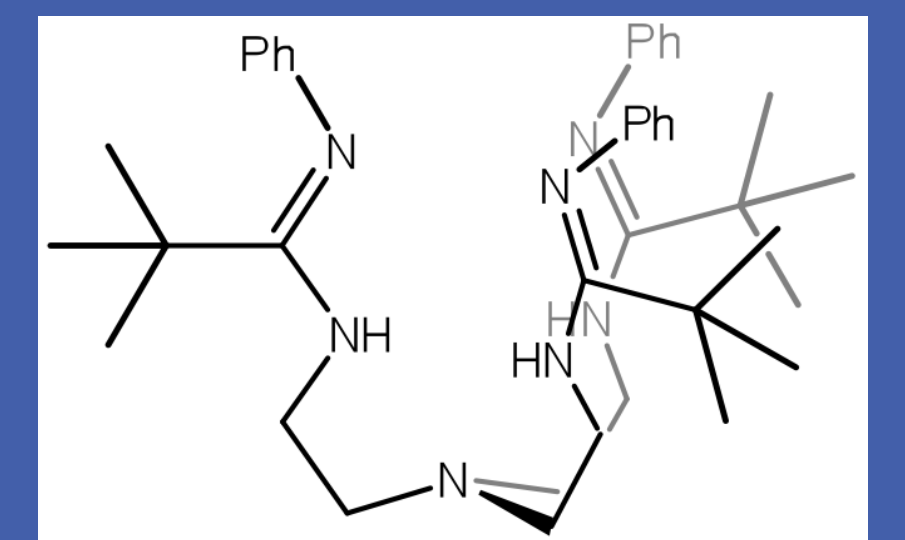
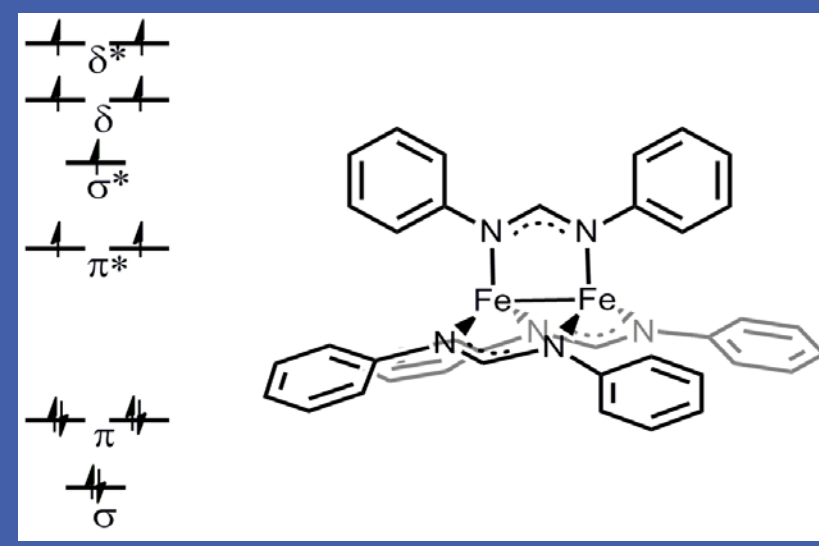


Tripodal Amidinate Ligands For Bimetallic Coordination Chemistry: Synthesis and Metallation

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Introduction

Most bimetallic complexes have a common structural motif in which each metal center has four bidentate ligands bridging the two metals. Double-decker ligands developed in our research group metallate with three bidentate ligands tied to an amine base and have two planes of heteroatoms to chelate to the bimetallic unit. This structural arrangement caps off one metal center, isolating the reactivity of the complex to a single metal site. In this way the supporting role of the second center can be assessed. One such ligand, a tris-phenyl amide, has been used to make two novel dirhodium complexes similar to catalysts used for carbene transfers. (See Figure 1 below.)

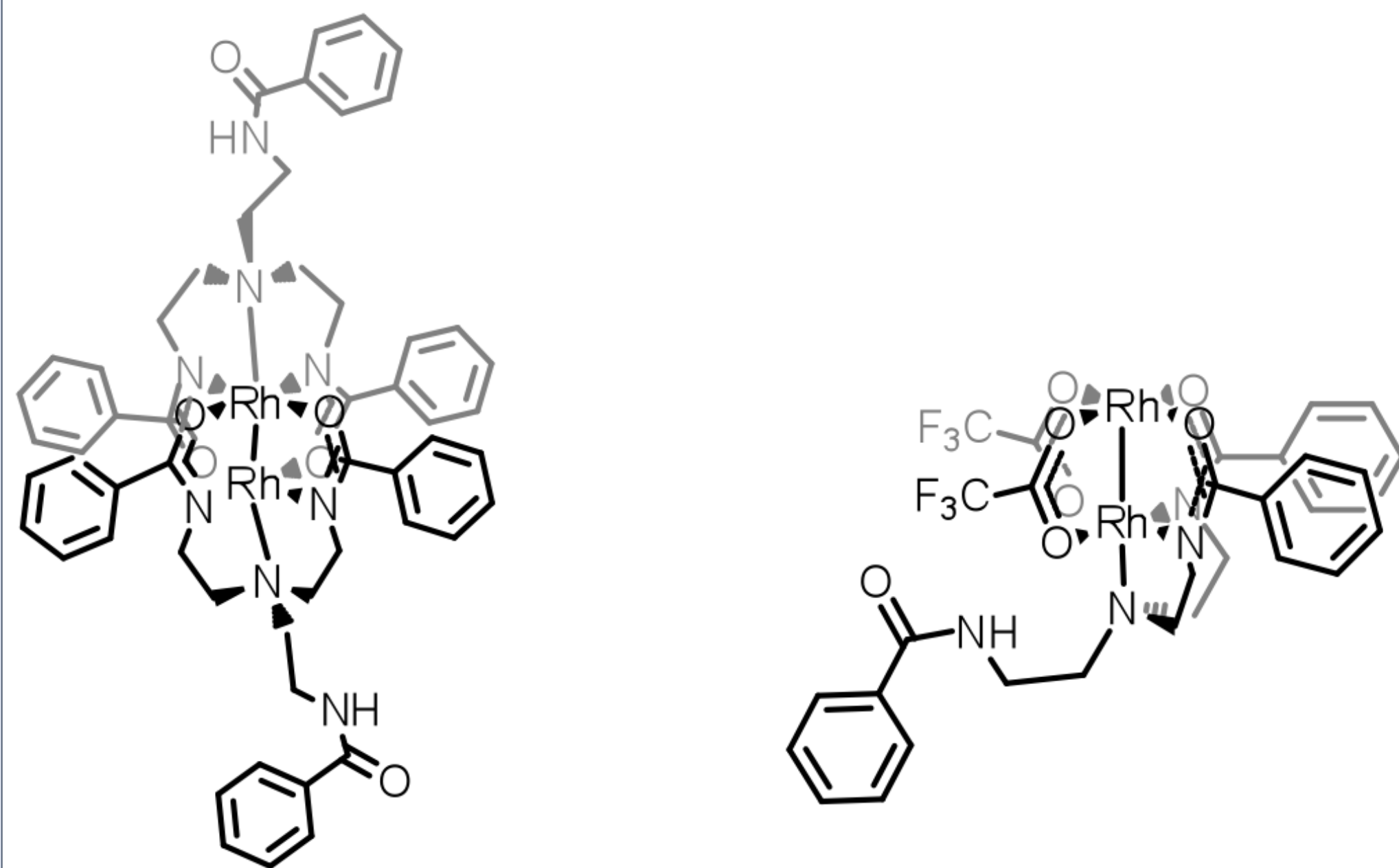


Figure 1: Dirhodium complexes with phenyl amide ligands

Objectives

This project focuses on making similar complexes with more strongly donating ligands. Amidine groups are good candidates for these ligands because they have two nitrogen donors instead of nitrogen and oxygen as is the case with amide ligands. This report describes the synthesis of a new amidine-based ligand with tert-butyl groups in the bridgehead position and phenyl groups on the second nitrogen donor. Attempts to prepare dirhodium complexes with this ligand system have been unsuccessful, but current research is focused on making complexes of these ligands with first-row metals. These should be interesting because the ligands should coordinate in a trigonal fashion, with three ligands binding to the metal, rather than the usual four. Trigonal bimetallic complexes are rare and expected to possess interesting electronic properties.

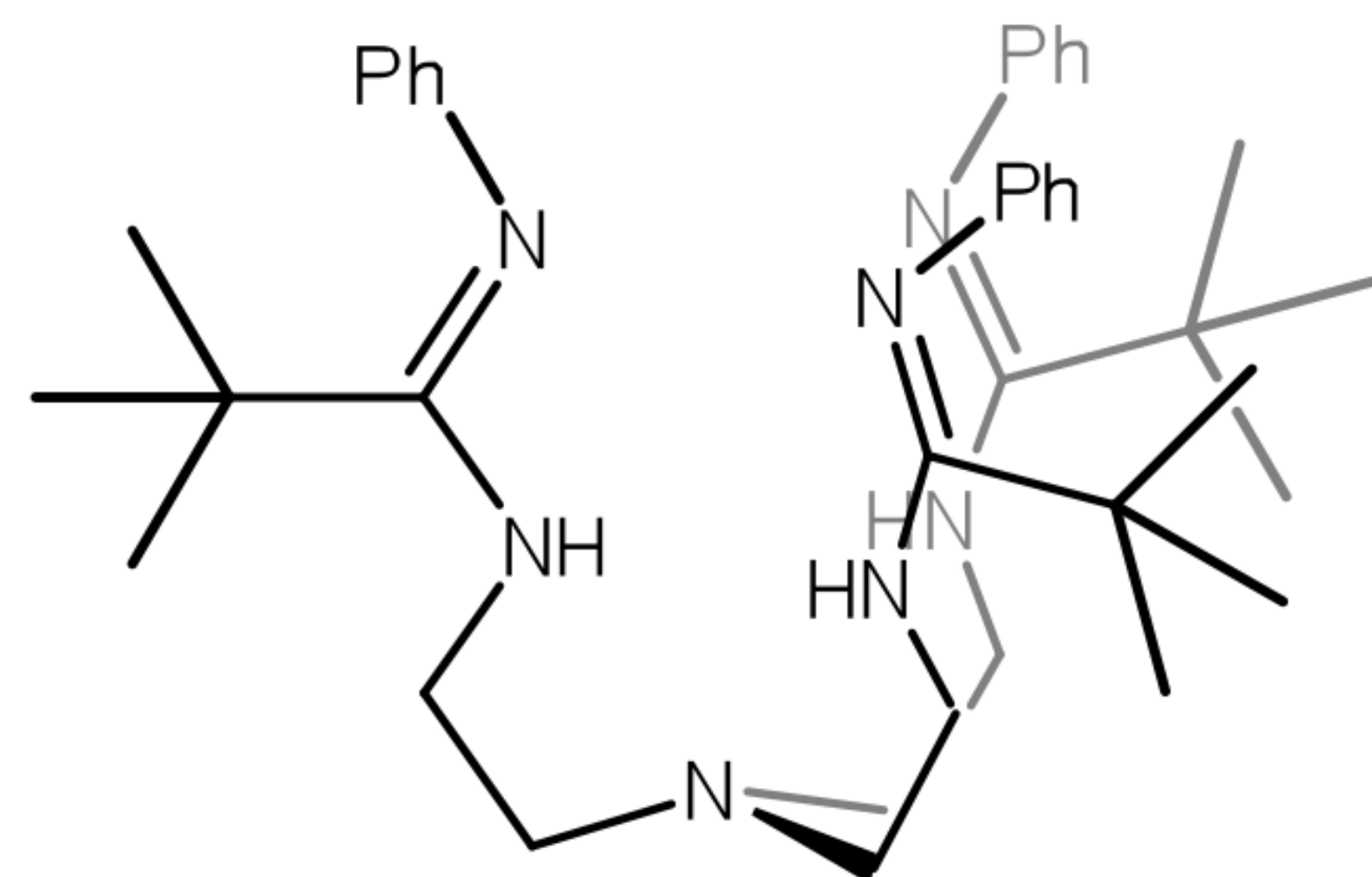


Figure 2: tert-butyl amidine ligand courtesy of graduate student Christopher Zall.

Results and Discussion:

Two types of double-decker ligands were prepared in this study. The first tris-amide ligand, **1**, contains nitrogen and oxygen atoms for coordination to a metal with a t-butyl group as the backbone. This was prepared in one step with good yield from tren and three equivalents of acyl chloride. This is analogous to the previously made phenyl amide ligand. Another ligand, **2**, was also synthesized by converting the amide groups in **1** to amidines. This prep used PCl_5 to make an imidoyl chloride group and then converted it to an amidine group by condensation with aniline at low temperature.

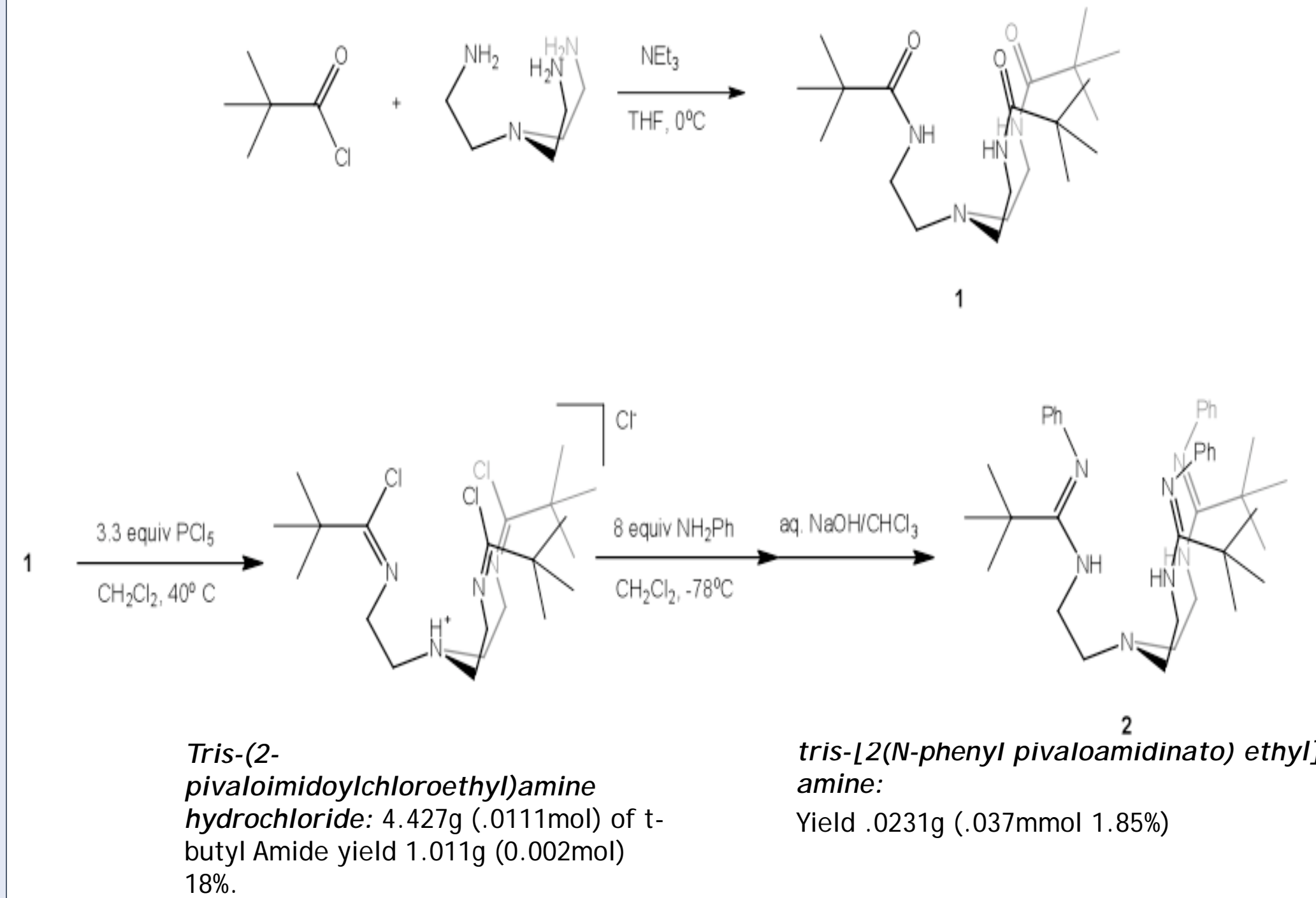


Figure 3: tert-Butyl amidine ligand synthesis

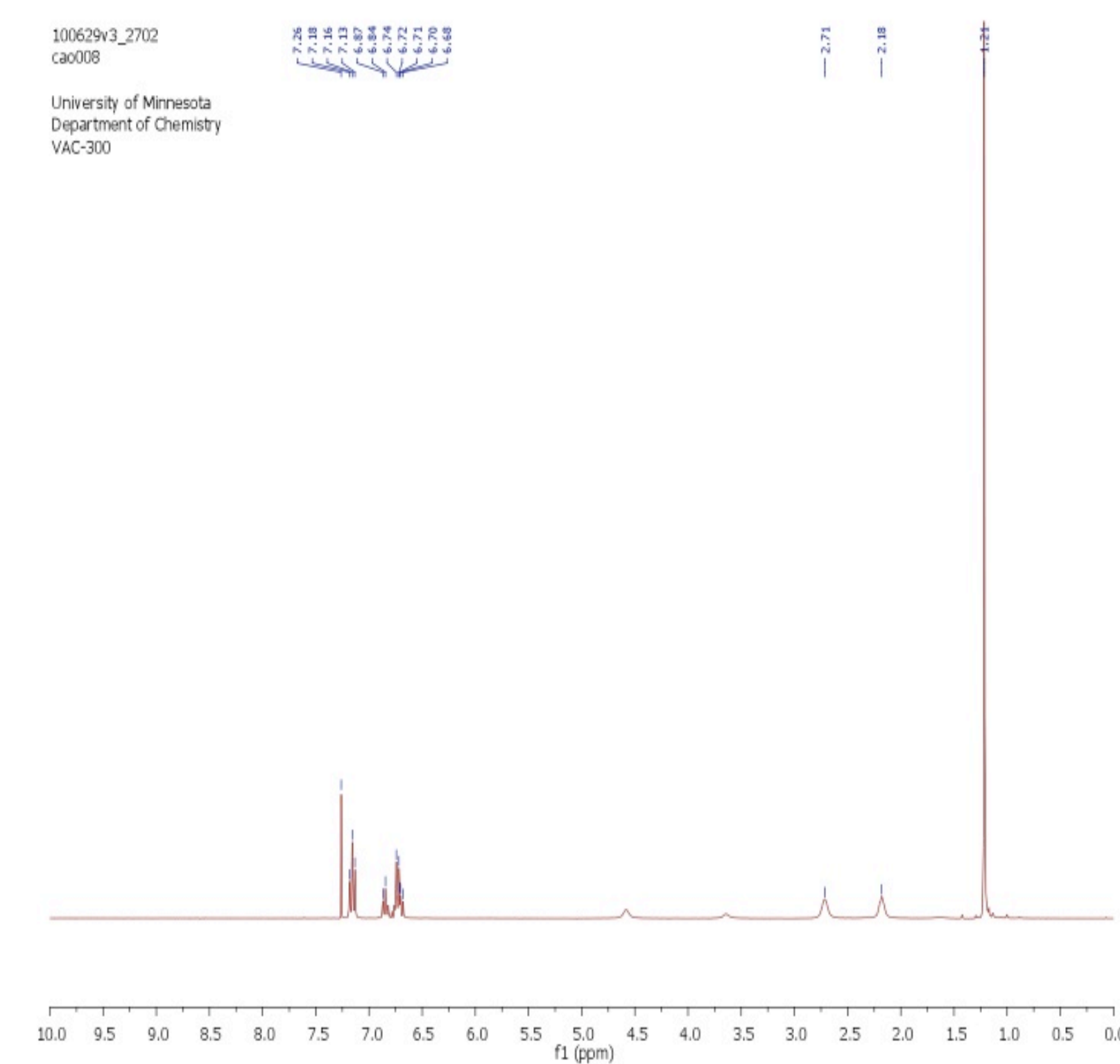


Figure 4: ^1H NMR spectrum of **2** in chloroform- d

Summary

- Reactivity of bimetallic complexes is particularly interesting because of the additional electrons introduced with the second metal.

- Bimetallic complexes commonly found in the literature usually have four bidentate ligands bridging the two metals. The tripodal ligands prepared in this study should provide a framework for making complexes with three bidentate bridging groups.

- When metallated, the novel ligands synthesized in this project cap off one metal atom, leaving only one site open for reactivity.

- Potential complexes created would be similar to catalysts used for carbene transfer.

Metallation: Dirhodium Complexes

Metallation of the tris-amidine ligands was attempted by refluxing the ligand with dirhodium precursors, according to literature precedents adapted in our group for tris-amidate ligands. Dirhodium-based products were observed in ESI-Mass spectra, but their isolation was unsuccessful. (1)

Crystal Structures

Although attempts to metallate associated with this project were unsuccessful, graduate student Christopher Zall has synthesized crystal quality dirhodium complexes. Crystal structures for these molecules can be seen below

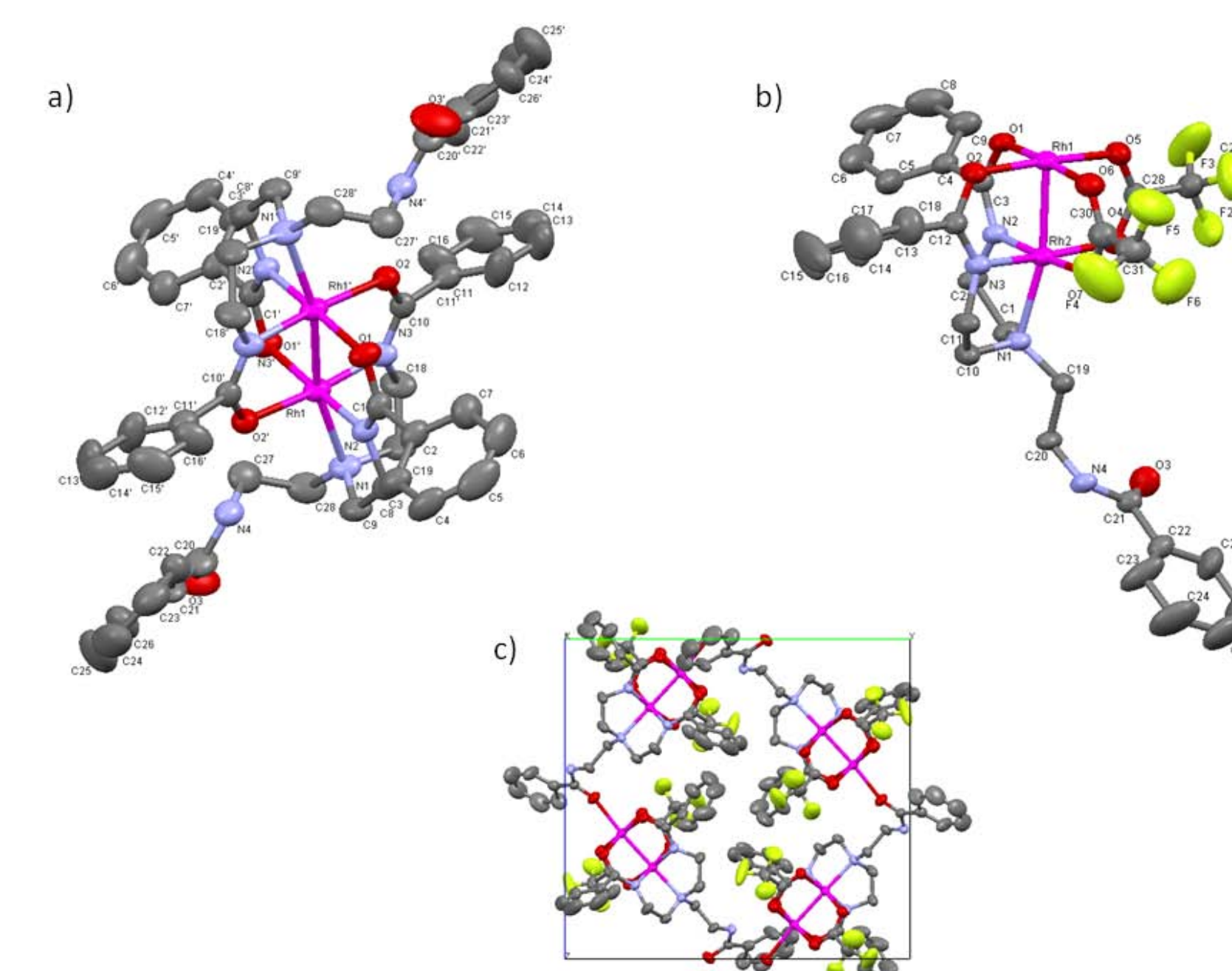


Figure 5: (a, b) Crystal structures of dirhodium complexes Rh_2L_2 and $\text{Rh}_2(\text{L})(\text{TFA})_2$ prepared with tripodal tris-amidate ligands (c) Packing diagram of $\text{Rh}_2(\text{L})(\text{TFA})_2$ showing networked dirhodium linkages

Future Targets: First-Row Metal Complexes

Trigonal bimetallic complexes are rare and can possess unique electronic properties. The trigonal ligand geometry leads to close orbital splittings, allowing a large number of unpaired electrons while retaining a strong bond between the two metals. (2)

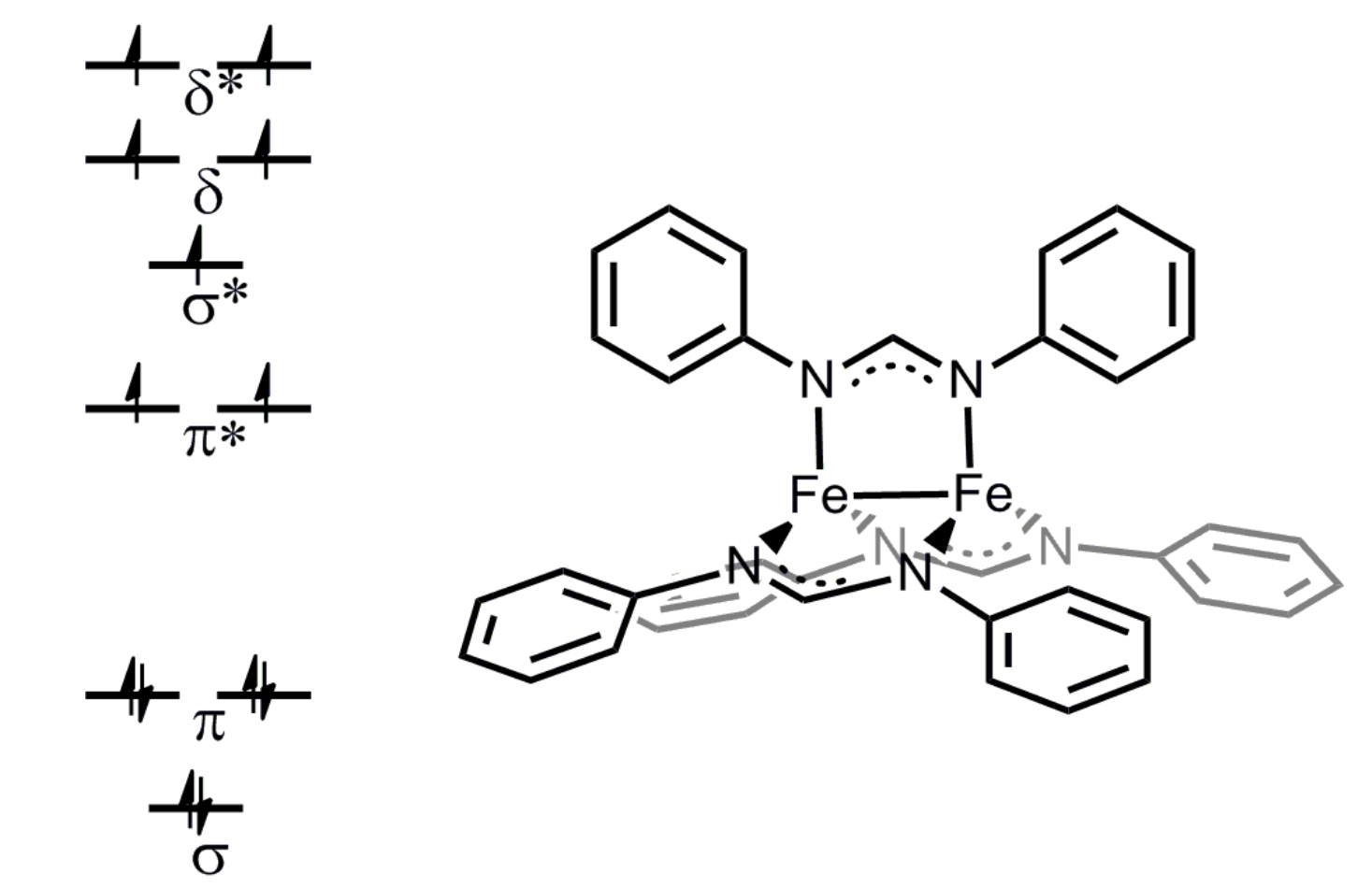


Figure 5: $\text{Fe}_2(\text{DPhF})_3$ Complex and molecular orbital diagram

Current work has been focused on redesigning these diiron complexes with a double-decker ligand framework. The electron-donating nitrogen "cap" could make the molecule more stable and selective. The framework should also allow stepwise metallation with two different metals, facilitating synthesis of mixed-metal complexes. A potential diiron complex with this new ligand structure is shown below in addition to other interesting bimetallic complexes that could be created.

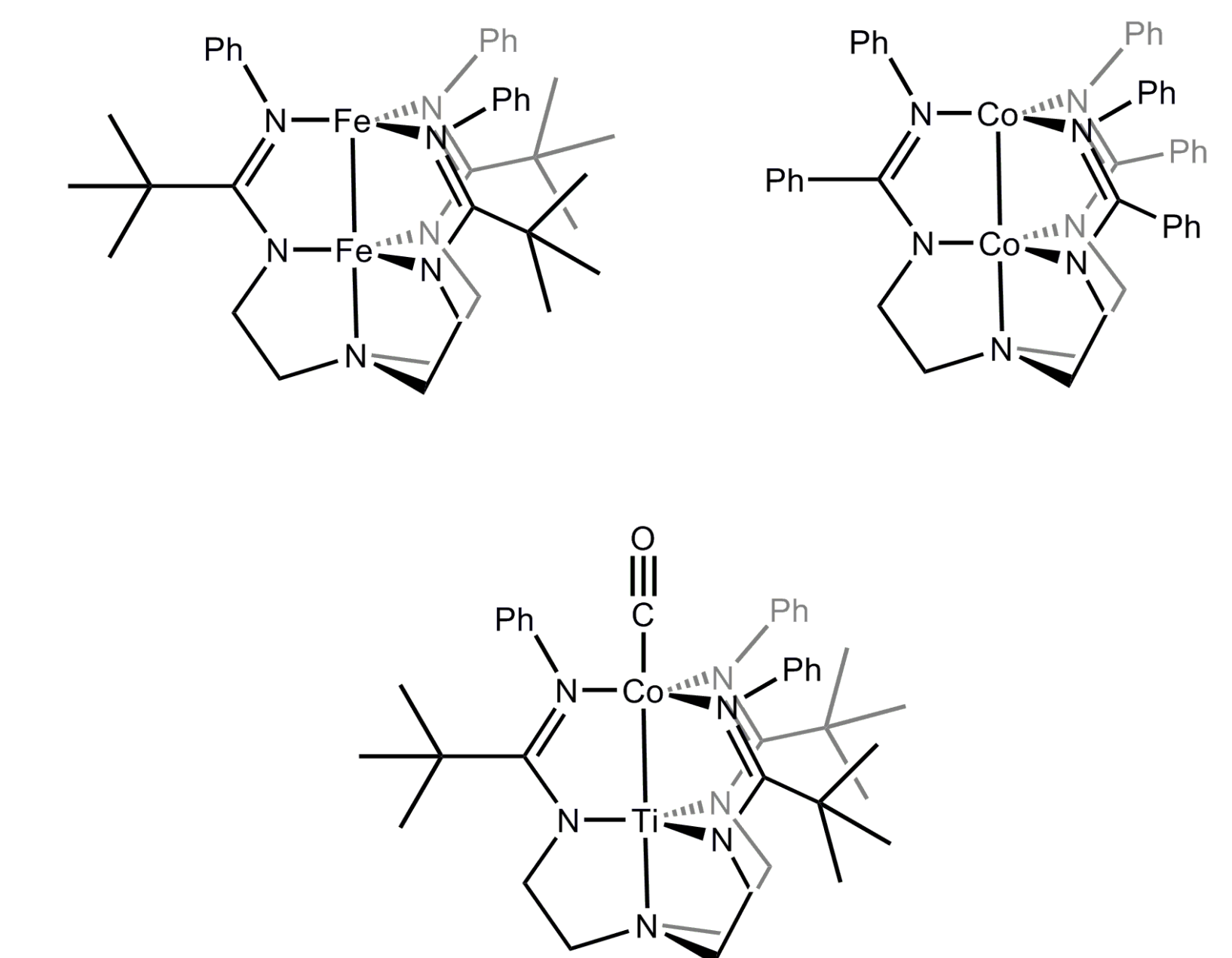


Figure 4: Potential homo- and heterobimetallic tris-amidinate complexes

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References:

(1) Doyle, M. P.; Winchester, W. R.; Protopopova, M. N.; Kazala, A. P.; Westrum, L. J. *Org. Synth.* 1996, 73, 13.

(2): Cotton, A. F.; Feng, X.; Murillo, C.A. *Inorganica Chimica Acta* 1997, 256(2): 303.