic structures, and TD-DFT calculated spectra that are consistent with the corresponding experimental data.
Table 5.9. Selected bond distances (Å) for [PhTtBu]Ni(phenSQ) and [PhTtBu]Ni(3,5-DBSQ) obtained by XRD and DFT. Electronic structure description are derived from experimental data and single-point DFT calculations.

<table>
<thead>
<tr>
<th>Bond Distances</th>
<th>Ni(phenSQ) (XRD)</th>
<th>Ni(phenSQ)1 (B3LYP, $S = 1/2$)</th>
<th>Ni(phenSQ)2 (BP86, $S = 1/2$)</th>
<th>Ni(phenSQ)3 (B3LYP, $S = 1/2$)</th>
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<tr>
<td>Ni–O1</td>
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<tr>
<td>C35–C22</td>
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<td>Low-spin NiII with SQ</td>
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</table>

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<tr>
<th>Bond Distances</th>
<th>Ni(3,5-DBSQ) (XRD)</th>
<th>Ni(3,5-DBSQ)1 (B3LYP, $S = 1/2$)</th>
<th>Ni(3,5-DBSQ)2 (BP86, $S = 1/2$)</th>
<th>Ni(3,5-DBSQ)3 (B3LYP, $S = 1/2$)</th>
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<tr>
<td>O2–C27</td>
<td>1.287(2)</td>
<td>1.290</td>
<td>1.302</td>
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<tr>
<td>C22–C27</td>
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<td>1.472</td>
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<tr>
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<td>Ni1–S1(eq)</td>
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<td>Ni1–S3(eq)</td>
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<tr>
<td>Electronic Structures (Expt. and DFT)</td>
<td>high-spin NiII with AF coupled SQ</td>
<td>Low-spin NiII with AF coupled SQ</td>
<td>high-spin NiII with AF coupled SQ</td>
<td>high-spin NiII with AF coupled SQ</td>
</tr>
</tbody>
</table>
The TD-DFT calculated electronic spectrum using the Ni(phenSQ)3 model together with the experimental electronic spectrum are shown in Figure 5.24. EDDMs for selected TD-DFT calculated electronic transitions are shown as well. Regions with a gain and a loss in electron density are depicted in blue and white, respectively. The intense feature at 397 (15967 M⁻¹ cm⁻¹) nm in the calculated spectrum reflects a semiquinonate π→π* transition. This feature is in excellent agreement with the transition at 398 (12877 M⁻¹ cm⁻¹) nm in the experimental spectrum. In the calculated spectrum, both features at 547 (3497 M⁻¹ cm⁻¹) and 555 (4864 M⁻¹ cm⁻¹) nm have ligand field and LMCT (SQ to Ni) character, whereas the feature at 586 (3511 M⁻¹ cm⁻¹) nm has LLCT ([PhTtBu] to SQ) character. These three transitions likely contribute to the experimentally observed transitions at 536 (11375 M⁻¹ cm⁻¹) and 586 (10011 M⁻¹ cm⁻¹) nm.

The TD-DFT calculated electronic spectrum derived from the Ni(3,5-DBSQ)3 model together with the experimental electronic spectrum are shown in Figure 5.25. The experimentally observed transitions at 460 (sh, 3057 M⁻¹ cm⁻¹), 522 (5811 M⁻¹ cm⁻¹), and 566 (sh, 5040 M⁻¹ cm⁻¹) nm likely correspond to the calculated transitions at 512 (1668 M⁻¹ cm⁻¹), 538 (3304 M⁻¹ cm⁻¹), and 570 (6450 M⁻¹ cm⁻¹) nm, respectively. The calculated transition at 512 (1668 M⁻¹ cm⁻¹) nm has the SQ π→π* character. The calculated transitions at 538 (3304 M⁻¹ cm⁻¹) and 570 (6450 M⁻¹ cm⁻¹) nm have ligand field character.
Figure 5.24. Comparison of the experimental electronic spectrum and TD-DFT calculated spectrum, the latter derived from the Ni(phenSQ)₃ model.
Figure 5.25. Comparison of the experimental electronic spectrum and TD-DFT calculated spectrum on Ni(3,5-DBSQ)3 model.
A qualitative MO diagram corresponding to the Ni(phenSQ)3 model is shown in Figure 5.26. The Ni(II) is high-spin, with two unpaired spin-up electrons occupying Ni(d_{z^2}) and Ni(d_{x^2-y^2})-based MOs. The spin-up electron in the Ni(d_{z^2})-based MO is coupled to the spin-down electron in the phenSQ π*-based MO with spatial overlap of $S = 0.31$, leading to the strong antiferromagnetic coupling observed in SQUID magnetometry. The calculated coupling constant, $J = -273.21 \text{ cm}^{-1}$ is in good agreement with the SQUID derived value, $J = -320 \text{ cm}^{-1}$.

![Figure 5.26. Qualitative MO diagram of Ni(phenSQ)3 model.](image-url)
5.6 Redox Properties of [PhTt^{tBu}]M(PhenSQ) (M = Mn, Fe, Ni, Co) and [PhTt^{tBu}]M(3,5-DBSQ) (M = Ni, Co)

5.6.1 Redox Properties of [PhTt^{tBu}]M(PhenSQ) (M = Mn, Fe, Ni, Co)

The redox properties of [PhTt^{tBu}]M(phenSQ) (M = Mn, Fe, Ni, Co) were probed using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The redox events for [PhTt^{Bu}]Mn(phenSQ) were irreversible on the electrochemical timescale, exhibiting $E_c = -1.11$ V assigned as a phenSQ/phenCat reduction and an $E_a = 0.09$ V assigned as phenSQ/phenQ oxidation, Figure 5.2.

For all other [PhTt^{Bu}]M(phenSQ) complexes (M = Fe, Ni, Co), the reduction events are assigned to phenSQ/phenCat couple and the oxidation events are assigned to phenSQ/phenQ couple, Figure 5.28. Specifically, the CV of [PhTt^{Bu}]Fe(phenSQ) showed irreversible oxidation and reduction events, Figure 5.28. Interestingly, while the oxidation process was irreversible regardless of the scan rates up to 1 V/s, the evidence of back current of the reduction process at faster scan rates (1 V/s) provided evidence that electrochemically generated [PhTt^{Bu}]Fe(phenCat)$^-$ is only partially stable even at scan rates up to 1 V/s, Figure 5.29. The CV of [PhTt^{Bu}]Ni(phenSQ) exhibited a quasi-reversible oxidation and reversible reduction processes, Figure 5.28, suggesting greater kinetic stabilities of [PhTt^{Bu}]Ni(phenQ)$^+$ and [PhTt^{Bu}]Ni(phenCat)$^-$ compared to [PhTt^{Bu}]Fe(phenQ)$^+$ and [PhTt^{Bu}]Fe(phenCat)$^-$, respectively. Finally, the CV of [PhTt^{Bu}]Co(phenSQ) exhibited an irreversible oxidation and reversible reduction processes, Figure 5.28.
Figure 5.27. Cyclic Voltammogram of [PhTt^tBu]Mn(phenSQ) in THF (1.0 mM) with decamethylferrocene added as internal standard. Electrolyte: n-Bu_4NPF_6 (0.1 M); Scan rate: 100 mV/s.

Figure 5.28. Cyclic Voltammograms of [PhTt^tBu]M(phenSQ) (M = Fe, Ni, Co) in THF (1.0 mM) containing 0.1 M n-Bu_4NClO_4 (scan rate: 100 mV/s).
Figure 5.29. Cyclic voltammograms (negative potentials) of [PhTtBu]Fe(phenSQ) in THF (1.0 mM) containing 0.1 M n-Bu4NClO4 at various scan rates. Brown: 100 mV/s; Red: 200 mV/s; Green: 300 mV/s; Purple: 500 mV/s; Blue: 1000 mV/s.

To garner information regarding the redox potentials at thermodynamic equilibrium for the irreversible events, the DPV were collected on [PhTtBu]M(phenSQ) (M = Fe, Ni, Co), Figure 5.30. The oxidation of [PhTtBu]Fe(phenSQ), [PhTtBu]Ni(phenSQ) and [PhTtBu]Co(phenSQ) occurred at -0.10 V, 0.05 V and 0.05 V (vs. Fc+/Fc0), respectively. These events are attributed to the PhenSQ/PhenQ redox events, which occurred at similar potentials for other MII(phenSQ) complexes. The higher potentials of the phenSQ/phenQ couple for [PhTtBu]Ni(phenSQ) and [PhTtBu]Co(phenSQ) compared to that for [PhTtBu]Fe(phenSQ) can be attributed to a) greater ligand-field stabilization energy for high-spin NiII (d8) and high-spin CoII (d7) vs. high-spin FeII (d6) and b) stronger antiferromagnetic exchange in [PhTtBu]Ni(phenSQ) and [PhTtBu]Co(phenSQ). Both
effects stabilize the Ni and Co analogues so that they are more difficult to oxidize. A similar trend was observed in Pierpont’s [Tp$^{\text{Cum,Me}}$]M(3,5-DBSQ) series (M = Zn(II), Co(II), Cu(II)). The Zn$^{\text{II}}$ analogue, due to its d$^{10}$ electronic configuration enjoys no LFSE nor any exchange interaction between Zn$^{\text{II}}$ and semiquinonate radical displayed oxidation potentials 0.17 V and 0.15 V lower than those of the Co(II) and Cu(II) analogues, respectively. The reductions of [PhTt$^{\text{Bu}}$]Fe(phenSQ), [PhTt$^{\text{Bu}}$]Ni(phenSQ) and [PhTt$^{\text{Bu}}$]Co(phenSQ) occurred at -0.92 V, -1.00 V and -0.91 V, respectively. These events are assigned as phenSQ/phenCat reductions.
Figure 5.30. Differential Pulse Voltammograms of \([\text{PhTt}^{\text{Bu}}]M(\text{phenSQ})\) (M = Fe, Ni, Co) in THF (1.0 mM) containing 0.1 M \(n\)-Bu\(_4\)NClO\(_4\).
5.6.2 Redox Properties of $[\text{PhTt}^{\text{Bu}}]M(3,5\text{-DBSQ})$ (M = Ni, Co)

As shown in Figure 5.31, $[\text{PhTt}^{\text{Bu}}]\text{Ni}(3,5\text{-DBSQ})$ and $[\text{PhTt}^{\text{Bu}}]\text{Co}(3,5\text{-DBSQ})$ exhibited reversible reductions at -0.94 V and -0.83 V, respectively. These events are assigned to the 3,5-DBSQ/3,5-DBC redox couple.

$[\text{PhTt}^{\text{Bu}}]\text{Ni}(3,5\text{-DBSQ})$ and $[\text{PhTt}^{\text{Bu}}]\text{Co}(3,5\text{-DBSQ})$ also showed irreversible oxidations at $E_a = 0.46$ V and 0.47 V, respectively. The oxidation event for $[\text{PhTt}^{\text{Bu}}]\text{Ni}(3,5\text{-DBSQ})$ was assigned to the 3,5-DBSQ/3,5-DBQ oxidation. The oxidation event for $[\text{PhTt}^{\text{Bu}}]\text{Co}(3,5\text{-DBSQ})$ is a 2e$^-$ oxidation process (3,5-DBSQ/3,5-DBQ and Co$^{II}$/Co$^{III}$ oxidations) given that the current for the oxidation event is approximately twice the current for the reduction event.

Figure 5.31. Cyclic voltammograms of $[\text{PhTt}^{\text{Bu}}]M(3,5\text{-DBSQ})$ (M = Ni, Co) in THF (1.0 mM) containing 0.1 M $n$-Bu$_4$NClO$_4$ and decamethylferrocene ($\text{Me}_{10}\text{Fc}$) as the internal standard (scan rate: 100 mV/s).
5.7 O$_2$ Reactivity of [PhTt$^{Bu}$]M(PhenSQ) (M = Fe, Co) and [PhTt$^{Bu}$]M(3,5-DBSQ) (M = Co, Ni)

5.7.1 O$_2$ Reactivity of [PhTt$^{Bu}$]Fe(PhenSQ) and [PhTt$^{Bu}$]Co(PhenSQ)

Numerous Fe$^{III}$-catecholate model compounds for the catechol dioxygenases react with O$_2$ in hours or days at room temperature. In contrast, both [PhTt$^{Bu}$]Fe(phenSQ) and [PhTt$^{Bu}$]Co(phenSQ) reacted with O$_2$ at extremely low temperature (-90 °C) within seconds, affording the opportunity to follow the course of the reactions by in situ spectroscopic methods, Scheme 5.4.

![Scheme 5.4. O$_2$ reactivity of [PhTt$^{Bu}$]Fe(PhenSQ) and [PhTt$^{Bu}$]Co(PhenSQ).](image)

The reaction of [PhTt$^{Bu}$]Fe(phenSQ) with O$_2$ was monitored by electronic absorption spectroscopy.$^{91}$ During the oxygenation of [PhTt$^{Bu}$]Fe(phenSQ) at -90 °C in toluene, optical intermediates were detected, Figure 5.32 (top). Upon warming to 0 °C, the intermediates decayed to the thermodynamic products in a few minutes, Figure 5.32 (bottom). To identify the final products, the reaction was performed on a preparative scale. After the reaction the organic products were deligated from the iron via addition of EDTANa$_2$ and subjected to $^1$H NMR, Figure 5.33, and LIFDI mass spectrosocopies, Figure 5.34. The formation of an intradiol cleavage product, specifically diphenic anhydride, was confirmed by these methods.
Figure 5.32. Electronic absorption spectral changes during the oxygenation of [PhTlBu]Fe(phenSQ) at -90 °C in toluene (top) and upon warming the solution to 0 °C generating the thermodynamic products (bottom).
Figure 5.33. $^1$H NMR spectra of the authentic diphenic anhydride (top) and the crude products of $[\text{PhTt}^{\text{Bu}}]\text{Fe}($phenSQ$) + \text{O}_2$ (bottom).
Figure 5.34. Calculated LIFDI mass spectrum of diphenic anhydride (top) and experimental LIFDI mass spectrum of the crude products of [PhTtBu]Fe(phenSQ) + O₂ (bottom).
Similarly, the reaction of [PhTt\textsuperscript{Bu}]Co(phenSQ) with O\textsubscript{2} at -90 °C in toluene produced intermediate(s) exhibiting an intense optical feature at 332 nm, Figure 5.35.\textsuperscript{91} The products of this reaction were analyzed by \textsuperscript{1}H NMR spectroscopy after deligation by EDTANa\textsubscript{2}. The one-electron oxidation product, phenanthrenequinone (phenQ), was produced in 43% yield based on proton integration, Figure 5.36. The LIFDI mass spectrum further confirmed the production of phenQ, Figure 5.37.

![Figure 5.35. Electronic absorption spectral changes during the oxygenation of [PhTt\textsuperscript{Bu}]Co(phenSQ) at -90 °C in toluene and upon warming the solution to 20 °C to generate the thermodynamic products.](image)

Figure 5.35. Electronic absorption spectral changes during the oxygenation of [PhTt\textsuperscript{Bu}]Co(phenSQ) at -90 °C in toluene and upon warming the solution to 20 °C to generate the thermodynamic products.
Figure 5.36. $^1$H NMR spectra of the authentic phenQ (top) and the crude products of [PhTt$_{Bu}$]Co(phenSQ) + O$_2$ (bottom).
Figure 5.37. Calculated LIFDI mass spectrum of phenQ (top) and experimental LIFDI mass spectrum of the crude products of [PhTt^{Bu}]Co(phenSQ) + O₂ (bottom).
The distinct outcome of the \( \text{O}_2 \) reactions of \([\text{PhTt}^{\text{Bu}}]\text{Fe(phenSQ)}\) and \([\text{PhTt}^{\text{Bu}}]\text{Co(phenSQ)}\) prompted further interrogation into the nature of reactive intermediates, which could provide information as to why distinct products are formed.

Figures 5.38 and 5.39 display the LIFDI mass spectra of the intermediates produced at -80 °C by reacting \([\text{PhTt}^{\text{Bu}}]\text{Fe(phenSQ)}\) and \([\text{PhTt}^{\text{Bu}}]\text{Co(phenSQ)}\), respectively, with \( \text{O}_2 \). In these spectra, \( m/z = 661.3016 \) for \([\text{PhTt}^{\text{Bu}}]\text{Fe(phenSQ)} + \text{O}_2 \) and \( m/z = 664.1901 \) for \([\text{PhTt}^{\text{Bu}}]\text{Co(phenSQ)} + \text{O}_2 \) match nicely with the molecular ion for \([\text{PhTt}^{\text{Bu}}]\text{Fe(phenSQ)}\) and \([\text{PhTt}^{\text{Bu}}]\text{Co(phenSQ)}\), respectively. However, the electronic absorption spectral changes shown in Figure 5.32 and Figure 5.35 indicated that \([\text{PhTt}^{\text{Bu}}]\text{Fe(phenSQ)}\) and \([\text{PhTt}^{\text{Bu}}]\text{Co(phenSQ)}\) were completely converted to the intermediates. Therefore, the molecular ion peaks are unlikely to be produced by unreacted starting materials. Alternatively, these features could derive from the \( \text{O}_2 \) adducts of \([\text{PhTt}^{\text{Bu}}]\text{Fe(phenSQ)}\) and \([\text{PhTt}^{\text{Bu}}]\text{Co(phenSQ)}\), i.e. \( \text{M}^{\text{III}}-\text{superoxo species} \) (\( \text{M} = \text{Fe}, \text{Co} \)). The superoxo moieties are expected to be quite labile and \( \text{O}_2 \) may well be released from the \( \text{M}^{\text{III}}-\text{superoxo species} \) under the operating condition of the mass spectrometer. If this hypothesis is accurate, \( \text{O}_2 \) loss may be observed by the electronic spectroscopy upon replacing the \( \text{O}_2 \)-saturated atmosphere with an \( \text{N}_2 \)-saturated atmosphere. \([\text{PhTt}^{\text{Bu}}]\text{Co(phenSQ)}\) seems to be a good candidate for this experiment as the LIFDI spectrum of \([\text{PhTt}^{\text{Bu}}]\text{Co(phenSQ)} + \text{O}_2 \) at -80 °C, Figure 5.39, shows predominantly the \( m/z = 664.1901 \) peak, which according to the hypothesis is indicative of a high conversion of \([\text{PhTt}^{\text{Bu}}]\text{Co(phenSQ)}\) to its \( \text{O}_2 \) adduct. Indeed, when we purged the solution of the intermediate produced by
[PhTt^{Bu}]Co(phenSQ) + O₂ with excess dry N₂, we found that this intermediate can be converted back to [PhTt^{Bu}]Co(phenSQ) to some extent, Figure 5.41.

The observation of O₂ release from the intermediate supports our assumption that the m/z = 664.1901 peak is produced by the O₂ adduct of [PhTt^{Bu}]Co(phenSQ), i.e. a Co^{III}-superoxo species. The thermal decay of this species led predominantly to the formation of phenQ instead of diphenic anhydride, an intradiol product, through one-electron oxidation of phenSQ, Scheme 5.6. Likewise, it is proposed that the m/z = 661.3016 peak observed in the mass spectrum of [PhTt^{Bu}]Fe(phenSQ) + O₂, Figure 5.38, is produced by the O₂ adduct of [PhTt^{Bu}]Fe(phenSQ), i.e. an Fe^{III}-superoxo species. Analogous to the cobalt counterpart, the thermal decay of this species also may lead to the formation of phenQ which was observed in the mass spectrum at m/z = 208.0517, Figure 5.34.

Furthermore, a major peak at m/z = 764.35 was also observed in the mass spectrum of [PhTt^{Bu}]Fe(phenSQ) + O₂ at -80 °C, Figure 5.38. This peak corresponds to the thioether-transferred product [PhTt^{Bu}]Fe(phenSQ) + CH₂S^{Bu} and is suggestive of the Fe(II) being oxidized to Fe(III). Interestingly, m/z = 780.35 and = 796.37 were also detected, which correspond to [PhTt^{Bu}]Fe(phenSQ) + CH₂S^{Bu} + O and [PhTt^{Bu}]Fe(phenSQ) + CH₂S^{Bu} + 2O, respectively, Figure 5.38 (bottom). The observations of m/z = 780.35 and = 796.37 peaks are consistent with the formation of O₂ adduct of the thioether-transferred intermediate, Scheme 5.5. The difference in the stability between the O₂ adduct of [PhTt^{Bu}]Fe(phenSQ) (m/z = 693.2, not observed by LIFDI) and O₂ adduct of [PhTt^{Bu}]Fe(phenSQ) + CH₂S^{Bu} (m/z = 796.37, observed by LIFDI) may lie in the formation of an Fe(III)-alkylperoxo intermediate in the latter case (m/z = 796.26), Scheme 5.5. The Fe(III)-alkylperoxo intermediate gains
additional stability compared to the Fe(III)-superoxo intermediate through the formation of a C–OO bond. Thus, it is easier for the Fe(III)-alkylperoxo intermediate to be observed by the LIFDI mass spectroscopy.

In the mass spectrum of [PhTt^Bu]Co(phenSQ) + O₂ at -80 °C, two low intensity features at $m/z = 767.2642$ and $= 561.1627$ were observed corresponding to [PhTt^Bu]Co(phenSQ) + CH₂S^Bu and [PhTt^Bu]Co(phenSQ) - CH₂S^Bu, respectively (Figure 5.40). The presence of these two peaks suggests that the Co(II) is oxidized to Co(III)⁺ which further suggests the formation of a Co(III)-superoxo intermediate, Scheme 5.6.
Figure 5.38. Top: LIFDI mass spectra of the intermediates produced by [PhTt\(^{tBu}\)]Fe(phenSQ) + O\(_2\) at -80 °C. Bottom: LIFDI mass spectra of the intermediates relevant to the thioether-transferring and subsequent oxygenation during the reaction of [PhTt\(^{tBu}\)]Fe(phenSQ) + O\(_2\) at -80 °C.
Figure 5.39. LIFDI mass spectra of the intermediates produced by [PhTt^tBu]Co(phenSQ) + O_2 at -80 °C.
Figure 5.40. LIFDI mass spectra of the intermediates relevant to thioether-transferring during the reaction of [PhTtBu]Co(phenSQ) + O₂ at -80 °C.
Figure 5.41. Electronic absorption spectra showing O₂ binding and release starting from [PhTt²Bu]Co(phenSQ). Yellow spectrum: [PhTt²Bu]Co(phenSQ) at room temperature. Blue spectrum: [PhTt²Bu]Co(phenSQ) at -80 °C. Red spectrum: [PhTt²Bu]Co(phenSQ) + O₂ at -80 °C. The disappearance of the band at 508 nm indicates that nearly all [PhTt²Bu]Co(phenSQ) was converted to the Co³⁺-superoxo intermediate. Pink spectrum: Upon purging N₂ into the solution of the Co³⁺-superoxo intermediate at -80 °C and then warming the solution to room temperature. The reappearance of the band at 508 nm indicates that a certain amount of the Co³⁺-superoxo intermediate was converted back to [PhTt²Bu]Co(phenSQ).
Scheme 5.5. Proposed mechanism for the formations of phenQ and diphenic anhydride from the reaction of [PhTl^tBu]Fe(phenSQ) + O₂.
Scheme 5.6. Proposed mechanism for the formations of phenQ from the reaction of $[{\text{PhTt}^\text{Bu}}]{\text{Co(phenSQ)}} + \text{O}_2$. 
5.7.2 O₂ Reactivity of [PhTt^tBu]Co(3,5-DBSQ) and [PhTt^tBu]Ni(3,5-DBSQ)

The reaction of [PhTt^tBu]Co(3,5-DBSQ) with O₂ produces 16% of muconic anhydride, an intradiol cleavage product, and 4% of phenyl boronic ester, Scheme 5.7, Figure 5.4. This represents the first example of cobalt-mediated intradiol cleavage with O₂. [PhTt^tBu]Ni(3,5-DBSQ) showed no reactivity with O₂, Scheme 5.7. The electronic spectroscopy was used to monitor the O₂ uptake at -80 °C by [PhTt^tBu]Co(3,5-DBSQ) and [PhTt^tBu]Ni(3,5-DBSQ), respectively, Figure 5.4. The increase in the absorptivity near 300 nm is suggestive of O₂ uptake by [PhTt^tBu]Co(3,5-DBSQ) at -80 °C. No spectral change was observed for [PhTt^tBu]Ni(3,5-DBSQ) under O₂ atmosphere, indicating that [PhTt^tBu]Ni(3,5-DBSQ) does not uptake O₂. The difference in the O₂ uptake capacity is a reflection of the distinct O₂ binding ability of Co^{II} (l.s.) vs. Ni^{II} (h.s.).

Scheme 5.7. O₂ reactivity of [PhTt^tBu]Co(3,5-DBSQ) and [PhTt^tBu]Ni(3,5-DBSQ).
Figure 5.42. $^1$H NMR spectrum of the products from the reaction of [PhTt$_{12}$]Co(3,5-DBSQ) with O$_2$. The spectrum was recorded in CDCl$_3$. Proton signals from the muconic anhydride are labeled.

Figure 5.43. High resolution CI (methane) mass spectra of the muconic anhydride derived from the reaction of [PhTt$_{12}$]Co(3,5-DBSQ) with O$_2$. Top: calculated spectrum of muconic anhydride, (M + H$^+$) m/z = 237.1491; Bottom: experimental spectrum, (M + H$^+$) m/z = 237.1509.
Figure 5.44. Low-field region of the $^1$H NMR spectrum of 4,6-di-tert-butyl-2-phenylbenzo[1,3,2]dioxaborole recorded in CDCl$_3$. Top: authentic compound. Bottom: crude product of the reaction of [PhTt$^{[3]}$]Co(3,5-DBSQ) with O$_2$. 
Figure 5.45. High resolution EI–MS of 4,6-di-tert-butyl-2-phenylbenzo[1,3,2]dioxaborole derived from the reaction of [PhTt\textsuperscript{Bu}]Co(3,5-DBSQ) with O\textsubscript{2}. Top: calculated spectrum, (M\textsuperscript{+}) m/z = 308.1951; Bottom: experimental spectrum, (M\textsuperscript{+}) m/z = 308.1963.

Figure 5.46. Electronic absorption spectroscopy monitoring the O\textsubscript{2} uptake at -80 °C by [PhTt\textsuperscript{Bu}]Ni(3,5-DBSQ) (left) and [PhTt\textsuperscript{Bu}]Co(3,5-DBSQ) (right), respectively.
5.8 Conclusions

A series of [PhTt\textsuperscript{tBu}]-supported five-coordinate M\textsuperscript{II}-semiquinonate complexes (M = Fe, Mn, Ni, Co) were prepared in a modular way from the corresponding metal iodide precursors. These M\textsuperscript{II}-semiquinonate complexes were studied by comprehensive spectroscopic techniques in conjunction with the DFT calculations.

[PhTt\textsuperscript{tBu}]Fe(phenSQ), [PhTt\textsuperscript{tBu}]Mn(phenSQ) and [PhTt\textsuperscript{tBu}]Ni(phenSQ) are best described as high-spin M\textsuperscript{II} complexes with antiferromagnetically coupled SQ radicals. Notably, [PhTt\textsuperscript{tBu}]Fe(phenSQ) is the first and only well-characterized mononuclear Fe\textsuperscript{II}-o-semiquinonate species up to date.

Interestingly, at room temperature [PhTt\textsuperscript{tBu}]Co(phenSQ) is best described as a high-spin Co\textsuperscript{II}-SQ complex, whereas at low temperature the low-spin Co\textsuperscript{II}-SQ electronic structure predominates. Such a temperature-induced spin transition is supported by variable temperature X-ray diffraction analysis, variable temperature electronic spectroscopy, and variable temperature magnetic susceptibility measurement. [PhTt\textsuperscript{tBu}]Co(3,5-DBSQ) undergoes the spin transition at a higher temperature, making it mostly low-spin at room temperature.

From an electronic structure perspective, these complexes are relevant to the proposed or observed intermediates in the catalytic cycles of the catechol dioxygenases. Indeed, [PhTt\textsuperscript{tBu}]Fe(phenSQ) and [PhTt\textsuperscript{tBu}]Co(3,5-DBSQ) exhibited the intradiol cleavage activity in the presence of O\textsubscript{2}. [PhTt\textsuperscript{tBu}]Co(phenSQ) also reacted with O\textsubscript{2}. But instead of forming intradiol cleavage products, the reaction yielded mostly the autoxidation product, phenQ. [PhTt\textsuperscript{tBu}]Ni(3,5-DBSQ) showed no reactivity with O\textsubscript{2}. These reactivity patterns show that the metal ions, the redox potentials of the dioxolene ligands, and perhaps the spin-states of the complexes may play vial roles in effecting the intradiol dioxygenase reactivity.
Based on the $^1$H NMR, electronic, and mass spectroscopic data, plausible mechanisms are provided for the O$_2$ reactivity of [PhTt$^{tBu}$]Fe(phenSQ) and [PhTt$^{tBu}$]Co(phenSQ). O$_2$ addition to [PhTt$^{tBu}$]Co(phenSQ) forms a Co$^{III}$-superoxo species. The thermal decay of this species led to the formation of phenQ instead of diphenic anhydride, an intradiol product, through one-electron oxidation of phenSQ. On the other hand, O$_2$ addition to [PhTt$^{tBu}$]Fe(phenSQ) forms an Fe$^{III}$-superoxo species. The thermal decay of this species leads to the formation of phenQ and diphenic anhydride. These results provide the first direct experimental evidence that the Fe$^{II}$-semiquinonate species may be responsible for the intradiol reactivity.

The future work in this area may be directed towards the preparation of new Fe$^{II}$-semiquinonate complexes and elucidation of their electronic structures. These efforts may develop more effective metal complexes for the intradiol cleavage reactions. They may also help understand the O$_2$ activation mechanism of the intradiol dioxygenase through the stabilization and characterization of the O$_2$ adducts of Fe$^{II}$-semiquinonate complexes, such as Fe$^{III}$-superoxo complexes or Fe$^{III}$-alkylperoxo complexes.
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