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Philip S. May April 7, 2010

Development of redox-active pincer ligands for Co(II) that display base-dependent nuclearity

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An abstract of
A thesis submitted to the Faculty of Emory College of Arts and Sciences
of Emory University in partial fulfillment
of the requirements of the degree of
Bachelor of Sciences with Honors

Department of Chemistry

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Abstract

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Pincer ligands offer an opportunity for exploring coordination geometry due to the extreme variability in ligand design. Past research with amidate ligands has focused on tripodal tetradentate ligand systems, and this work investigates the coordination chemistry of the pincer analogs of these systems. The NNN pincer ligands reported here are of the form $NH(o\text{-}PhNHC(O)R)_2$ (R = ^{i}Pr, ^{t}Bu) and have been complexed with Co(II) metal ions. Structures for experiments involving the ligand when R = ^{t}Bu have yet to be obtained. When R = ^{i}Pr, the complexes produced have been a dinuclear dimeric complex with a Co_2N_2 diamond-core structure when the ligand is treated with 3.1 equivalents of base, and a monomeric complex with a 2:1 ligand:metal ration when the ligand is treated with 2.1 equivalents of base. The dimeric complex has a relatively rare geometry, as the Co_2N_2 diamond-core is not often seen with amidate ligands. The monomeric complex has unique electrochemical properties, demonstrating four electrochemical events with only one cobalt center. These complexes offer great opportunities and possibilities in the area of coordination chemistry and catalysis.

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I would like to thank everyone who helped me accomplish this thesis. The graduate students in the MacBeth research group have been invaluable in teaching me about chemistry and working in a lab, and helping me to understand the data I collected and even offering some of their own to permit my thesis to be presented in context. Matt Jones and Kelly Kluge in particular have worked with me since I started in the MacBeth group, and I thank them for their guidance and assistance throughout my time in the lab. Dr. Savita Sharma has also been an incredible asset to me this past year, taking my project to new levels with experiments I would never have had time to accomplish. I would also like to thank Dr. Kenneth Hardcastle and Sheri Lense for the crystal structures included in this thesis. Dean Preetha Ram, Dr. Jose Soría, and Dr. David Lynn through INSPIRE have been available to me as mentors and advisors since before I stepped foot on campus, and their support during my four years has helped me to shape my own research career. I would also like to thank my parents, who have been gracious enough to fund my four years at Emory University and to offer unconditional love and support whenever I need it. Finally, I would like to thank my advisor, Dr. Cora MacBeth, for all the incredible opportunities she has presented to me while working in her lab and writing this thesis. Her patience in explaining issues as well as frequent availability made the last three years of chemistry research a joy. Thank you to everyone who offered support, and to everyone who I may I have forgotten but aided me in the completion of this work.

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1. Introduction

A ligand is the ion or molecule that binds to a metal to form a coordination complex. Ligands are traditionally seen as Lewis bases with the metal acting as the complementary Lewis acid and coordinate covalent bonds form between the ligand and the metal. Varying ligands permits for much control over the reactivity of the metal complex in a number of different ways, including sterics, coordination number, electron richness/poorness, and redox potential.[1] They are classified in a number of ways, one of the most important being their denticity, which is the number of atoms in one ligand that bonds to a metal center.[2] Any polydentate ligands are chelating ligands, and the terms bidentate, tridentate, tetradentate, etc. indicate the number of binding sites available in the one ligand (2, 3, and 4, respectively).[3] Ligands are also classified as either "strong field" when they are π-acceptors or "weak field" ligands when they are π-donors, which affects whether or not the metal center is "low spin" or "high spin", respectively Modifying the spin state of the metal center then modifies the reactivity of the entire coordination complex.[1] With this ability to affect metal ion reactivity so greatly, ligands are critical in all areas of chemistry.

Our group has used tetraamine, tripodal ligand systems with *o*-phenylamine moieties in order to explore coordination geometries vary the electronic features of the resulting transition-metal centers.[4-6] These ligands are tetradentate with a central tertiary N atom attached to three arms, each with one N-donor atom. The most common types of these ligands are those derived from tris(2-aminoethyl)amine, more commonly referred to as "tren" [7] (Figure 1).

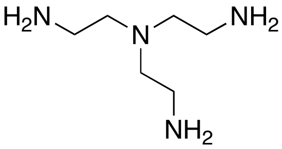


Figure 1. tris(2-aminoethyl)amine, “tren”

From the tren ligand, we substituted the 2-aminoethyl backbone with *o*-phenylamine (Figure 2) in order to make the ligand less flexible upon metal ion chelation[4] and hopefully permit the end compounds to be redox-active.[8-10]

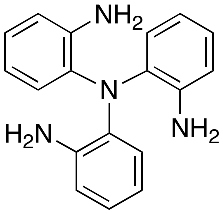


Figure 2. tris(2-aminophenyl)amine ($N(o\text{-}PhNH_2)_3$) ligand scaffold

Additionally, primary amines are very modular and therefore highly functional.[11] When a bulky R group is attached to the arms following the N, a sterically protected, 3-fold-symmetric “pocket” is created, leaving the metal center available to bond to additional ligands, but only those which can enter this space.[12] Based on this, the *o*-phenylamine scaffold was further modified to make the ligands of the tris(amidate) variety ($[N(o\text{-}PhNC(O)R_3]^{3-}$).[4-6]

In general, amidate ligands are monoanionic N,O chelating ligands that can be derived from primary amine and acyl chlorides.[13] Amidates have easily varied steric and electronic properties which permits for modular synthesis of a simple, tunable ligand set.[14] However, they are also able to bind through multiple bonding modes with one metal ion: chelation through both the N and O, just through the N, or just through the O (Figure 3).[5,6,14]

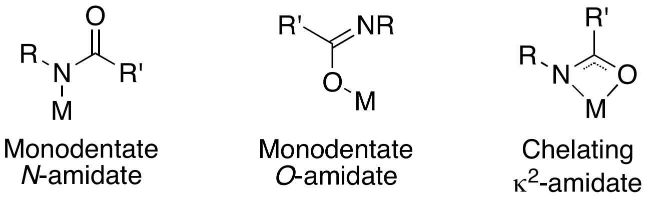


Figure 3. Possible coordination modes of amidate donors[5,6,14]

Previous work with tripodal amidates has shown coordination both as monodentate *N*-amidates[4] and as chelating κ^2-amidates.[5,6] The monodentate *N*-amidate has allowed access to cobalt in unique coordination geometries,[4] and the chelating κ^2-amidate has provided stabilization of aluminum[5] and been able to bind with nickel in unique coordination.[6] From the tetradentate tripodal ligand structure, we have decided to explore further the tridentate pincer ligand (Figure 4).

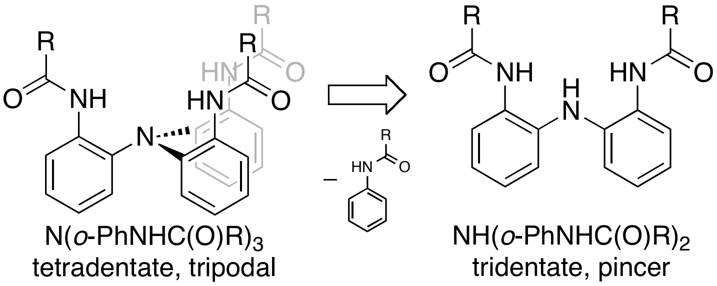
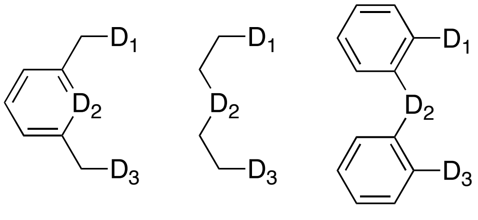


Figure 4. Visual comparison of tripodal ligand versus the pincer ligand, showing the loss of one ligand arm

This change permits for greater number of open coordination sites, permitting for new exploration of reactivity and accessibility.

Pincer ligands presented an opportunity for new and different coordination geometries and hopefully different reactivity of the complexes. A pincer ligand is a tridentate ligand that typically coordinates to a metal center in a meridional fashion (with octahedral geometries)[15] or pseudo-meridional fashion (in trigonal bipyramidal, square pyramidal, or square planar geometries), except notably with group 11 metals.[16] By the 1970s, pincer ligands and complexes had been synthesized and studied, but exploration their usage in organometallic and inorganic chemistry was not begun until the late 1990s.[17] The ligand backbone as well as the coordinating atoms can all be changed in order to control various aspects of the coordination, including bite angle, steric hindrance, and frontier orbitals. Additionally, the meridional coordination creates two thermodynamically stable internal five-membered rings which are in the same plane, yielding exceptional thermostability and high reactivity.[15] Pincer ligands are often chosen for use in research due to this robustness that they are able to confer on their complexes.[18] Being used extensively in the areas of reaction mechanism studies, catalysis, and design of new materials, pincer ligand systems are now integral to many concepts in chemistry.[15] Additionally, pincer complexes can be used as very efficient Lewis acid catalysts, resulting in extremely high enantioselectivity under aerobic conditions, and then the complexes can still be easily recovered during the purification of the product.[19] Pincer ligands are typically classified by the three atoms through which they bind, with the most popular being PNP and PCP.[17] They are further classified by the structure of the ligand backbone, with an aryl backbone (Figure 5, **I**), a purely alkane backbone (Figure 5, **II**), or an alkane backbone with aryl support (Figure 5, **III**).[15]



I **II** **III**

Figure 5. Ligand backbone types for pincer ligands, (I) aryl (II) alkane (III) alkane with aryl support. D = C,P,N,S,O

The structure in Figure 5, **III** is the style of pincer ligand in Figure 4. This would be classified as an NNN pincer ligand, an area which has not had much exploration,[18,20,21] however this work intends to investigate this type of pincer ligand based on previous work from the MacBeth lab.[4-6]

Previous work with NNN pincer ligands has used all of the major classifications of pincer ligand structures. The Morales-Morales group has used NNN pincers modeled after Figure 5, **I** for novel organic transformations based on the robustness that these pincers afford to the transition metal complexes (Figure 6, **I**).[18] The van Koten lab also uses Figure 5, **I** type NNN pincer ligands in their work with ruthenium(II)-catalyzed reactions.[20] Additionally, the Schrock group has used Figure 5, **II** and **III** type NNN pincer ligands with tantalum (Figure 6, **II** and **III**).[21]

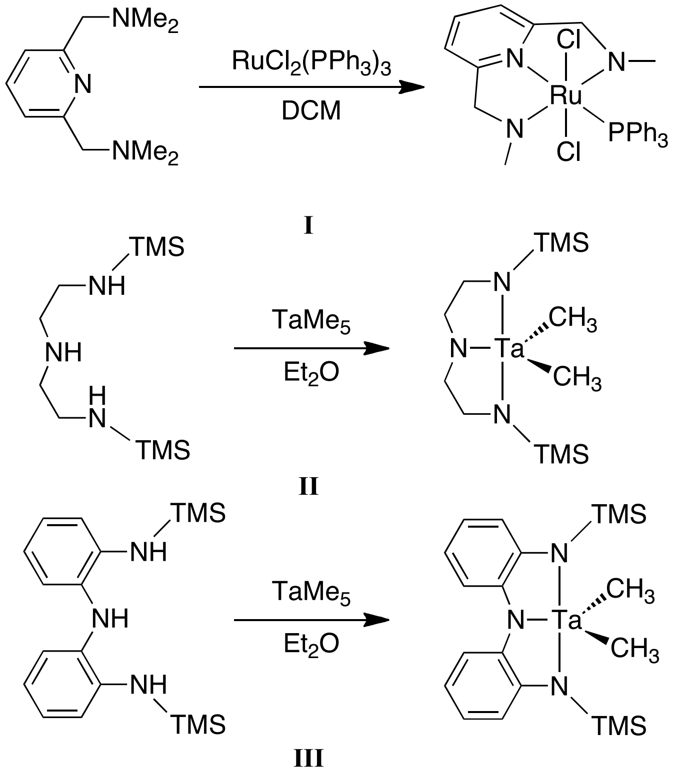


Figure 6. Usages of different ligand backbones corresponding to Figure 5, (I) aryl ruthenium complex[20] (II) alkane tantalum complex [21] (III) alkane with aryl support tantalum complex[21]

Herein I will describe how NNN pincer ligands as depicted in Figure 4 will be used to explore the coordination chemistry of cobalt using different substituent R groups.

2. Results and Discussion

2.1. Ligand synthesis

The triamine ligand NH(*o*-PhNH$_2$)$_2$ was synthesized by first preparing bis(2-nitrophenyl-amine) via an S$_N$Ar reaction.[22] The Pd-catalyzed reduction of this species afforded NH(*o*-PhNH$_2$)$_2$ in high yield (91.8%) (Figure 7). The diamidoamine analogue was readily prepared by acylation of a NH(*o*-PhNH$_2$)$_2$ with isobutyryl chloride to form (NH(*o*-PhNHC(O)^{i}Pr)$_2$ (**H$_3$L^{iPr}**) in high yield (92.5%) as a white solid and with pivaloyl chloride to form (NH(*o*-PhNHC(O)^{t}Bu)$_2$ (**H$_3$L^{tBu}**) in high yield (92%) as a bluish-green-white solid (Figure 8).

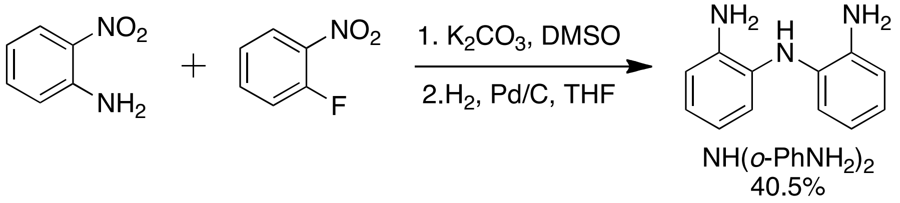


Figure 7. Reaction scheme for synthesis of ligand precursor, NH(*o*-PhNH$_2$)$_2$

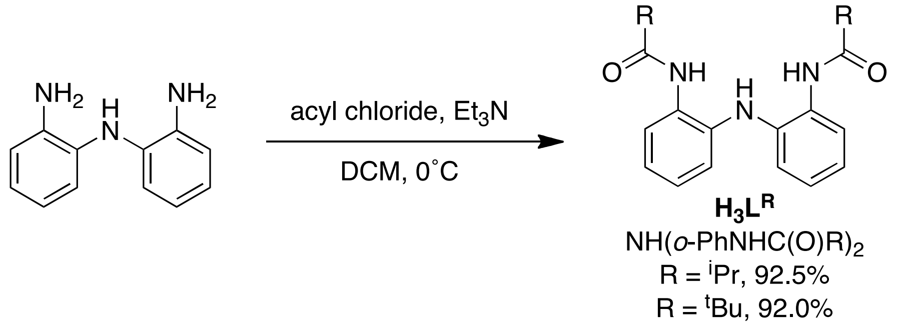


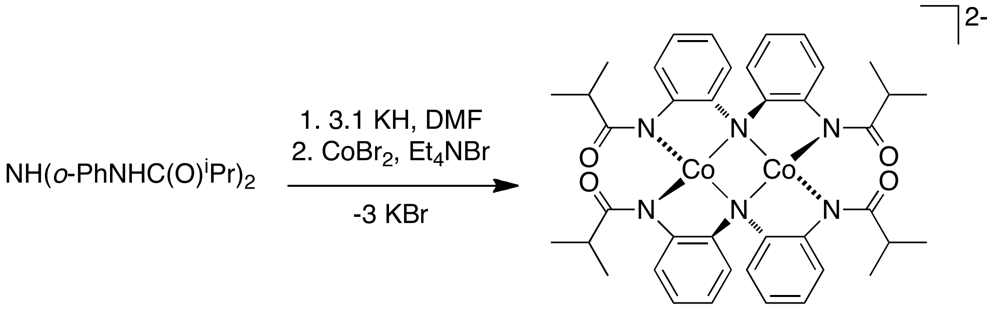
Figure 8. Reaction scheme for syntheses of ligands, **H$_3$L^{iPr}** and **H$_3$L^{tBu}**

The synthesis of the ligands was followed by ^{1}H NMR spectroscopy. The aryl protons initially appeared in the region of 8.21 ppm to 7.10 ppm, as the functionality changed from a nitro group to an amine, they shifted more downstream in the region of 6.93 ppm to 6.79 ppm, and as the functionality changed again from an amine to an amide, the aryl protons shifted back upstream to the region of 7.67 ppm to 6.88 ppm. The proton on the terminal amine group that became an amide shifted upon acylation from 3.64 ppm to 7.83 ppm in $\mathbf{H_3L^{iPr}}$ and 7.65 ppm in $\mathbf{H_3L^{tBu}}$. The hydrogens associated with the isopropyl functional group of $\mathbf{H_3L^{iPr}}$ appeared at 1.16 ppm and those associated with the tert-butyl functional group of $\mathbf{H_3L^{tBu}}$ appeared at 1.22 ppm.

2.2. Cobalt chemistry with $\mathbf{H_3L^{iPr}}$

The structural features of $\mathbf{H_3L^{iPr}}$ were evaluated by treating the ligand with approximately 3 and 2 equivalents of KH to deprotonate the ligand. The ligand treated with approximately 3 equivalents was theorized to yield an anionic complex of the form $[Co(N(\textit{o}\text{-}PhNC(O)^iPr)_2)]^-$, and the ligand treated with approximately 2 equivalents was theorized to yield a neutral complex of the form $[Co(NH(\textit{o}\text{-}PhNC(O)^iPr)_2)]$. The actual results were much more interesting.

The complex containing the triply-deprotonated ligand was prepared as outlined in Figure 9. $\mathbf{H_3L^{iPr}}$ was treated with 3.1 equivalents of KH in a solution of dry dimethylformamide (DMF). Once the deprotonation was completed, $CoBr_2$ was added followed by in situ salt metathesis with 1 equivalent of tetraethylammonium bromide. The resulting red complex was purified by recrystallization by slow diffusion of diethyl ether into a DMF solution of the metal salt to give red crystals. Rather than the expected result as indicated above, the actual result was the formation of the diamond-core cobalt dimer complex $(Et_4N)_2[Co(N(\textit{o}\text{-}PhNC(O)^iPr)_2)]_2$ (Figure 10). Table 1 presents selected bond lengths and bond angles from the complex. The UV-visible absorption spectra of the complex in various solvents are also presented in Figure 11.



(Et$_4$N)$_2$[Co$_2$(L^{iPr})$_2$]
77%

Figure 9. Reaction scheme for the synthesis of cobalt diamond-core dimer, **(Et$_4$N)$_2$[Co$_2$(L^{iPr})$_2$]**

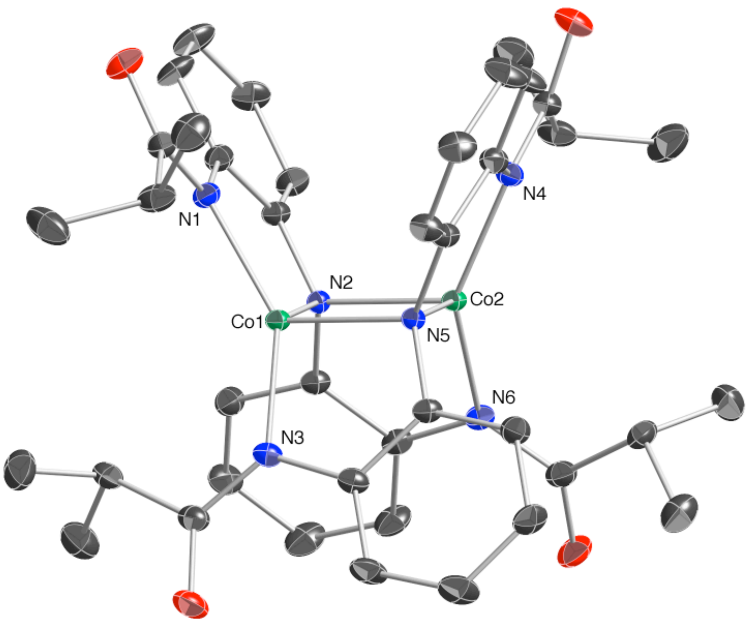


Figure 10. Molecular structure and numbering scheme of **(Et$_4$N)$_2$[Co$_2$(L^{iPr})$_2$]** (35% probability), with hydrogen atoms and counter ions omitted for clarity.

Parameter	Value
Co – N2	2.044 Å
Co – N5	2.040 Å
Co1 – N1; Co2 – N6	1.989 Å
Co1 – N3; Co2 – N4	1.985 Å
N2 – Co – N5	98.616°
Co1 – N2 – Co2	81.304°
Co1 – N5 – Co2	81.463°
N1 – Co1 – N3; N6 – Co2 – N4	143.845°
N1 – Co1 – N2; N3 – Co1 – N5; N6 – Co2 – N5; N4 – Co2 – N2	85.352°
N1 – Co1 – N5; N3 – Co1 – N2; N6 – Co2 – N2; N4 – Co2 – N5	119.083°
Co1 – Co2 distance	2.663 Å

Table 1. Selected bond distances and bond angles for **$(Et_4N)_2[Co_2(L^{iPr})_2]$**

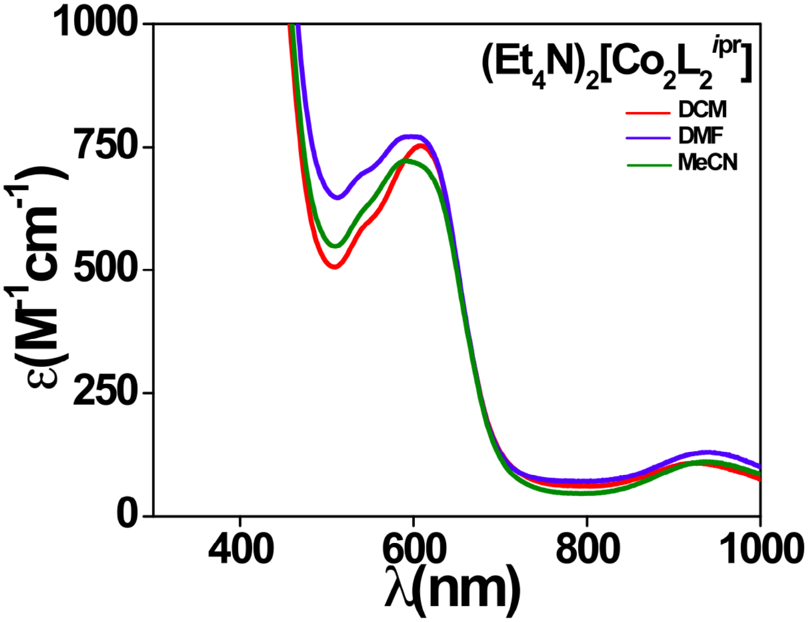


Figure 11. UV-Visible absorption spectra of **$[Co_2(L^{iPr})_2](Et_4N)_2$**, obtained by Dr. Savita Sharma.

Each Co^{II} ion is four-coordinate and displays a seesaw coordination environment with a τ_4 value of 0.686.[23] The diamond-core plane is defined by the Co^{II} ions and the amido nitrogen from each ligand, and each ligand binds to each metal through one of its amidate nitrogens. The complex is symmetrical about its inversion center, making it C_i symmetric. There are consistently two maxima in the UV-visible spectra, one at 600 ± 9 nm and another at 926 nm. These two peaks correspond to the *d*-*d* band transitions of the cobalt.

The diamond-core arrangement of Co_2N_2 has been reported before by Fout et al. involving Co(I),[24] and by O'Connor and Bunker involving Co(III),[25] and the Co(II)-Co(II) distance in $\mathbf{(Et_4N)_2Co_2(L^{iPr})_2}$ is 2.663 Å, which is longer than the 2.254 Å reported for the Co(I)-Co(I) bond length,[24] and shorter than the 2.991 Å reported for the Co(III)-Co(III) distance.[25] This distribution is expected based on the relative sizes of the Co(I), Co(II), and Co(III) ions. Additionally, the Co(II)-Co(II) distance in $\mathbf{(Et_4N)_2Co_2(L^{iPr})_2}$ is greater than the reported Co(II)-Co(II) bond length of 2.302 Å.[26]

The complex containing the doubly-deprotonated ligand was prepared as outlined in Figure 12. $\mathbf{H_3L^{iPr}}$ was treated with 2.1 equivalents of KH in a solution of dry DMF. Once the deprotonation was completed, $CoBr_2$ was added. After attempts at crystallization failed, assuming that the complex was actually anionic rather than neutral, 1 equivalent of Et_4NBr was added for in situ salt metathesis. The resulting green complex was purified by recrystallization by slow diffusion of diethyl ether into a DMF solution of the metal complex to give green crystals. The result was the formation of the 2:1 ligand:cobalt complex $(Et_4N)_2[Co(N(o\text{-}PhNC(O)^iPr)(o\text{-}PhNHC(O)^iPr))_2]$ (Figure 13). Table 2 presents selected bond lengths and bond angles from the complex. The UV-visible absorption spectra of the complex in various solvents are presented in Figure 14.

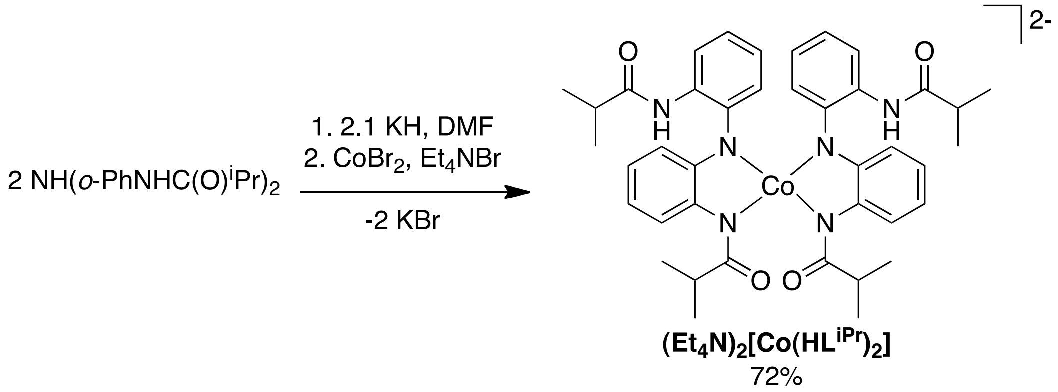


Figure 12. Reaction scheme for the synthesis of 2:1 ligand:metal complex, **$(Et_4N)_2[Co(HL^{iPr})_2]$**

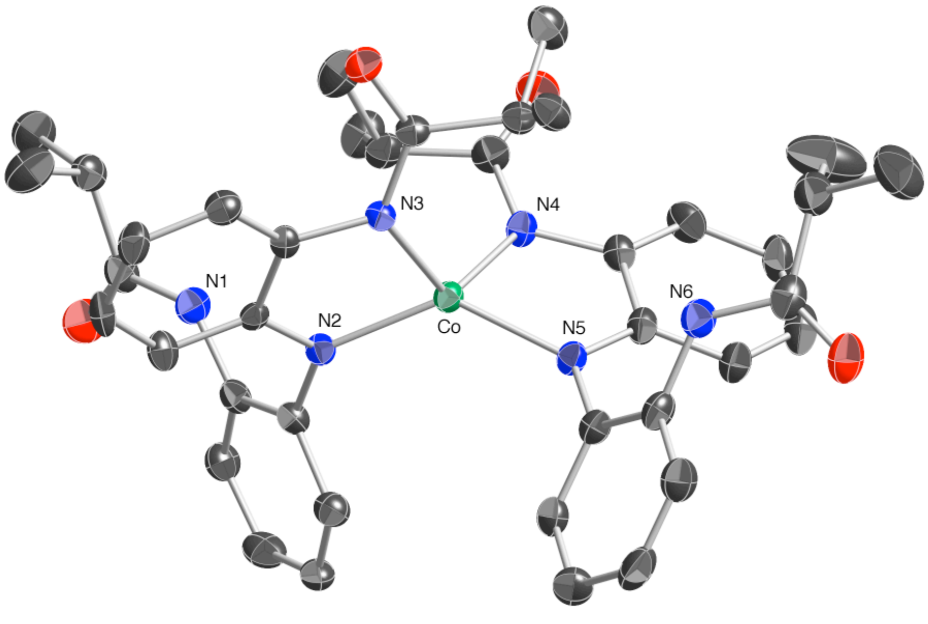


Figure 13. Molecular structure and numbering scheme of **$(Et_4N)_2[Co(HL^{iPr})_2]$** (35% probability), with hydrogen atoms and counter ions omitted for clarity.

Parameter	Value
Co – N2	1.996 Å
Co – N3	2.035 Å
Co – N4	2.029 Å
Co – N5	1.996 Å
N2 – Co – N3	82.329°
N2 – Co – N4	123.504°
N2 – Co – N5	132.040°
N3 – Co – N4	117.141°
N3 – Co – N5	123.357°
N4 – Co – N5	83.067°

Table 2. Selected bond distances and bond angles for **$(Et_4N)_2[Co(HL^{iPr})_2]$**

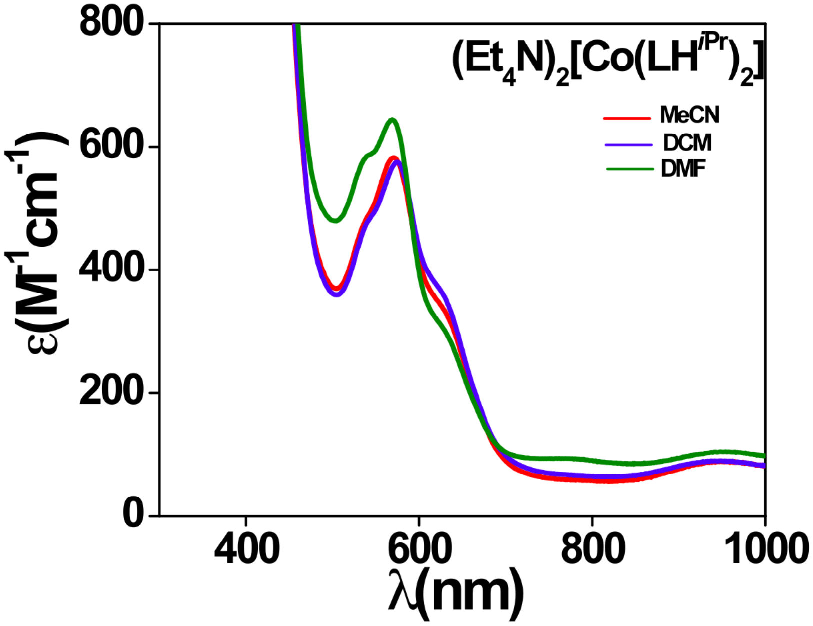


Figure 14. UV-Visible absorption spectra of **$(Et_4N)_2[Co(HL^{iPr})_2]$** obtained by Dr. Savita Sharma.

The Co^{II} ion is four-coordinate and displays a seesaw coordination environment with a τ_4 value of 0.741.[23] Each ligand binds to the Co^{II} center through the central amido nitrogen and one of the amidate nitrogens. Each adducted ligand also has one amidate nitrogen free. There are consistently two maxima in the UV-visible spectra, one at 569 ± 4 nm and another at 636 ± 2 nm. These two peaks correspond to the *d-d* band transitions of the cobalt.

When comparing the two compounds, **$(Et_4N)_2[Co_2(L^{iPr})_2]$** and **$(Et_4N)_2[Co(HL^{iPr})_2]$**, through solid-state UV-visible spectroscopy (Figure 15), the two maxima from the solution-state UV-visible are present, showing that the complexes do not change between the solid- and solution-state. In addition to the maxima from the solution-state, there are also two maxima in the region under 300 nm. It is thought that these maxima correspond to intra-ligand charge transfer.

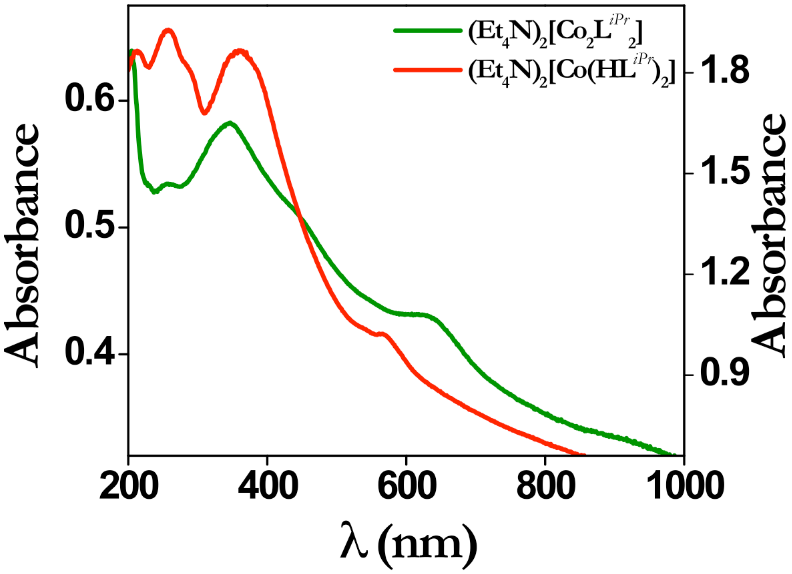


Figure 15. Solid-state UV-visible absorption spectra of **$(Et_4N)_2[Co_2(L^{iPr})_2]$**, represented here in green, and **$(Et_4N)_2[Co(HL^{iPr})_2]$**, represented here in red, obtained by Dr. Savita Sharma

The cobalt chemistry performed with **H_3L^{iPr}** offers the first example of base dependent nuclearity of pincer ligands. The number of Co(II) metal centers chelated by **L^{iPr}** is directly dependent on the quantity of base added to the system, and not on the ratio of ligand to $CoBr_2$. With the mononuclear cobalt complex **$(Et_4N)_2[Co(HL^{iPr})_2]$**, no change in end product was observed when the ligand:$CoBr_2$ ratio was 1:1 as opposed to when it was 2:1. The deciding factor was the fact that with both ratios, 2.1 equivalents of base were introduced for deprotonation, and the doubly-deprotonated ligand **HL^{iPr}** chelated in the 2:1 ligand:$CoBr_2$ ratio. If the product were dependent on the ligand:$CoBr_2$

ratio, then when the ratio was 1:1, the original theorized neutral complex should have been the product.

2.3. Electrochemistry of the L^{iPr} complexes

The electrochemistry data included herein was obtained by Dr. Savita Sharma and used with her permission. Both complexes were investigated using cyclic voltammetry (Figures 16 and 17), yielding interesting results.

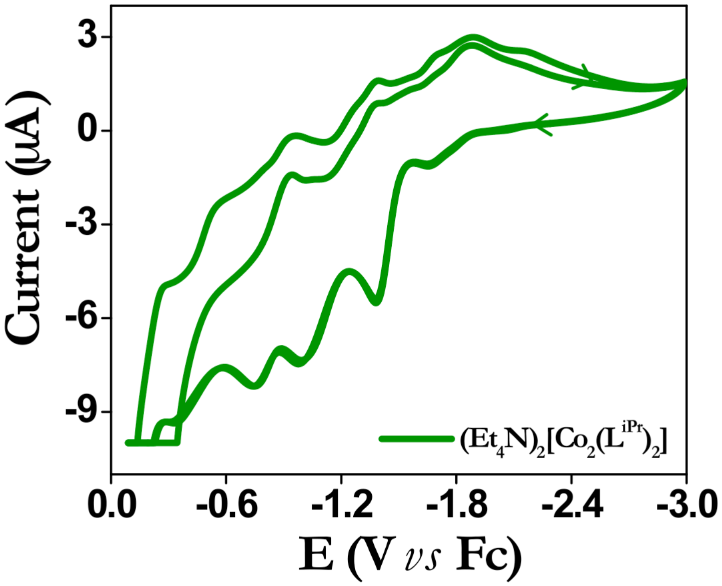


Figure 16. Cyclic voltammogram of **$(Et_4N)_2[Co_2(L^{iPr})_2]$**, obtained by Dr. Savita Sharma

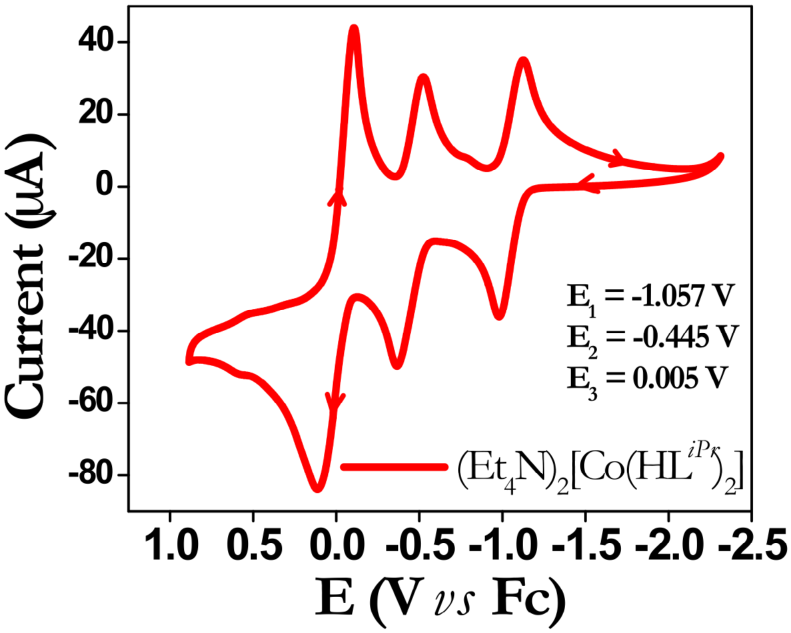


Figure 17. Cyclic volatmmogram of **$(Et_4N)_2[Co(HL^{iPr})_2]$**, obtained by Dr. Savita Sharma

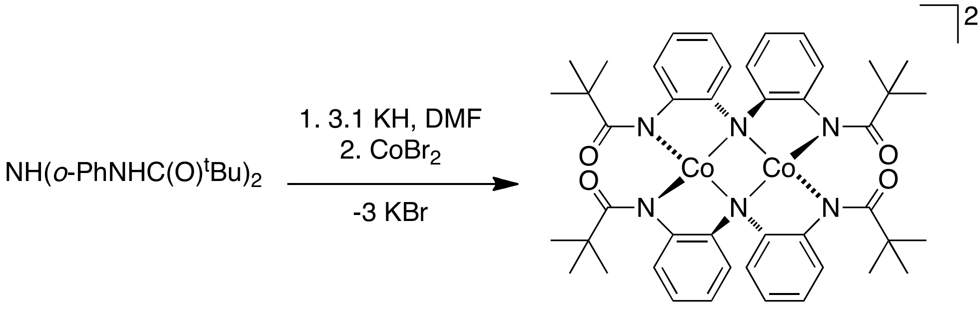
Unfortunately, the results from the cyclic voltammetry of **$(Et_4N)_2[Co_2(L^{iPr})_2]$** are at this time too complicated and unable to be interpreted knowledgably. However, the results from the cyclic voltammetry of **$(Et_4N)_2[Co(HL^{iPr})_2]$** are understandable and demonstrate that the metal complex is in fact redox active with three peaks in the cyclic voltammogram. The peak at E_1 most likely corresponds to the Co(II)-Co(III) electron transfer, and the peaks at E_2 and E_3 most likely correspond to the Co(III)-Co(IV) electron transfer or a ligand radical. The creation of a ligand radical demonstrates that the ligand in **$(Et_4N)_2[Co(HL^{iPr})_2]$** is redox-active. Having a ligand that is redox-active permits for a combination of the redox properties of both the ligand and the metal wherein both components may be oxidated or reduced indepently of each other.[27]

The electrochemical features offered by the monomeric complex **$(Et_4N)_2[Co(HL^{iPr})_2]$** are quite unique. This complex while only showing three peaks actually involves four electron transfers, since E_3 is a two-electron transfer. Other Co(II) complexes which involve chelation by two ligands only provide for three electron transfers.[28] In this complex, all of the nitrogens are participating in bonding with the cobalt center, and the complex has an overall positive charge. A dinuclear cobalt complex has been needed to observe four electron transfers,[29] but this complex still offers four electrochemical events while being mononuclear. In this complex, the ligands themselves are neutral. This differs significantly from **$(Et_4N)_2[Co(HL^{iPr})_2]$**, where the metal complex has a negative charge and the ligands are dianionic. The dinuclear complex reported by Szymczak, et al. is actually a reductive species, with the cobalt metal centers being reduced all the way down to Co(I),[29] whereas **$(Et_4N)_2[Co(HL^{iPr})_2]$** is thought to be oxidative with the metal center being oxidized up to Co(IV). The dianionic nature of the ligand contributes to the oxidative nature of the complex.

2.4. Cobalt chemistry with H_3L^{tBu}

The structural features of **H_3L^{tBu}** were attempted to be evaluated by treating the ligand with approximately 3 and 2 equivalents of KH to deprotonate the ligand. Based on the structures obtained with the cobalt complexes of **H_3L^{iPr}**, the ligand treated with approximately 3 equivalents is theorized to yield an anionic complex either of the form $[Co(N(o\text{-}PhNC(O)^tBu)_2)]^-$ or in the form of the diamond-core complex $[Co_2(N(o\text{-}PhNC(O)^tBu)_2)_2]^{2-}$. The ligand treated with approximately 2 equivalents is theorized to yield the 2:1 ligand:metal complex $[Co(N(o\text{-}PhNC(O)^tBu)(o\text{-}PhNHC(O)^tBu))]^{2-}$. Unfortunately, results of these experiments have still not yielded conclusive structural data.

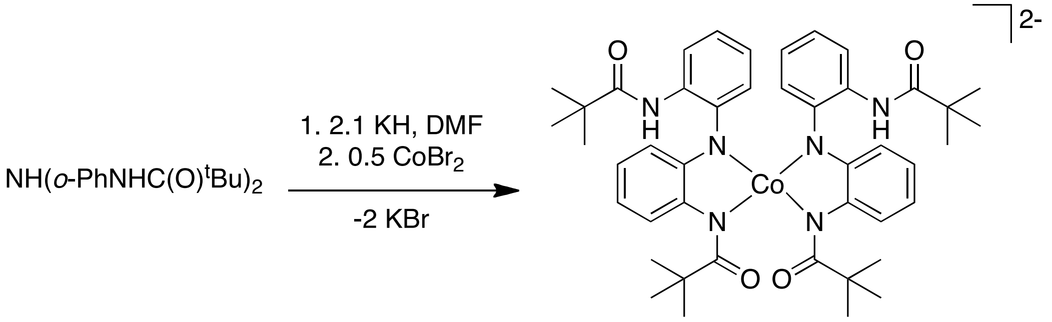
The experiments with the triply-deprotonated ligand were conducted according to Figure 18, which also shows the theoretical result of the reaction. **H_3L^{tBu}** was treated with 3.1 equivalents of KH in a solution of dry DMF. Once the deprotonation was completed, $CoBr_2$ was added. No salt metathesis was attempted with these reactions due to the added non-polarity afforded to the complex with the tert-butyl group. The resulting red complex has been attempted to be purified by recrystallization, but to no avail. Multiple attempted at recrystallization yield a red oil, and continued efforts are underway to obtain a structure for the result of this reaction.



$K_2[Co_2(L^{tBu})_2]$
$K_2[Co_2(N(o\text{-}PhNC(O)^tBu)_2)_2]$
theoretical result

Figure 18. Reaction scheme for the theoretical diamond-core dimer, **$K_2[Co_2(L^{tBu})_2]$**

The experiments with the doubly-deprotonated ligand were conducted as outlined in Figure 19, which also shows a theoretical result of the reaction. **H_3L^{tBu}** was treated with 2.1 equivalents of KH in a solution of dry DMF. Once the deprotonation was completed, one-half equivalent of $CoBr_2$ was added. As with the triply-deprotonated ligand experiments, salt metathesis was not attempted in these experiments either. The results of this experiment are more interesting, however. There are apparently two products from this reaction, neither of which has been characterized. One is a green solid that is insoluble in acetonitrile, but attempts at recrystallization through slow diffusion of diethyl ether into a DMF solution have only yielded a green powder. Since the reaction that yielded the 2:1 ligand:metal complex **$(Et_4N)_2[Co(HL^{iPr})_2]$** resulted in green crystals, it is theorized that this green product is the analagous 2:1 ligand:metal complex. The other product is a red solution that after slow diffusion of diethyl ether into a DMF/acetonitrile solution of the complex yields red microcrystalline material that is unsuitable for X-ray diffraction. Continued efforts are underway to obtain structures for both products of this reaction.



$K_2[Co(HL^{tBu})_2]$

$K_2[Co(N(o\text{-}PhNC(O)^tBu)(o\text{-}PhNHC(O)^tBu))]$

theoretical result

Figure 19. Reaction scheme for the theoretical 2:1 ligand:metal complex, **$K_2[Co(HL^{tBu})_2]$**

3. Conclusions and Future Direction

Ligands of the NNN-pincer type with amidate functionality of the form NH(*o*-PhNHC(O)R$)_2$ (R = ^{i}Pr, ^{t}Bu) have been successfully synthesized and characterized, as have cobalt complexes with the ligand NH(*o*-PhNHC(O)^{i}Pr$)_2$ (**H_3L^{iPr}**). When **H_3L^{iPr}** was treated with 3.1 equivalents of base, the triply-deprotonated **L^{iPr}** formed a dinuclear dimeric complex with a Co_2N_2 diamond-core structure $(Et_4N)_2$[Co_2(N(*o*-PhNC(O)^{i}Pr$)_2)_2$] (**$(Et_4N)_2[Co_2(L^{iPr})_2]$**). When treated with 2.1 equivalents of base, the doubly-deprotonated **HL^{iPr}** formed a mononuclear complex with a 2:1 ligand:cobalt ratio $(Et_4N)_2$[Co(N(*o*-PhNC(O)^{i}Pr)(*o*-PhNHC(O)^{i}Pr))] (**$(Et_4N)_2[Co(HL^{iPr})_2]$**). The Co_2N_2 diamond-core structure has not often been reported with amido ligands, and holds great potential for future work. The mononuclear complex demonstrates unique electrochemical properties that need to be further explored. With both complexes, further experimentation needs to be conducted in order to determine exactly which redox events are metal-based, and which are ligand-based. The redox-activity of the ligand coupled with the redox-activity of the cobalt metal center offers opportunities for efficient catalysts and materials in the future. Unfortunately, cobalt complexes with the ligand NH(*o*-PhNHC(O)^{t}Bu$)_2$ (**H_3L^{tBu}**) have not been as successful. The reactions are going to completion and the products are thought to be cobalt-ligand complexes, however growing crystals suitable for X-ray diffraction is proving difficult.

Future research with these complexes offers many possibilities. The diamond-core dimer should be explored to see if exogenous ligand binding will result in monomerization, and if so, what types of exogenous ligands will cause this.

Additionally, it should be investigated if the complex can be used for the catalytic reduction of oxygen. There also need to be further electrochemical studies with the diamond-core dimer to try and understand exactly what is occurring in the cyclic voltammogram. The mononucleaer 2:1 complex needs to be further explored with respect to its unique electrochemistry. Additional work needs to be completed with the $\mathbf{H_3L^{tBu}}$ ligand to obtain structural information and insight into how changing the terminal R group on each ligand arm will affect the nuclearity of complex formation.

4. Experimental

4.1 General Considerations

All manipulations were carried out using standard Schlenk techniques or conducted in an MBraun Labmaster 130 drybox under a nitrogen atmosphere. All reagents used were purchased from commercial vendors and used as received unless otherwise noted. Anhydrous solvents were purchased from Sigma-Aldrich and further purified by sparging with Ar gas followed by passage through activated alumina columns. Deuterated chloroform ($CDCl_3$-d_1) was purchased from Aldrich and degassed and dried according to standard procedures[30] prior to use. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 MHz spectrometer at ambient temperature. Chemical shifts were referenced to residual solvent peaks. Infrared spectra were recorded as KBr pellets on a Varian Scimitar 800 Series FT-IR spectrophotometer. UV-Visible absorption spectra were recorded on a Cary 50 spectrophotometer using 1.0 cm quartz cuvettes. Solution state magnetic moments were measured using the Evans method.[31] The Mass Spectrometry Centre at Emory University recorded Mass spectra on a JEOL JMS-SX102/SX102A/E mass spectrometer. X-ray diffraction studies were carried out in the X-ray Crystallography Centre at Emory University on a Bruker Smart 1000 CCD diffractometer. Cyclic voltammetric experiments were carried out using a CH Instruments (Austin, TX) Model 660C potentiostat. All experiments were conducted in DCM with a 0.10 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. Electrochemical experiements were conducted in a three-component cell consisting of a Pt auxiliary electrode, a non-aqueous reference electrode ($Ag/AgNO_3$), and a platinum working electrode. All electrochemical measurements and referenced and reported versus the ferrocene/ferrocenium couple. Characterization data except for ^{1}H NMR data and electrochemical data were obtained by Dr. Savita Sharma.

4.2. Ligand Syntheses

4.2.1 Bis(2-nitrophenyl)amine [NH(*o*-PhNO$_2$)$_2$]

A mixture of 2-nitroaniline (10.0 g, 74.1 mmol), 1-fluoro-2-nitrobenzene (7.79 mL, 74.1 mmol), and potassium *t*-butoxide (8.72 g, 77.8 mmol) was stirred under N_2 in dimethyl sulfoxide (DMSO, 120 mL) at room temperature for one hour. The solution was then diluted with water (500 mL) and filtered to give a bright orange solid. The solid was stirred in MeOH (2.0 L) and the temperature raised over 20 min until the MeOH was boiling. The solution was then allowed to cool to room temperature overnight, stored for 6 h at 0˚C, and filtered through a Buchner funnel with coarse porosity filter paper to yield an iridescent orange solid. The solid was washed with additional MeOH at room temperature and dried under vacuum to afford the dry product (44.2%, 8.44 g). ^{1}H NMR (δ, $CDCl_3$, 300 MHz): 11.02 (s, 1H), 8.21 (dd, 2H, *J* = 1.5), 7.56 (m, 4H), 7.10 (td, 2H, *J* = 1.8 Hz, *J* = 1.5 Hz). ^{13}C NMR (δ, $CDCl_3$, 75.5 MHz): 137.40, 134.30, 127.01, 121.32, 119.20. HRMS(ESI): $C_{12}H_9N_3O_4$ *m/z* Calcd. 259.0593, Found 260.06584 $[M+1]^+$. FTIR (KBr, cm^{-1}): ν(NO_2) 1514, 1334, ν(NH) 3303. UV-vis (CH_2Cl_2) λ_{max}, nm (ε, M^{-1} cm^{-1}): 430 (14100), 268 (35700).

4.2.2. Bis(2-aminophenyl)amine [NH(*o*-PhNH$_2$)$_2$]

To a THF (50.0 mL) solution of NH(*o*-PhNO$_2$)$_2$ (5.00g, 19.3 mmol) was added 5% Pd/C (2.42 g, 1.16 mmol, 6 mol%). The reaction mixture was placed in a pressure safe reaction bottle and shaken under H_2 at 50 psi for 4 h. The reaction mixture was filtered through a pad of celite on a medium porosity fritted funnel and washed with THF. The filtrate was concentrated *in vacuo* to yield a brown oil. This was dissolved in diethyl ether (20.0 mL), hexanes (5.0 mL) added, and stored overnight at 0˚C to produce a purple solid. The supernatant was decanted and the solid was dried overnight under vacuum to yield a white/purple solid (91.8%, 3.53 g). ^{1}H NMR (δ, $CDCl_3$, 300 MHz): 6.93 (m, 4H, ArH), 6.79 (m, 4H,ArH), 5.05 (s, 1H, NH), 3.64 (s, 4H, NH). ^{13}C NMR (δ, $CDCl_3$, 75.5 MHz): 138.56, 131.21, 124.12, 122.61, 120.84, 118.78. HRMS(ESI): $C_{12}H_{13}N_3$ *m/z* Calcd. 199.11095 Found 200.11751 $[M+1]^+$. FTIR (KBr, cm^{-1}): ν(NH_2) 3413, 3375, and 3344.

4.2.3. 2,2'-Bisisobutylamidodiphenylamine [NH(*o*-PhNHC(O)^{i}Pr)$_2$] – H_3L^{iPr}

A solution of NH(*o*-$PhNH_2$)$_2$ (1.8 g, 9.05 mmol) in dichloromethane (DCM, 100 mL) was lowered to 0˚C under an atmosphere of N_2. Triethylamine (2.77 mL, 19.8 mmol) was then added, followed by isobutyryl chloride (2.10 mL, 19.8 mmol). The mixture was warmed to room temperature and stirred overnight. The resulting solid was extracted through aqueous $NaHCO_3$ (saturated, 3 x 50 mL), dried over magnesium sulfate, and concentrated *in vacuo* to produce a white powdery solid (92.5%, 2.84g). ^{1}H NMR (δ, $CDCl_3$, 300 MHz): 7.83 (s, 2H, NH(CO)), 7.67 (d, 2H, *J* = 1.6 Hz, ArH), 7.04 (m, 4H, ArH), 6.88 (d, 2H, *J* = 1.2 Hz, ArH), 5.75 (s, 1H, NH), 2.58 (q, 2H, *J* = 6.8 Hz, CH), 1.16 (d, 12H, *J* = 7.2 Hz, CH_3). ^{13}C NMR (δ, $CDCl_3$, 75.5 MHz): 176.48, 136.02, 129.26, 126.27, 124.18, 123.0, 121.11, 36.20, 19.76. HRESI-MS: $C_{20}H_{25}N_3O_2$ *m/z* Calcd.

339.19468 Found 340.20150 $[M+1]^+$. FTIR (KBr, cm^{-1}): $\nu(NH_{amide})$ 3230, $\nu(NH_{amine})$ 3367, $\nu(CO)$ 1660.

4.2.4. 2,2'-Bistertpentylamidodiphenylamine [$NH(o\text{-}PhNHC(O)^tBu)_2$] – H_3L^{tBu}

A solution of $NH(o\text{-}PhNH_2)_2$ (3.52 g, 17.7 mmol) in dichloromethane (DCM, 100 mL) was lowered to 0˚C under an atmosphere of N_2. Triethylamine (5.43 mL, 39.0 mmol) was then added, followed by pivaloyl chloride (4.80 mL, 39.0 mmol). The mixture was warmed to room temperature and stirred overnight. The resulting solid was extracted through aqueous $NaHCO_3$ (saturated, 3 x 75 mL), dried over magnesium sulfate, and concentrated *in vacuo* to produce a purple oil. The oil was stored overnight at 0˚C, washed with hexanes, and dried again to produce a bluish-green-white solid (92%, 5.95g). ^1H NMR (δ, $CDCl_3$, 300 MHz): 7.69 (d, 2H, J = 5.7 Hz, ArH), 7.65 (s, 2H, NH(CO)), 7.06 (m, 4H, ArH), 6.90 (d, 2H, J = 7.5 Hz, ArH), 5.31 (s, 1H, NH), 1.22 (s, 18H, CH_3).

4.3. Complex syntheses

4.3.1. Diamond-core dimer $(Et_4N)_2[Co_2(N(o\text{-}PhNC(O)^iPr)_2)_2]$ – $(Et_4N)_2[Co_2(L^{iPr})_2]$

To a solution of $NH(o\text{-}PhNHC(O)^iPr)_2$ (46 mg, 0.135 mmol) in dry dimethylformamide (DMF, 10 mL) was added potassium hydride (16.9 mg, 0.421 mmol) as a solid. After 2 h of stirring, to the dark yellow solution $CoBr_2$ (29.6 mg, 0.135 mmol) was added as a solid. The reaction was stirred overnight and tetraethylammonium bromide (28.5 mg, 0.135 mmol) was added to the red solution as a solid. After stirring for 1 hr, the reaction mixture was concentrated in *in vacuo*. The resulting red solid was dissolved in acetonitrile (MeCN, 10 mL) and filtered through a medium porosity frit. The product was recrystallized by slow diffusion of diethyl ether into DMF solution to yield red crystals (77%, 41.3 mg). ^{1}H NMR (δ, CD_2Cl_2, 400 MHz): -46.28 (s), -40.05 (s), -1.12 (s), 0.71 (s), 10.92 (s), 25.99 (s), 28.64 (s), 65.20 (s). FTIR (KBr, cm^{-1}): ν(CO) 1592. $\mu_{\text{eff}} = 4.73\ \mu_B$ (Evans Method, CD_2Cl_2, 298K). UV-vis (DMF) λ_{max}, nm (ε, M^{-1}cm^{-1}): 600 (770), 926 (133); UV-vis (DCM) λ_{max}, nm (ε, M^{-1}cm^{-1}): 609 (749), 926 (106); UV-vis (CH_3CN) λ_{max}, nm (ε, M^{-1}cm^{-1}): 595 (720); UV-vis (solid, silicon oil) λ_{max}, nm: 253, 343, 455 (sh), 644.

4.3.2. 2:1 ligand:metal complex $(Et_4N)_2[Co(N(o\text{-}PhNC(O)^iPr)(o\text{-}PhNHC(O)^iPr))]$ – $(Et_4N)_2[Co(HL^{iPr})_2]$

To a solution of $NH(o\text{-}PhNHC(O)^iPr)_2$ (114 mg, 0.336 mmol) in dry dimethylformamide (DMF, 10 mL) was added potassium hydride (29.0 mg, 0.740 mmol) as a solid. After 2 h of stirring, to the yellow solution $CoBr_2$ (36.7 mg, 0.168 mmol) was added as a solid. The reaction was stirred overnight, tetraethylammonium bromide (70.0 mg, 0.336 mmol) was added to the green solution as a solid, and 1 hr later the green reaction mixture was concentrated *in vacuo*. The resulting green solid was dissolved in acetonitrile (MeCN, 10 mL) and filtered through a medium porosity frit. The product was recrystallized by slow diffusion of diethyl ether into DMF solution to yield green crystals (72%, 120.1 mg). FTIR (KBr, cm^{-1}): ν(CO) 1592, ν(NH) 3388. $\mu_{\text{eff}} = 1.826\ \mu_B$ (Evans Method, CD_2Cl_2, 298K). UV-vis (DMF) λ_{max}, nm (ε, M^{-1}cm^{-1}): 569 (640), 634 (sh) (290); UV-vis (DCM) λ_{max}, nm (ε, M^{-1}cm^{-1}): 573 (570), 636 (sh) (330); UV-vis (CH_3CN) λ_{max}, nm (ε, M^{-1}cm^{-1}): 569 (580), 636 (sh) (307); UV-vis (solid, silicon oil) λ_{max}, nm: 211, 255, 360, 573.

4.3.3. Proposed $K_2[Co(N(o\text{-}PhNC(O)^tBu)_2)]$

To a solution of $NH(o\text{-}PhNHC(O)^tBu)_2$ (91 mg, 0.249 mmol) in dry dimethylformamide (DMF, 10 mL) was added potassium hydride (34.9 mg, 0.870 mmol) as a solid. After 2 h of stirring, to the dark yellow solution $CoBr_2$ (54.5 mg, 0.249 mmol) was added as a solid. The reaction was stirred overnight, and the green solution was concentrated *in vacuo*. The resulting green solid was dissolved in acetonitrile (MeCN, 10 mL) and filtered through a medium porosity frit. The resulting blue-green solid was dissolved in dry tetrahydrofuran (THF, 10 mL) and filtered through a medium porosity frit. The resulting filtrate was concentrated *in vacuo* and attempted to be recrystallized by slow diffusion of diethyl ether into DMF solution, but the result was a green powder. A crystalline form has yet to be obtained.

4.3.4. Proposed $K_2[Co(N(o\text{-}PhNC(O)^tBu)(o\text{-}PhNHC(O)^tBu))]$

To a solution of $NH(o\text{-}PhNHC(O)^tBu)_2$ (123 mg, 0.337 mmol) in dry dimethylformamide (DMF, 10 mL) was added potassium hydride (33.8 mg, 0.843 mmol) as a solid. After 4 h of stirring, to the dark yellow solution $CoBr_2$ (36.8 mg, 0.168 mmol) was added as a solid. The reaction was stirred overnight, and the red solution was concentrated *in vacuo*. The resulting red solid was dissolved in acetonitrile (MeCN, 10 mL) and filtered through a medium porosity frit. The resulting filtrate was concentrated *in vacuo* and attempted to be recrystallized by slow diffusion of diethyl ether into DMF, but the result was a red oil. A crystalline form has yet to be obtained.

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Appendix A. Crystal Data for $(Et_4N)_2[Co_2(L^{iPr})_2]$

Table 1. Crystal data and structure refinement for PSM_1_20N.

Identification code	PSM_1_20N	
Empirical formula	C28 H42 Co N4 O2	
Formula weight	525.59	
Temperature	172(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	I4(1)22	
Unit cell dimensions	a = 18.7790(8) Å	α= 90°.
	b = 18.7790(8) Å	β= 90°.
	c = 35.798(3) Å	γ = 90°.
Volume	12624.1(13) $Å^3$	
Z	16	
Density (calculated)	1.106 Mg/m^3	
Absorption coefficient	0.571 mm^{-1}	
F(000)	4496	
Crystal size	0.44 x 0.40 x 0.37 mm^3	
Theta range for data collection	1.22 to 30.71°.	
Index ranges	-26<=h<=25, -26<=k<=26, -50<=l<=50	
Reflections collected	120959	
Independent reflections	9495 [R(int) = 0.0500]	
Completeness to theta = 30.71°	97.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8166 and 0.7874	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9495 / 0 / 320	
Goodness-of-fit on F^2	1.063	
Final R indices [I>2sigma(I)]	R1 = 0.0506, wR2 = 0.1505	
R indices (all data)	R1 = 0.0665, wR2 = 0.1573	
Absolute structure parameter	0.504(18)	
Largest diff. peak and hole	0.811 and -0.540 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for PSM_1_20N. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	5355(1)	5530(1)	9350(1)	18(1)
C(2)	5752(2)	5347(2)	9041(1)	24(1)
C(3)	6101(2)	5856(2)	8828(1)	31(1)
C(4)	6015(2)	6571(2)	8923(1)	35(1)
C(5)	5640(2)	6765(2)	9233(1)	29(1)
C(6)	5303(1)	6263(1)	9464(1)	18(1)
C(7)	4898(2)	7035(1)	9960(1)	24(1)
C(8)	4401(2)	7115(2)	10293(1)	30(1)
C(9)	4806(2)	7449(2)	10617(1)	45(1)
C(10)	3768(2)	7569(2)	10182(1)	47(1)
C(1B)	1238(2)	4669(2)	1973(1)	22(1)
C(2B)	1758(2)	4311(2)	1754(1)	31(1)
C(3B)	1546(2)	3905(2)	1438(1)	35(1)
C(4B)	842(2)	3879(2)	1335(1)	29(1)
C(5B)	333(2)	4236(2)	1543(1)	25(1)
C(6B)	529(1)	4635(1)	1858(1)	19(1)
C(7B)	2036(1)	5106(2)	2459(1)	25(1)
C(8B)	2082(2)	5577(2)	2805(1)	31(1)
C(9B)	2543(2)	6234(2)	2701(1)	48(1)
C(10B)	2436(2)	5186(2)	3132(1)	41(1)
C(1S)	6862(2)	7355(2)	280(1)	30(1)
C(2S)	6898(2)	7850(2)	621(1)	41(1)
C(3S)	8191(2)	7423(2)	183(1)	31(1)
C(4S)	8308(2)	6768(2)	423(1)	38(1)
C(5S)	-507(2)	5752(2)	9605(1)	46(1)
C(6S)	78(2)	5664(2)	9900(1)	38(1)
C(7S)	661(2)	4914(2)	10376(1)	37(1)
C(8S)	795(2)	5518(2)	10656(1)	42(1)
Co(1)	4495(1)	5505(1)	10000	15(1)
Co(1B)	501(1)	5501(1)	2500	15(1)
N(1)	5000	5000	9571(1)	19(1)

N(2)	4895(1)	6393(1)	9792(1)	20(1)
N(1B)	1387(1)	5080(1)	2293(1)	20(1)
N(2B)	0	5000	2068(1)	14(1)
N(1S)	7458(1)	7458(1)	0	21(1)
N(2S)	0	5000	10138(1)	24(1)
O(1)	5245(1)	7577(1)	9865(1)	39(1)
O(1B)	2575(1)	4795(1)	2351(1)	33(1)

Table 3. Bond lengths [Å] and angles [°] for PSM_1_20N.

C(1)-C(2)	1.378(4)
C(1)-N(1)	1.434(3)
C(1)-C(6)	1.439(3)
C(2)-C(3)	1.387(4)
C(2)-H(2A)	0.9500
C(3)-C(4)	1.396(5)
C(3)-H(3A)	0.9500
C(4)-C(5)	1.364(5)
C(4)-H(4A)	0.9500
C(5)-C(6)	1.404(4)
C(5)-H(5A)	0.9500
C(6)-N(2)	1.424(3)
C(7)-O(1)	1.256(3)
C(7)-N(2)	1.347(3)
C(7)-C(8)	1.522(4)
C(8)-C(10)	1.515(5)
C(8)-C(9)	1.522(5)
C(8)-H(8A)	1.0000
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(1B)-C(6B)	1.396(4)
C(1B)-N(1B)	1.408(4)
C(1B)-C(2B)	1.422(4)
C(2B)-C(3B)	1.421(4)
C(2B)-H(2BA)	0.9500
C(3B)-C(4B)	1.372(4)
C(3B)-H(3BA)	0.9500
C(4B)-C(5B)	1.385(4)
C(4B)-H(4BA)	0.9500
C(5B)-C(6B)	1.403(4)

C(5B)-H(5BA)	0.9500
C(6B)-N(2B)	1.421(3)
C(7B)-O(1B)	1.231(3)
C(7B)-N(1B)	1.359(3)
C(7B)-C(8B)	1.524(4)
C(8B)-C(10B)	1.532(5)
C(8B)-C(9B)	1.553(5)
C(8B)-H(8BA)	1.0000
C(9B)-H(9BA)	0.9800
C(9B)-H(9BB)	0.9800
C(9B)-H(9BC)	0.9800
C(10B)-H(10A)	0.9800
C(10B)-H(10B)	0.9800
C(10B)-H(10C)	0.9800
C(1S)-N(1S)	1.515(4)
C(1S)-C(2S)	1.534(4)
C(1S)-H(1SA)	0.9900
C(1S)-H(1SB)	0.9900
C(2S)-H(2SA)	0.9800
C(2S)-H(2SB)	0.9800
C(2S)-H(2SC)	0.9800
C(3S)-C(4S)	1.516(4)
C(3S)-N(1S)	1.525(3)
C(3S)-H(3SA)	0.9900
C(3S)-H(3SB)	0.9900
C(4S)-H(4SA)	0.9800
C(4S)-H(4SB)	0.9800
C(4S)-H(4SC)	0.9800
C(5S)-C(6S)	1.532(5)
C(5S)-H(5SA)	0.9800
C(5S)-H(5SB)	0.9800
C(5S)-H(5SC)	0.9800
C(6S)-N(2S)	1.519(4)
C(6S)-H(6SA)	0.9900
C(6S)-H(6SB)	0.9900
C(7S)-N(2S)	1.514(4)

C(7S)-C(8S)	1.533(5)
C(7S)-H(7SA)	0.9900
C(7S)-H(7SB)	0.9900
C(8S)-H(8SA)	0.9800
C(8S)-H(8SB)	0.9800
C(8S)-H(8SC)	0.9800
Co(1)-N(2)#1	1.975(2)
Co(1)-N(2)	1.975(2)
Co(1)-N(1)	2.040(2)
Co(1)-N(1)#2	2.040(2)
Co(1)-Co(1)#3	2.6807(9)
Co(1B)-N(1B)#4	1.985(2)
Co(1B)-N(1B)	1.985(2)
Co(1B)-N(2B)#4	2.041(2)
Co(1B)-N(2B)	2.041(2)
Co(1B)-Co(1B)#5	2.6637(9)
N(1)-C(1)#3	1.434(3)
N(1)-Co(1)#3	2.040(2)
N(2B)-C(6B)#5	1.421(3)
N(2B)-Co(1B)#5	2.041(2)
N(1S)-C(1S)#6	1.515(3)
N(1S)-C(3S)#6	1.525(3)
N(2S)-C(7S)#5	1.514(4)
N(2S)-C(6S)#5	1.519(4)

C(2)-C(1)-N(1)	121.3(2)
C(2)-C(1)-C(6)	120.2(2)
N(1)-C(1)-C(6)	118.5(2)
C(1)-C(2)-C(3)	121.6(3)
C(1)-C(2)-H(2A)	119.2
C(3)-C(2)-H(2A)	119.2
C(2)-C(3)-C(4)	118.4(3)
C(2)-C(3)-H(3A)	120.8
C(4)-C(3)-H(3A)	120.8
C(5)-C(4)-C(3)	121.0(3)
C(5)-C(4)-H(4A)	119.5

C(3)-C(4)-H(4A)	119.5
C(4)-C(5)-C(6)	122.1(3)
C(4)-C(5)-H(5A)	119.0
C(6)-C(5)-H(5A)	119.0
C(5)-C(6)-N(2)	127.8(2)
C(5)-C(6)-C(1)	116.5(2)
N(2)-C(6)-C(1)	115.7(2)
O(1)-C(7)-N(2)	127.4(3)
O(1)-C(7)-C(8)	116.8(2)
N(2)-C(7)-C(8)	115.8(2)
C(10)-C(8)-C(7)	109.3(3)
C(10)-C(8)-C(9)	111.0(3)
C(7)-C(8)-C(9)	109.3(3)
C(10)-C(8)-H(8A)	109.1
C(7)-C(8)-H(8A)	109.1
C(9)-C(8)-H(8A)	109.1
C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(8)-C(10)-H(10A)	109.5
C(8)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(8)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(6B)-C(1B)-N(1B)	117.0(2)
C(6B)-C(1B)-C(2B)	118.1(3)
N(1B)-C(1B)-C(2B)	124.9(3)
C(3B)-C(2B)-C(1B)	120.1(3)
C(3B)-C(2B)-H(2BA)	120.0
C(1B)-C(2B)-H(2BA)	120.0
C(4B)-C(3B)-C(2B)	120.1(3)
C(4B)-C(3B)-H(3BA)	119.9

C(2B)-C(3B)-H(3BA)	119.9
C(3B)-C(4B)-C(5B)	120.2(3)
C(3B)-C(4B)-H(4BA)	119.9
C(5B)-C(4B)-H(4BA)	119.9
C(4B)-C(5B)-C(6B)	120.7(3)
C(4B)-C(5B)-H(5BA)	119.7
C(6B)-C(5B)-H(5BA)	119.7
C(1B)-C(6B)-C(5B)	120.7(2)
C(1B)-C(6B)-N(2B)	119.3(2)
C(5B)-C(6B)-N(2B)	120.0(2)
O(1B)-C(7B)-N(1B)	125.8(3)
O(1B)-C(7B)-C(8B)	118.9(3)
N(1B)-C(7B)-C(8B)	115.3(2)
C(7B)-C(8B)-C(10B)	111.5(3)
C(7B)-C(8B)-C(9B)	107.4(3)
C(10B)-C(8B)-C(9B)	108.7(3)
C(7B)-C(8B)-H(8BA)	109.7
C(10B)-C(8B)-H(8BA)	109.7
C(9B)-C(8B)-H(8BA)	109.7
C(8B)-C(9B)-H(9BA)	109.5
C(8B)-C(9B)-H(9BB)	109.5
H(9BA)-C(9B)-H(9BB)	109.5
C(8B)-C(9B)-H(9BC)	109.5
H(9BA)-C(9B)-H(9BC)	109.5
H(9BB)-C(9B)-H(9BC)	109.5
C(8B)-C(10B)-H(10A)	109.5
C(8B)-C(10B)-H(10B)	109.5
H(10A)-C(10B)-H(10B)	109.5
C(8B)-C(10B)-H(10C)	109.5
H(10A)-C(10B)-H(10C)	109.5
H(10B)-C(10B)-H(10C)	109.5
N(1S)-C(1S)-C(2S)	114.6(3)
N(1S)-C(1S)-H(1SA)	108.6
C(2S)-C(1S)-H(1SA)	108.6
N(1S)-C(1S)-H(1SB)	108.6
C(2S)-C(1S)-H(1SB)	108.6

H(1SA)-C(1S)-H(1SB)	107.6
C(1S)-C(2S)-H(2SA)	109.5
C(1S)-C(2S)-H(2SB)	109.5
H(2SA)-C(2S)-H(2SB)	109.5
C(1S)-C(2S)-H(2SC)	109.5
H(2SA)-C(2S)-H(2SC)	109.5
H(2SB)-C(2S)-H(2SC)	109.5
C(4S)-C(3S)-N(1S)	114.1(3)
C(4S)-C(3S)-H(3SA)	108.7
N(1S)-C(3S)-H(3SA)	108.7
C(4S)-C(3S)-H(3SB)	108.7
N(1S)-C(3S)-H(3SB)	108.7
H(3SA)-C(3S)-H(3SB)	107.6
C(3S)-C(4S)-H(4SA)	109.5
C(3S)-C(4S)-H(4SB)	109.5
H(4SA)-C(4S)-H(4SB)	109.5
C(3S)-C(4S)-H(4SC)	109.5
H(4SA)-C(4S)-H(4SC)	109.5
H(4SB)-C(4S)-H(4SC)	109.5
C(6S)-C(5S)-H(5SA)	109.5
C(6S)-C(5S)-H(5SB)	109.5
H(5SA)-C(5S)-H(5SB)	109.5
C(6S)-C(5S)-H(5SC)	109.5
H(5SA)-C(5S)-H(5SC)	109.5
H(5SB)-C(5S)-H(5SC)	109.5
N(2S)-C(6S)-C(5S)	113.9(3)
N(2S)-C(6S)-H(6SA)	108.8
C(5S)-C(6S)-H(6SA)	108.8
N(2S)-C(6S)-H(6SB)	108.8
C(5S)-C(6S)-H(6SB)	108.8
H(6SA)-C(6S)-H(6SB)	107.7
N(2S)-C(7S)-C(8S)	115.1(3)
N(2S)-C(7S)-H(7SA)	108.5
C(8S)-C(7S)-H(7SA)	108.5
N(2S)-C(7S)-H(7SB)	108.5
C(8S)-C(7S)-H(7SB)	108.5

H(7SA)-C(7S)-H(7SB)	107.5
C(7S)-C(8S)-H(8SA)	109.5
C(7S)-C(8S)-H(8SB)	109.5
H(8SA)-C(8S)-H(8SB)	109.5
C(7S)-C(8S)-H(8SC)	109.5
H(8SA)-C(8S)-H(8SC)	109.5
H(8SB)-C(8S)-H(8SC)	109.5
N(2)#1-Co(1)-N(2)	141.63(13)
N(2)#1-Co(1)-N(1)	120.01(7)
N(2)-Co(1)-N(1)	86.08(7)
N(2)#1-Co(1)-N(1)#2	86.08(7)
N(2)-Co(1)-N(1)#2	120.02(7)
N(1)-Co(1)-N(1)#2	97.84(11)
N(2)#1-Co(1)-Co(1)#3	109.18(7)
N(2)-Co(1)-Co(1)#3	109.18(7)
N(1)-Co(1)-Co(1)#3	48.92(5)
N(1)#2-Co(1)-Co(1)#3	48.92(5)
N(1B)#4-Co(1B)-N(1B)	143.85(14)
N(1B)#4-Co(1B)-N(2B)#4	85.36(7)
N(1B)-Co(1B)-N(2B)#4	119.08(7)
N(1B)#4-Co(1B)-N(2B)	119.08(7)
N(1B)-Co(1B)-N(2B)	85.35(7)
N(2B)#4-Co(1B)-N(2B)	98.52(10)
N(1B)#4-Co(1B)-Co(1B)#5	108.08(7)
N(1B)-Co(1B)-Co(1B)#5	108.07(7)
N(2B)#4-Co(1B)-Co(1B)#5	49.26(5)
N(2B)-Co(1B)-Co(1B)#5	49.26(5)
C(1)#3-N(1)-C(1)	113.3(3)
C(1)#3-N(1)-Co(1)#3	107.94(11)
C(1)-N(1)-Co(1)#3	121.40(11)
C(1)#3-N(1)-Co(1)	121.40(11)
C(1)-N(1)-Co(1)	107.95(11)
Co(1)#3-N(1)-Co(1)	82.16(11)
C(7)-N(2)-C(6)	121.3(2)
C(7)-N(2)-Co(1)	126.09(19)
C(6)-N(2)-Co(1)	111.79(16)

C(7B)-N(1B)-C(1B)	123.6(2)
C(7B)-N(1B)-Co(1B)	124.99(19)
C(1B)-N(1B)-Co(1B)	110.92(17)
C(6B)-N(2B)-C(6B)#5	116.2(3)
C(6B)-N(2B)-Co(1B)#5	119.98(11)
C(6B)#5-N(2B)-Co(1B)#5	107.50(11)
C(6B)-N(2B)-Co(1B)	107.50(11)
C(6B)#5-N(2B)-Co(1B)	119.97(11)
Co(1B)#5-N(2B)-Co(1B)	81.48(10)
C(1S)#6-N(1S)-C(1S)	104.5(3)
C(1S)#6-N(1S)-C(3S)	111.53(18)
C(1S)-N(1S)-C(3S)	112.17(18)
C(1S)#6-N(1S)-C(3S)#6	112.17(18)
C(1S)-N(1S)-C(3S)#6	111.54(18)
C(3S)-N(1S)-C(3S)#6	105.2(3)
C(7S)#5-N(2S)-C(7S)	111.5(4)
C(7S)#5-N(2S)-C(6S)#5	109.0(2)
C(7S)-N(2S)-C(6S)#5	108.0(2)
C(7S)#5-N(2S)-C(6S)	108.0(2)
C(7S)-N(2S)-C(6S)	109.0(2)
C(6S)#5-N(2S)-C(6S)	111.5(4)

Symmetry transformations used to generate equivalent atoms:

#1 -y+1,-x+1,-z+2 #2 y+0,x+0,-z+2 #3 -x+1,-y+1,z+0

#4 y-1/2,x+1/2,-z+1/2 #5 -x+0,-y+1,z+0 #6 y+0,x+0,-z+0

Table 4. Anisotropic displacement parameters (Å^2x 10^3) for PSM_1_20N. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	17(1)	17(1)	19(1)	3(1)	-1(1)	-4(1)
C(2)	30(1)	25(1)	18(1)	2(1)	3(1)	-5(1)
C(3)	36(2)	35(2)	21(1)	5(1)	8(1)	-8(1)
C(4)	40(2)	32(2)	34(2)	16(1)	7(1)	-12(1)
C(5)	36(2)	23(1)	29(1)	3(1)	2(1)	-10(1)
C(6)	22(1)	16(1)	17(1)	4(1)	-2(1)	-5(1)
C(7)	28(1)	14(1)	29(1)	-1(1)	3(1)	-1(1)
C(8)	37(2)	18(1)	33(2)	-4(1)	12(1)	0(1)
C(9)	62(2)	43(2)	31(2)	-7(2)	-1(2)	-7(2)
C(10)	39(2)	36(2)	66(3)	-3(2)	10(2)	6(2)
C(1B)	21(1)	24(1)	21(1)	3(1)	1(1)	4(1)
C(2B)	20(1)	46(2)	27(1)	-7(1)	5(1)	11(1)
C(3B)	31(2)	52(2)	22(1)	-11(1)	5(1)	16(1)
C(4B)	36(2)	34(2)	18(1)	-10(1)	1(1)	9(1)
C(5B)	23(1)	30(1)	21(1)	-5(1)	-2(1)	3(1)
C(6B)	22(1)	22(1)	13(1)	1(1)	1(1)	5(1)
C(7B)	20(1)	23(1)	31(2)	3(1)	1(1)	3(1)
C(8B)	19(1)	35(2)	37(2)	-8(1)	-9(1)	4(1)
C(9B)	50(2)	26(2)	68(3)	0(2)	-21(2)	-6(2)
C(10B)	32(2)	53(2)	38(2)	1(2)	-6(1)	2(2)
C(1S)	28(1)	35(2)	29(1)	0(1)	2(1)	2(1)
C(2S)	44(2)	44(2)	34(2)	-11(1)	5(1)	9(2)
C(3S)	21(1)	31(2)	41(2)	3(1)	-8(1)	0(1)
C(4S)	32(2)	38(2)	43(2)	3(2)	-14(1)	5(1)
C(5S)	58(2)	40(2)	41(2)	7(2)	-16(2)	-1(2)
C(6S)	43(2)	30(2)	40(2)	5(1)	-7(1)	-4(1)
C(7S)	32(2)	34(2)	44(2)	4(1)	-4(1)	7(1)
C(8S)	44(2)	47(2)	37(2)	-1(2)	-10(2)	0(2)
Co(1)	15(1)	15(1)	17(1)	1(1)	1(1)	-4(1)
Co(1B)	15(1)	15(1)	16(1)	0(1)	0(1)	3(1)
N(1)	24(2)	14(1)	17(1)	0	0	-9(1)

N(2)	22(1)	14(1)	24(1)	0(1)	4(1)	-4(1)
N(1B)	17(1)	23(1)	21(1)	1(1)	2(1)	3(1)
N(2B)	15(1)	16(1)	12(1)	0	0	1(1)
N(1S)	20(1)	20(1)	23(1)	0(1)	0(1)	3(1)
N(2S)	24(2)	20(2)	28(1)	0	0	0(1)
O(1)	46(1)	19(1)	53(2)	-6(1)	14(1)	-13(1)
O(1B)	17(1)	44(1)	39(1)	-5(1)	-1(1)	6(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for PSM_1_20N.

	x	y	z	U(eq)
H(2A)	5788	4859	8972	29
H(3A)	6391	5720	8623	37
H(4A)	6220	6929	8769	42
H(5A)	5606	7256	9295	35
H(8A)	4227	6633	10370	35
H(9A)	5218	7152	10679	68
H(9B)	4492	7485	10834	68
H(9C)	4969	7926	10545	68
H(10A)	3507	7335	9980	71
H(10B)	3936	8036	10097	71
H(10C)	3453	7631	10398	71
H(2BA)	2247	4342	1819	37
H(3BA)	1892	3652	1297	42
H(4BA)	704	3615	1121	35
H(5BA)	-153	4211	1471	29
H(8BA)	1594	5736	2879	37
H(9BA)	2591	6545	2920	72
H(9BB)	2314	6497	2498	72
H(9BC)	3016	6075	2621	72
H(10A)	2467	5506	3347	61
H(10B)	2916	5036	3058	61
H(10C)	2152	4767	3198	61
H(1SA)	6871	6856	368	36
H(1SB)	6402	7432	152	36
H(2SA)	6468	7790	772	61
H(2SB)	6933	8345	536	61
H(2SC)	7318	7730	771	61
H(3SA)	8558	7434	-16	37
H(3SB)	8257	7853	339	37
H(4SA)	8765	6809	553	57

H(4SB)	8312	6343	264	57
H(4SC)	7923	6729	606	57
H(5SA)	-424	6190	9463	69
H(5SB)	-972	5778	9729	69
H(5SC)	-500	5343	9435	69
H(6SA)	546	5649	9772	45
H(6SB)	76	6087	10065	45
H(7SA)	1079	4876	10209	44
H(7SB)	623	4461	10516	44
H(8SA)	1231	5418	10797	63
H(8SB)	392	5552	10828	63
H(8SC)	849	5968	10521	63

Table 6. Torsion angles [°] for PSM_1_20N.

N(1)-C(1)-C(2)-C(3)	-179.6(3)
C(6)-C(1)-C(2)-C(3)	-1.1(4)
C(1)-C(2)-C(3)-C(4)	-2.9(5)
C(2)-C(3)-C(4)-C(5)	4.7(5)
C(3)-C(4)-C(5)-C(6)	-2.3(5)
C(4)-C(5)-C(6)-N(2)	-179.6(3)
C(4)-C(5)-C(6)-C(1)	-1.7(4)
C(2)-C(1)-C(6)-C(5)	3.4(4)
N(1)-C(1)-C(6)-C(5)	-178.1(2)
C(2)-C(1)-C(6)-N(2)	-178.4(2)
N(1)-C(1)-C(6)-N(2)	0.1(3)
O(1)-C(7)-C(8)-C(10)	71.3(4)
N(2)-C(7)-C(8)-C(10)	-106.4(3)
O(1)-C(7)-C(8)-C(9)	-50.4(4)
N(2)-C(7)-C(8)-C(9)	131.9(3)
C(6B)-C(1B)-C(2B)-C(3B)	-2.8(5)
N(1B)-C(1B)-C(2B)-C(3B)	179.6(3)
C(1B)-C(2B)-C(3B)-C(4B)	2.3(5)
C(2B)-C(3B)-C(4B)-C(5B)	-1.2(5)
C(3B)-C(4B)-C(5B)-C(6B)	0.6(5)
N(1B)-C(1B)-C(6B)-C(5B)	-180.0(2)
C(2B)-C(1B)-C(6B)-C(5B)	2.3(4)
N(1B)-C(1B)-C(6B)-N(2B)	-0.9(4)
C(2B)-C(1B)-C(6B)-N(2B)	-178.7(2)
C(4B)-C(5B)-C(6B)-C(1B)	-1.2(4)
C(4B)-C(5B)-C(6B)-N(2B)	179.8(3)
O(1B)-C(7B)-C(8B)-C(10B)	-50.2(4)
N(1B)-C(7B)-C(8B)-C(10B)	131.0(3)
O(1B)-C(7B)-C(8B)-C(9B)	68.8(4)
N(1B)-C(7B)-C(8B)-C(9B)	-110.0(3)
C(2)-C(1)-N(1)-C(1)#3	-43.6(2)
C(6)-C(1)-N(1)-C(1)#3	137.9(2)
C(2)-C(1)-N(1)-Co(1)#3	87.4(3)
C(6)-C(1)-N(1)-Co(1)#3	-91.1(2)

C(2)-C(1)-N(1)-Co(1)	179.1(2)
C(6)-C(1)-N(1)-Co(1)	0.6(2)
N(2)#1-Co(1)-N(1)-C(1)#3	16.3(2)
N(2)-Co(1)-N(1)-C(1)#3	-133.94(18)
N(1)#2-Co(1)-N(1)-C(1)#3	106.28(16)
Co(1)#3-Co(1)-N(1)-C(1)#3	106.28(16)
N(2)#1-Co(1)-N(1)-C(1)	149.46(14)
N(2)-Co(1)-N(1)-C(1)	-0.76(15)
N(1)#2-Co(1)-N(1)-C(1)	-120.54(13)
Co(1)#3-Co(1)-N(1)-C(1)	-120.54(13)
N(2)#1-Co(1)-N(1)-Co(1)#3	-89.99(8)
N(2)-Co(1)-N(1)-Co(1)#3	119.78(7)
N(1)#2-Co(1)-N(1)-Co(1)#3	0.0
O(1)-C(7)-N(2)-C(6)	-1.3(5)
C(8)-C(7)-N(2)-C(6)	176.1(2)
O(1)-C(7)-N(2)-Co(1)	167.3(3)
C(8)-C(7)-N(2)-Co(1)	-15.3(4)
C(5)-C(6)-N(2)-C(7)	-12.7(4)
C(1)-C(6)-N(2)-C(7)	169.4(2)
C(5)-C(6)-N(2)-Co(1)	177.2(2)
C(1)-C(6)-N(2)-Co(1)	-0.7(3)
N(2)#1-Co(1)-N(2)-C(7)	55.1(2)
N(1)-Co(1)-N(2)-C(7)	-168.7(2)
N(1)#2-Co(1)-N(2)-C(7)	-71.9(3)
Co(1)#3-Co(1)-N(2)-C(7)	-124.9(2)
N(2)#1-Co(1)-N(2)-C(6)	-135.32(18)
N(1)-Co(1)-N(2)-C(6)	0.84(17)
N(1)#2-Co(1)-N(2)-C(6)	97.63(18)
Co(1)#3-Co(1)-N(2)-C(6)	44.68(18)
O(1B)-C(7B)-N(1B)-C(1B)	2.0(5)
C(8B)-C(7B)-N(1B)-C(1B)	-179.3(3)
O(1B)-C(7B)-N(1B)-Co(1B)	173.2(2)
C(8B)-C(7B)-N(1B)-Co(1B)	-8.1(4)
C(6B)-C(1B)-N(1B)-C(7B)	173.1(3)
C(2B)-C(1B)-N(1B)-C(7B)	-9.3(4)
C(6B)-C(1B)-N(1B)-Co(1B)	0.8(3)

C(2B)-C(1B)-N(1B)-Co(1B)	178.4(2)
N(1B)#4-Co(1B)-N(1B)-C(7B)	51.8(2)
N(2B)#4-Co(1B)-N(1B)-C(7B)	-75.3(2)
N(2B)-Co(1B)-N(1B)-C(7B)	-172.5(2)
Co(1B)#5-Co(1B)-N(1B)-C(7B)	-128.2(2)
N(1B)#4-Co(1B)-N(1B)-C(1B)	-136.01(18)
N(2B)#4-Co(1B)-N(1B)-C(1B)	96.82(18)
N(2B)-Co(1B)-N(1B)-C(1B)	-0.35(17)
Co(1B)#5-Co(1B)-N(1B)-C(1B)	43.99(18)
C(1B)-C(6B)-N(2B)-C(6B)#5	138.3(3)
C(5B)-C(6B)-N(2B)-C(6B)#5	-42.7(2)
C(1B)-C(6B)-N(2B)-Co(1B)#5	-89.6(2)
C(5B)-C(6B)-N(2B)-Co(1B)#5	89.5(3)
C(1B)-C(6B)-N(2B)-Co(1B)	0.6(3)
C(5B)-C(6B)-N(2B)-Co(1B)	179.6(2)
N(1B)#4-Co(1B)-N(2B)-C(6B)	151.75(14)
N(1B)-Co(1B)-N(2B)-C(6B)	-0.11(14)
N(2B)#4-Co(1B)-N(2B)-C(6B)	-118.85(13)
Co(1B)#5-Co(1B)-N(2B)-C(6B)	-118.85(13)
N(1B)#4-Co(1B)-N(2B)-C(6B)#5	15.94(19)
N(1B)-Co(1B)-N(2B)-C(6B)#5	-135.91(17)
N(2B)#4-Co(1B)-N(2B)-C(6B)#5	105.34(16)
Co(1B)#5-Co(1B)-N(2B)-C(6B)#5	105.34(16)
N(1B)#4-Co(1B)-N(2B)-Co(1B)#5	-89.40(8)
N(1B)-Co(1B)-N(2B)-Co(1B)#5	118.74(7)
N(2B)#4-Co(1B)-N(2B)-Co(1B)#5	0.0
C(2S)-C(1S)-N(1S)-C(1S)#6	173.5(3)
C(2S)-C(1S)-N(1S)-C(3S)	52.6(3)
C(2S)-C(1S)-N(1S)-C(3S)#6	-65.1(3)
C(4S)-C(3S)-N(1S)-C(1S)#6	-65.2(3)
C(4S)-C(3S)-N(1S)-C(1S)	51.6(3)
C(4S)-C(3S)-N(1S)-C(3S)#6	173.0(3)
C(8S)-C(7S)-N(2S)-C(7S)#5	-56.4(3)
C(8S)-C(7S)-N(2S)-C(6S)#5	-176.1(3)
C(8S)-C(7S)-N(2S)-C(6S)	62.6(4)
C(5S)-C(6S)-N(2S)-C(7S)#5	-67.2(4)

C(5S)-C(6S)-N(2S)-C(7S)	171.6(3)
C(5S)-C(6S)-N(2S)-C(6S)#5	52.5(3)

Symmetry transformations used to generate equivalent atoms:

#1 -y+1,-x+1,-z+2 #2 y+0,x+0,-z+2 #3 -x+1,-y+1,z+0

#4 y-1/2,x+1/2,-z+1/2 #5 -x+0,-y+1,z+0 #6 y+0,x+0,-z+0

Appendix B. Crystal Data for $(Et_4N)_2[Co(HL^{iPr})_2]$

Table 1. Crystal data and structure refinement for PSM16B.

Identification code	PSM16B	
Empirical formula	C56 H86 Co N8 O4	
Formula weight	994.26	
Temperature	172(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pca2(1)	
Unit cell dimensions	a = 17.364(4) Å	α= 90°.
	b = 16.539(4) Å	β= 90°.
	c = 19.385(5) Å	γ = 90°.
Volume	5567(2) Å^3	
Z	4	
Density (calculated)	1.186 Mg/m^3	
Absorption coefficient	0.359 mm^{-1}	
F(000)	2148	
Crystal size	0.17 x 0.11 x 0.07 mm^3	
Theta range for data collection	1.70 to 30.63°.	
Index ranges	-24<=h<=23, -23<=k<=23, -26<=l<=26	
Reflections collected	97086	
Independent reflections	16016 [R(int) = 0.1821]	
Completeness to theta = 30.63°	95.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9753 and 0.9415	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	16016 / 1 / 622	
Goodness-of-fit on F^2	1.006	
Final R indices [I>2sigma(I)]	R1 = 0.0662, wR2 = 0.1229	
R indices (all data)	R1 = 0.1796, wR2 = 0.1544	
Absolute structure parameter	-0.012(15)	
Largest diff. peak and hole	0.826 and -0.553 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for PSM16B. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	-355(2)	9001(2)	4401(2)	34(1)
C(2)	-469(3)	9789(3)	4613(3)	45(1)
C(3)	-1003(3)	10298(3)	4295(3)	52(1)
C(4)	-1432(3)	10002(3)	3737(3)	56(1)
C(5)	-1323(2)	9228(3)	3509(2)	42(1)
C(6)	-793(2)	8686(3)	3829(2)	34(1)
C(7)	-1090(2)	7582(2)	3064(2)	32(1)
C(8)	-745(3)	7349(3)	2437(2)	39(1)
C(9)	-1158(3)	7037(3)	1889(2)	50(1)
C(10)	-1948(3)	6932(3)	1952(3)	59(2)
C(11)	-2315(3)	7129(3)	2569(3)	48(1)
C(12)	-1893(2)	7450(3)	3114(2)	40(1)
C(13)	-2968(3)	7976(3)	3851(3)	46(1)
C(14)	-3196(3)	8139(3)	4593(3)	57(1)
C(15)	-4068(3)	8216(4)	4673(3)	88(2)
C(16)	-2785(4)	8854(5)	4880(3)	120(3)
C(17)	639(2)	8621(3)	5221(2)	40(1)
C(18)	1383(2)	8123(3)	5317(2)	40(1)
C(19)	1262(3)	7470(3)	5878(3)	58(2)
C(20)	2048(3)	8681(3)	5489(3)	58(1)
C(21)	618(2)	5763(2)	4594(2)	28(1)
C(22)	615(2)	4977(3)	4852(2)	38(1)
C(23)	1156(2)	4415(3)	4637(3)	45(1)
C(24)	1720(2)	4623(2)	4169(3)	41(1)
C(25)	1738(2)	5405(3)	3893(2)	36(1)
C(26)	1197(2)	5992(2)	4096(2)	25(1)
C(27)	1735(2)	7066(2)	3385(2)	31(1)
C(28)	1548(3)	7251(3)	2694(2)	39(1)
C(29)	2060(3)	7622(3)	2256(2)	40(1)
C(30)	2788(3)	7843(3)	2500(2)	48(1)
C(31)	3004(2)	7648(3)	3171(2)	41(1)

C(32)	2488(2)	7253(2)	3609(2)	33(1)
C(33)	3405(2)	7004(3)	4603(2)	41(1)
C(34)	3415(2)	6684(3)	5344(2)	44(1)
C(35)	4168(3)	6925(4)	5700(3)	63(2)
C(36)	3308(3)	5765(3)	5361(3)	66(2)
C(37)	-375(2)	6357(2)	5320(2)	30(1)
C(38)	-1050(2)	6950(2)	5352(2)	34(1)
C(39)	-1021(3)	7467(3)	6015(3)	53(1)
C(40)	-1799(2)	6461(3)	5332(2)	43(1)
Co(1)	209(1)	7377(1)	4141(1)	28(1)
N(1)	237(2)	8458(2)	4636(2)	33(1)
N(2)	-640(2)	7902(2)	3609(2)	32(1)
N(3)	-2264(2)	7627(2)	3761(2)	43(1)
N(4)	58(2)	6372(2)	4731(2)	26(1)
N(5)	1152(2)	6782(2)	3842(2)	29(1)
N(6)	2689(2)	7030(2)	4298(2)	39(1)
O(1)	485(2)	9124(2)	5663(2)	64(1)
O(2)	-3390(2)	8154(2)	3364(2)	59(1)
O(3)	-285(2)	5884(2)	5819(2)	44(1)
O(4)	3994(2)	7192(2)	4298(2)	63(1)
N(1C)	794(2)	9996(2)	2332(2)	45(1)
C(1C)	988(4)	9995(4)	3080(3)	85(2)
C(2C)	1383(3)	9308(3)	3413(3)	65(2)
C(3C)	453(4)	10796(4)	2110(3)	86(2)
C(4C)	-279(3)	11060(4)	2453(3)	83(2)
C(5C)	1506(4)	9827(4)	1894(3)	81(2)
C(6C)	2175(3)	10374(4)	2005(3)	92(2)
C(7C)	225(4)	9290(3)	2207(3)	81(2)
C(8C)	-96(4)	9218(4)	1510(3)	107(3)
N(2C)	9550(2)	4525(2)	2639(2)	35(1)
C(9C)	9059(3)	4516(3)	3288(2)	45(1)
C(10C)	8751(2)	5348(3)	3508(3)	50(1)
C(11C)	9097(3)	4862(3)	2017(2)	48(1)
C(12C)	8308(3)	4511(4)	1899(3)	71(2)
C(13C)	9790(2)	3656(3)	2473(2)	45(1)
C(14C)	10310(3)	3248(3)	3000(3)	59(1)

C(15C)	10866(3)	5042(3)	2217(3)	56(1)
C(16C)	10261(2)	5063(3)	2776(2)	42(1)

Table 3. Bond lengths [Å] and angles [°] for PSM16B.

C(1)-C(2)	1.380(6)
C(1)-N(1)	1.440(5)
C(1)-C(6)	1.441(5)
C(2)-C(3)	1.397(6)
C(2)-H(2A)	0.9500
C(3)-C(4)	1.402(7)
C(3)-H(3A)	0.9500
C(4)-C(5)	1.367(6)
C(4)-H(4A)	0.9500
C(5)-C(6)	1.428(6)
C(5)-H(5A)	0.9500
C(6)-N(2)	1.389(5)
C(7)-C(8)	1.408(6)
C(7)-C(12)	1.416(6)
C(7)-N(2)	1.418(5)
C(8)-C(9)	1.383(6)
C(8)-H(8A)	0.9500
C(9)-C(10)	1.387(6)
C(9)-H(9A)	0.9500
C(10)-C(11)	1.395(7)
C(10)-H(10A)	0.9500
C(11)-C(12)	1.390(6)
C(11)-H(11A)	0.9500
C(12)-N(3)	1.440(6)
C(13)-O(2)	1.229(5)
C(13)-N(3)	1.364(6)
C(13)-C(14)	1.517(7)
C(14)-C(16)	1.489(8)
C(14)-C(15)	1.527(7)
C(14)-H(14A)	1.0000
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800

C(16)-H(PSM16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-O(1)	1.224(5)
C(17)-N(1)	1.359(5)
C(17)-C(18)	1.543(6)
C(18)-C(20)	1.516(6)
C(18)-C(19)	1.547(7)
C(18)-H(18A)	1.0000
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-C(22)	1.393(6)
C(21)-N(4)	1.426(5)
C(21)-C(26)	1.443(5)
C(22)-C(23)	1.385(6)
C(22)-H(22A)	0.9500
C(23)-C(24)	1.379(6)
C(23)-H(23A)	0.9500
C(24)-C(25)	1.400(5)
C(24)-H(24A)	0.9500
C(25)-C(26)	1.409(5)
C(25)-H(25A)	0.9500
C(26)-N(5)	1.399(4)
C(27)-C(32)	1.411(5)
C(27)-C(28)	1.412(6)
C(27)-N(5)	1.424(5)
C(28)-C(29)	1.374(6)
C(28)-H(28A)	0.9500
C(29)-C(30)	1.399(6)
C(29)-H(29A)	0.9500
C(30)-C(31)	1.391(6)
C(30)-H(30A)	0.9500
C(31)-C(32)	1.396(6)

C(31)-H(31A)	0.9500
C(32)-N(6)	1.431(5)
C(33)-O(4)	1.220(5)
C(33)-N(6)	1.377(5)
C(33)-C(34)	1.530(6)
C(34)-C(35)	1.530(6)
C(34)-C(36)	1.533(7)
C(34)-H(34A)	1.0000
C(35)-H(35A)	0.9800
C(35)-H(35B)	0.9800
C(35)-H(35C)	0.9800
C(36)-H(36A)	0.9800
C(36)-H(36B)	0.9800
C(36)-H(36C)	0.9800
C(37)-O(3)	1.253(4)
C(37)-N(4)	1.367(5)
C(37)-C(38)	1.529(5)
C(38)-C(40)	1.532(5)
C(38)-C(39)	1.546(6)
C(38)-H(38A)	1.0000
C(39)-H(39A)	0.9800
C(39)-H(39B)	0.9800
C(39)-H(39C)	0.9800
C(40)-H(40A)	0.9800
C(40)-H(40B)	0.9800
C(40)-H(40C)	0.9800
Co(1)-N(5)	1.996(3)
Co(1)-N(2)	1.996(3)
Co(1)-N(1)	2.029(3)
Co(1)-N(4)	2.035(3)
N(3)-H(3B)	0.8800
N(6)-H(6A)	0.8800
N(1C)-C(1C)	1.489(7)
N(1C)-C(3C)	1.512(6)
N(1C)-C(5C)	1.526(7)
N(1C)-C(7C)	1.549(6)

C(1C)-C(2C)	1.476(7)
C(1C)-H(1C1)	0.9900
C(1C)-H(1C2)	0.9900
C(2C)-H(2CA)	0.9800
C(2C)-H(2CB)	0.9800
C(2C)-H(2CC)	0.9800
C(3C)-C(4C)	1.500(8)
C(3C)-H(3CA)	0.9900
C(3C)-H(3CB)	0.9900
C(4C)-H(4CA)	0.9800
C(4C)-H(4CB)	0.9800
C(4C)-H(4CC)	0.9800
C(5C)-C(6C)	1.488(8)
C(5C)-H(5CA)	0.9900
C(5C)-H(5CB)	0.9900
C(6C)-H(6CA)	0.9800
C(6C)-H(6CB)	0.9800
C(6C)-H(6CC)	0.9800
C(7C)-C(8C)	1.467(8)
C(7C)-H(7CA)	0.9900
C(7C)-H(7CB)	0.9900
C(8C)-H(8CA)	0.9800
C(8C)-H(8CB)	0.9800
C(8C)-H(8CC)	0.9800
N(2C)-C(9C)	1.520(5)
N(2C)-C(13C)	1.530(5)
N(2C)-C(11C)	1.543(5)
N(2C)-C(16C)	1.545(5)
C(9C)-C(10C)	1.535(6)
C(9C)-H(9CA)	0.9900
C(9C)-H(9CB)	0.9900
C(10C)-H(10B)	0.9800
C(10C)-H(10C)	0.9800
C(10C)-H(10D)	0.9800
C(11C)-C(12C)	1.505(6)
C(11C)-H(11B)	0.9900

C(11C)-H(11C)	0.9900
C(12C)-H(12A)	0.9800
C(12C)-H(12B)	0.9800
C(12C)-H(12C)	0.9800
C(13C)-C(14C)	1.522(6)
C(13C)-H(13A)	0.9900
C(13C)-H(13B)	0.9900
C(14C)-H(14B)	0.9800
C(14C)-H(14C)	0.9800
C(14C)-H(14D)	0.9800
C(15C)-C(16C)	1.509(6)
C(15C)-H(15D)	0.9800
C(15C)-H(15E)	0.9800
C(15C)-H(15F)	0.9800
C(16C)-H(16D)	0.9900
C(16C)-H(16E)	0.9900
C(2)-C(1)-N(1)	126.7(4)
C(2)-C(1)-C(6)	119.7(4)
N(1)-C(1)-C(6)	113.2(4)
C(1)-C(2)-C(3)	122.2(4)
C(1)-C(2)-H(2A)	118.9
C(3)-C(2)-H(2A)	118.9
C(2)-C(3)-C(4)	118.9(4)
C(2)-C(3)-H(3A)	120.5
C(4)-C(3)-H(3A)	120.5
C(5)-C(4)-C(3)	120.1(4)
C(5)-C(4)-H(4A)	119.9
C(3)-C(4)-H(4A)	119.9
C(4)-C(5)-C(6)	122.5(4)
C(4)-C(5)-H(5A)	118.7
C(6)-C(5)-H(5A)	118.7
N(2)-C(6)-C(5)	125.2(4)
N(2)-C(6)-C(1)	118.2(4)
C(5)-C(6)-C(1)	116.5(4)
C(8)-C(7)-C(12)	115.8(4)

C(8)-C(7)-N(2)	120.7(4)
C(12)-C(7)-N(2)	123.4(4)
C(9)-C(8)-C(7)	123.0(4)
C(9)-C(8)-H(8A)	118.5
C(7)-C(8)-H(8A)	118.5
C(8)-C(9)-C(10)	119.5(5)
C(8)-C(9)-H(9A)	120.2
C(10)-C(9)-H(9A)	120.2
C(9)-C(10)-C(11)	119.9(4)
C(9)-C(10)-H(10A)	120.1
C(11)-C(10)-H(10A)	120.1
C(12)-C(11)-C(10)	120.0(4)
C(12)-C(11)-H(11A)	120.0
C(10)-C(11)-H(11A)	120.0
C(11)-C(12)-C(7)	121.8(4)
C(11)-C(12)-N(3)	120.2(4)
C(7)-C(12)-N(3)	117.9(4)
O(2)-C(13)-N(3)	122.5(5)
O(2)-C(13)-C(14)	122.0(5)
N(3)-C(13)-C(14)	115.5(4)
C(16)-C(14)-C(13)	111.8(5)
C(16)-C(14)-C(15)	111.9(5)
C(13)-C(14)-C(15)	111.7(5)
C(16)-C(14)-H(14A)	107.1
C(13)-C(14)-H(14A)	107.1
C(15)-C(14)-H(14A)	107.1
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(14)-C(16)-H(16A)	109.5
C(14)-C(16)-H(PSM16B)	109.5
H(16A)-C(16)-H(PSM16B)	109.5
C(14)-C(16)-H(16C)	109.5

H(16A)-C(16)-H(16C)	109.5
H(PSM16B)-C(16)-H(16C)	109.5
O(1)-C(17)-N(1)	127.3(4)
O(1)-C(17)-C(18)	117.5(4)
N(1)-C(17)-C(18)	115.1(4)
C(20)-C(18)-C(17)	109.8(4)
C(20)-C(18)-C(19)	111.9(4)
C(17)-C(18)-C(19)	110.0(4)
C(20)-C(18)-H(18A)	108.3
C(17)-C(18)-H(18A)	108.3
C(19)-C(18)-H(18A)	108.3
C(18)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(18)-C(20)-H(20A)	109.5
C(18)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(18)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(22)-C(21)-N(4)	126.2(4)
C(22)-C(21)-C(26)	119.2(3)
N(4)-C(21)-C(26)	114.4(3)
C(23)-C(22)-C(21)	121.1(4)
C(23)-C(22)-H(22A)	119.5
C(21)-C(22)-H(22A)	119.5
C(24)-C(23)-C(22)	120.8(4)
C(24)-C(23)-H(23A)	119.6
C(22)-C(23)-H(23A)	119.6
C(23)-C(24)-C(25)	119.9(4)
C(23)-C(24)-H(24A)	120.1
C(25)-C(24)-H(24A)	120.1
C(24)-C(25)-C(26)	120.9(4)

C(24)-C(25)-H(25A)	119.5
C(26)-C(25)-H(25A)	119.5
N(5)-C(26)-C(25)	125.6(4)
N(5)-C(26)-C(21)	116.3(3)
C(25)-C(26)-C(21)	118.1(3)
C(32)-C(27)-C(28)	117.2(4)
C(32)-C(27)-N(5)	122.7(4)
C(28)-C(27)-N(5)	119.8(4)
C(29)-C(28)-C(27)	122.3(4)
C(29)-C(28)-H(28A)	118.8
C(27)-C(28)-H(28A)	118.8
C(28)-C(29)-C(30)	119.5(4)
C(28)-C(29)-H(29A)	120.3
C(30)-C(29)-H(29A)	120.3
C(31)-C(30)-C(29)	119.9(4)
C(31)-C(30)-H(30A)	120.0
C(29)-C(30)-H(30A)	120.0
C(30)-C(31)-C(32)	120.2(4)
C(30)-C(31)-H(31A)	119.9
C(32)-C(31)-H(31A)	119.9
C(31)-C(32)-C(27)	120.7(4)
C(31)-C(32)-N(6)	122.1(4)
C(27)-C(32)-N(6)	117.2(4)
O(4)-C(33)-N(6)	122.7(4)
O(4)-C(33)-C(34)	122.2(4)
N(6)-C(33)-C(34)	115.1(4)
C(35)-C(34)-C(33)	110.1(4)
C(35)-C(34)-C(36)	110.6(4)
C(33)-C(34)-C(36)	111.2(4)
C(35)-C(34)-H(34A)	108.3
C(33)-C(34)-H(34A)	108.3
C(36)-C(34)-H(34A)	108.3
C(34)-C(35)-H(35A)	109.5
C(34)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5
C(34)-C(35)-H(35C)	109.5

H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5
C(34)-C(36)-H(36A)	109.5
C(34)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5
C(34)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5
O(3)-C(37)-N(4)	126.0(4)
O(3)-C(37)-C(38)	117.7(4)
N(4)-C(37)-C(38)	116.3(3)
C(37)-C(38)-C(40)	108.1(3)
C(37)-C(38)-C(39)	111.4(4)
C(40)-C(38)-C(39)	109.9(4)
C(37)-C(38)-H(38A)	109.1
C(40)-C(38)-H(38A)	109.1
C(39)-C(38)-H(38A)	109.1
C(38)-C(39)-H(39A)	109.5
C(38)-C(39)-H(39B)	109.5
H(39A)-C(39)-H(39B)	109.5
C(38)-C(39)-H(39C)	109.5
H(39A)-C(39)-H(39C)	109.5
H(39B)-C(39)-H(39C)	109.5
C(38)-C(40)-H(40A)	109.5
C(38)-C(40)-H(40B)	109.5
H(40A)-C(40)-H(40B)	109.5
C(38)-C(40)-H(40C)	109.5
H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5
N(5)-Co(1)-N(2)	132.03(13)
N(5)-Co(1)-N(1)	123.50(13)
N(2)-Co(1)-N(1)	83.05(13)
N(5)-Co(1)-N(4)	82.33(13)
N(2)-Co(1)-N(4)	123.38(13)
N(1)-Co(1)-N(4)	117.14(13)
C(17)-N(1)-C(1)	120.5(3)

C(17)-N(1)-Co(1)	125.6(3)
C(1)-N(1)-Co(1)	112.5(2)
C(6)-N(2)-C(7)	118.2(3)
C(6)-N(2)-Co(1)	112.8(3)
C(7)-N(2)-Co(1)	129.0(3)
C(13)-N(3)-C(12)	126.8(4)
C(13)-N(3)-H(3B)	116.6
C(12)-N(3)-H(3B)	116.6
C(37)-N(4)-C(21)	121.2(3)
C(37)-N(4)-Co(1)	123.8(3)
C(21)-N(4)-Co(1)	112.6(2)
C(26)-N(5)-C(27)	119.2(3)
C(26)-N(5)-Co(1)	113.8(2)
C(27)-N(5)-Co(1)	127.0(3)
C(33)-N(6)-C(32)	129.0(4)
C(33)-N(6)-H(6A)	115.5
C(32)-N(6)-H(6A)	115.5
C(1C)-N(1C)-C(3C)	111.5(4)
C(1C)-N(1C)-C(5C)	110.9(4)
C(3C)-N(1C)-C(5C)	108.6(4)
C(1C)-N(1C)-C(7C)	107.2(4)
C(3C)-N(1C)-C(7C)	111.5(4)
C(5C)-N(1C)-C(7C)	107.0(4)
C(2C)-C(1C)-N(1C)	122.1(5)
C(2C)-C(1C)-H(1C1)	106.8
N(1C)-C(1C)-H(1C1)	106.8
C(2C)-C(1C)-H(1C2)	106.8
N(1C)-C(1C)-H(1C2)	106.8
H(1C1)-C(1C)-H(1C2)	106.7
C(1C)-C(2C)-H(2CA)	109.5
C(1C)-C(2C)-H(2CB)	109.5
H(2CA)-C(2C)-H(2CB)	109.5
C(1C)-C(2C)-H(2CC)	109.5
H(2CA)-C(2C)-H(2CC)	109.5
H(2CB)-C(2C)-H(2CC)	109.5
C(4C)-C(3C)-N(1C)	117.4(5)

C(4C)-C(3C)-H(3CA)	107.9
N(1C)-C(3C)-H(3CA)	107.9
C(4C)-C(3C)-H(3CB)	107.9
N(1C)-C(3C)-H(3CB)	107.9
H(3CA)-C(3C)-H(3CB)	107.2
C(3C)-C(4C)-H(4CA)	109.5
C(3C)-C(4C)-H(4CB)	109.5
H(4CA)-C(4C)-H(4CB)	109.5
C(3C)-C(4C)-H(4CC)	109.5
H(4CA)-C(4C)-H(4CC)	109.5
H(4CB)-C(4C)-H(4CC)	109.5
C(6C)-C(5C)-N(1C)	116.2(5)
C(6C)-C(5C)-H(5CA)	108.2
N(1C)-C(5C)-H(5CA)	108.2
C(6C)-C(5C)-H(5CB)	108.2
N(1C)-C(5C)-H(5CB)	108.2
H(5CA)-C(5C)-H(5CB)	107.4
C(5C)-C(6C)-H(6CA)	109.5
C(5C)-C(6C)-H(6CB)	109.5
H(6CA)-C(6C)-H(6CB)	109.5
C(5C)-C(6C)-H(6CC)	109.5
H(6CA)-C(6C)-H(6CC)	109.5
H(6CB)-C(6C)-H(6CC)	109.5
C(8C)-C(7C)-N(1C)	116.6(5)
C(8C)-C(7C)-H(7CA)	108.1
N(1C)-C(7C)-H(7CA)	108.1
C(8C)-C(7C)-H(7CB)	108.1
N(1C)-C(7C)-H(7CB)	108.1
H(7CA)-C(7C)-H(7CB)	107.3
C(7C)-C(8C)-H(8CA)	109.5
C(7C)-C(8C)-H(8CB)	109.5
H(8CA)-C(8C)-H(8CB)	109.5
C(7C)-C(8C)-H(8CC)	109.5
H(8CA)-C(8C)-H(8CC)	109.5
H(8CB)-C(8C)-H(8CC)	109.5
C(9C)-N(2C)-C(13C)	108.5(3)

C(9C)-N(2C)-C(11C)	111.3(3)
C(13C)-N(2C)-C(11C)	108.3(3)
C(9C)-N(2C)-C(16C)	108.2(3)
C(13C)-N(2C)-C(16C)	111.0(3)
C(11C)-N(2C)-C(16C)	109.5(3)
N(2C)-C(9C)-C(10C)	114.6(4)
N(2C)-C(9C)-H(9CA)	108.6
C(10C)-C(9C)-H(9CA)	108.6
N(2C)-C(9C)-H(9CB)	108.6
C(10C)-C(9C)-H(9CB)	108.6
H(9CA)-C(9C)-H(9CB)	107.6
C(9C)-C(10C)-H(10B)	109.5
C(9C)-C(10C)-H(10C)	109.5
H(10B)-C(10C)-H(10C)	109.5
C(9C)-C(10C)-H(10D)	109.5
H(10B)-C(10C)-H(10D)	109.5
H(10C)-C(10C)-H(10D)	109.5
C(12C)-C(11C)-N(2C)	116.4(4)
C(12C)-C(11C)-H(11B)	108.2
N(2C)-C(11C)-H(11B)	108.2
C(12C)-C(11C)-H(11C)	108.2
N(2C)-C(11C)-H(11C)	108.2
H(11B)-C(11C)-H(11C)	107.3
C(11C)-C(12C)-H(12A)	109.5
C(11C)-C(12C)-H(12B)	109.5
H(12A)-C(12C)-H(12B)	109.5
C(11C)-C(12C)-H(12C)	109.5
H(12A)-C(12C)-H(12C)	109.5
H(12B)-C(12C)-H(12C)	109.5
C(14C)-C(13C)-N(2C)	115.9(4)
C(14C)-C(13C)-H(13A)	108.3
N(2C)-C(13C)-H(13A)	108.3
C(14C)-C(13C)-H(13B)	108.3
N(2C)-C(13C)-H(13B)	108.3
H(13A)-C(13C)-H(13B)	107.4
C(13C)-C(14C)-H(14B)	109.5

C(13C)-C(14C)-H(14C)	109.5
H(14B)-C(14C)-H(14C)	109.5
C(13C)-C(14C)-H(14D)	109.5
H(14B)-C(14C)-H(14D)	109.5
H(14C)-C(14C)-H(14D)	109.5
C(16C)-C(15C)-H(15D)	109.5
C(16C)-C(15C)-H(15E)	109.5
H(15D)-C(15C)-H(15E)	109.5
C(16C)-C(15C)-H(15F)	109.5
H(15D)-C(15C)-H(15F)	109.5
H(15E)-C(15C)-H(15F)	109.5
C(15C)-C(16C)-N(2C)	114.9(3)
C(15C)-C(16C)-H(16D)	108.5
N(2C)-C(16C)-H(16D)	108.5
C(15C)-C(16C)-H(16E)	108.5
N(2C)-C(16C)-H(16E)	108.5
H(16D)-C(16C)-H(16E)	107.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$) for PSM16B. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	30(2)	29(2)	43(3)	3(2)	3(2)	-1(2)
C(2)	49(3)	32(3)	53(3)	-9(2)	5(2)	1(2)
C(3)	53(3)	34(3)	68(4)	-7(2)	-6(3)	16(2)
C(4)	42(3)	45(3)	81(4)	13(3)	-2(3)	8(2)
C(5)	35(3)	41(3)	50(3)	2(2)	-8(2)	4(2)
C(6)	29(2)	32(3)	42(3)	7(2)	1(2)	3(2)
C(7)	32(2)	29(2)	36(3)	2(2)	-5(2)	-1(2)
C(8)	36(3)	33(3)	47(3)	2(2)	-3(2)	4(2)
C(9)	54(3)	53(3)	43(3)	-10(2)	-6(3)	4(3)
C(10)	56(4)	67(4)	53(4)	-5(3)	-31(3)	7(3)
C(11)	33(3)	54(3)	58(4)	0(3)	-8(3)	0(2)
C(12)	32(2)	43(3)	44(3)	5(2)	-11(2)	2(2)
C(13)	34(3)	41(3)	63(3)	12(2)	-1(2)	-6(2)
C(14)	48(3)	61(4)	60(4)	8(3)	6(3)	6(3)
C(15)	58(4)	109(6)	96(5)	-13(4)	23(4)	10(3)
C(16)	125(6)	161(8)	73(5)	-51(5)	28(4)	-70(6)
C(17)	43(3)	35(3)	42(3)	-5(2)	-3(2)	-4(2)
C(18)	39(3)	44(3)	37(3)	-6(2)	-8(2)	-2(2)
C(19)	51(3)	57(4)	66(4)	11(3)	-17(3)	-6(3)
C(20)	50(3)	52(3)	70(4)	11(3)	-9(3)	-11(2)
C(21)	26(2)	26(2)	32(2)	-3(2)	-4(2)	-1(2)
C(22)	39(3)	38(3)	38(3)	5(2)	2(2)	-4(2)
C(23)	44(3)	31(3)	60(3)	13(2)	1(3)	4(2)
C(24)	25(2)	34(2)	64(3)	-8(3)	-1(3)	10(2)
C(25)	22(2)	36(3)	51(3)	0(2)	3(2)	-2(2)
C(26)	25(2)	27(2)	23(2)	0(2)	-6(2)	-2(1)
C(27)	31(2)	31(2)	33(3)	-4(2)	3(2)	-1(2)
C(28)	41(3)	40(3)	37(3)	-2(2)	3(2)	0(2)
C(29)	46(3)	43(3)	32(3)	8(2)	9(2)	9(2)
C(30)	49(3)	51(3)	43(3)	5(2)	20(2)	-7(2)
C(31)	28(2)	50(3)	46(3)	1(2)	4(2)	-1(2)

C(32)	26(2)	36(3)	36(3)	-5(2)	4(2)	2(2)
C(33)	27(2)	47(3)	48(3)	-7(2)	1(2)	-1(2)
C(34)	33(3)	58(3)	41(3)	-7(2)	-4(2)	3(2)
C(35)	45(3)	86(4)	58(4)	-11(3)	-15(3)	-3(3)
C(36)	71(4)	66(4)	60(4)	7(3)	-19(3)	-8(3)
C(37)	29(2)	32(2)	30(2)	3(2)	2(2)	-8(2)
C(38)	33(2)	35(3)	34(2)	7(2)	8(2)	-2(2)
C(39)	43(3)	59(4)	58(4)	-18(3)	-3(3)	-3(2)
C(40)	34(2)	49(3)	45(3)	-8(2)	5(2)	-2(2)
Co(1)	25(1)	30(1)	30(1)	2(1)	-1(1)	0(1)
N(1)	30(2)	29(2)	39(2)	0(2)	-5(2)	0(2)
N(2)	34(2)	27(2)	34(2)	2(2)	-4(2)	1(2)
N(3)	32(2)	51(3)	46(2)	6(2)	1(2)	2(2)
N(4)	27(2)	26(2)	27(2)	0(1)	1(2)	-2(1)
N(5)	28(2)	28(2)	31(2)	1(1)	1(1)	0(1)
N(6)	26(2)	49(2)	41(3)	5(2)	1(2)	-3(2)
O(1)	76(3)	63(2)	52(2)	-24(2)	-13(2)	16(2)
O(2)	36(2)	65(2)	76(3)	1(2)	-13(2)	7(2)
O(3)	45(2)	49(2)	39(2)	13(2)	5(2)	3(2)
O(4)	27(2)	101(3)	60(3)	9(2)	1(2)	-5(2)
N(1C)	47(2)	36(2)	51(3)	7(2)	-2(2)	1(2)
C(1C)	106(5)	77(5)	71(4)	10(3)	-13(4)	-14(4)
C(2C)	58(3)	73(4)	64(4)	21(3)	0(3)	5(3)
C(3C)	106(5)	53(4)	99(5)	14(4)	-23(4)	-7(4)
C(4C)	69(4)	72(4)	109(5)	15(4)	17(4)	19(3)
C(5C)	95(5)	68(4)	81(5)	12(3)	6(4)	-2(4)
C(6C)	80(4)	94(5)	101(6)	24(4)	14(4)	-12(4)
C(7C)	89(4)	55(4)	98(5)	-4(4)	-21(4)	-25(3)
C(8C)	160(7)	68(5)	94(5)	34(4)	-75(5)	-44(4)
N(2C)	36(2)	33(2)	35(2)	-3(2)	-1(2)	-5(2)
C(9C)	40(3)	55(3)	42(3)	-3(2)	13(2)	-9(2)
C(10C)	45(3)	52(3)	51(3)	-13(2)	7(2)	5(2)
C(11C)	48(3)	50(3)	47(3)	-6(2)	-7(2)	3(2)
C(12C)	48(3)	85(4)	80(4)	-26(3)	-26(3)	4(3)
C(13C)	39(3)	36(3)	60(3)	-15(2)	13(2)	-6(2)
C(14C)	60(3)	50(3)	66(4)	8(3)	9(3)	13(3)

C(15C)	46(3)	69(4)	54(3)	-11(3)	7(3)	-23(3)
C(16C)	43(3)	43(3)	39(3)	-6(2)	-1(2)	-18(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for PSM16B.

	x	y	z	U(eq)
H(2A)	-174	9991	4988	54
H(3A)	-1075	10836	4455	62
H(4A)	-1800	10340	3516	67
H(5A)	-1611	9044	3123	50
H(8A)	-203	7409	2389	46
H(9A)	-903	6897	1472	60
H(10A)	-2237	6726	1575	71
H(11A)	-2853	7043	2618	58
H(14A)	-3032	7659	4870	68
H(15A)	-4318	7737	4476	132
H(15B)	-4247	8701	4431	132
H(15C)	-4199	8258	5163	132
H(16A)	-2229	8783	4821	179
H(PSM16B)	-2904	8907	5373	179
H(16C)	-2952	9343	4637	179
H(18A)	1501	7844	4871	48
H(19A)	1734	7151	5930	87
H(19B)	837	7114	5743	87
H(19C)	1138	7733	6318	87
H(20A)	2111	9079	5119	86
H(20B)	2522	8364	5535	86
H(20C)	1941	8962	5924	86
H(22A)	236	4824	5181	46
H(23A)	1137	3880	4815	54
H(24A)	2096	4236	4035	49
H(25A)	2122	5541	3563	44
H(28A)	1051	7114	2526	47
H(29A)	1920	7728	1791	48
H(30A)	3136	8126	2208	57
H(31A)	3504	7785	3333	50

H(34A)	2979	6938	5601	53
H(35A)	4223	7515	5689	95
H(35B)	4603	6676	5458	95
H(35C)	4159	6739	6180	95
H(36A)	3314	5577	5840	98
H(36B)	3727	5505	5105	98
H(36C)	2813	5624	5148	98
H(38A)	-1030	7315	4941	41
H(39A)	-541	7778	6025	80
H(39B)	-1044	7113	6420	80
H(39C)	-1461	7839	6022	80
H(40A)	-1818	6142	4906	64
H(40B)	-2240	6830	5346	64
H(40C)	-1818	6097	5731	64
H(3B)	-2010	7497	4137	51
H(6A)	2302	6888	4565	46
H(1C1)	1309	10480	3165	102
H(1C2)	499	10079	3334	102
H(2CA)	1453	9423	3905	98
H(2CB)	1886	9226	3196	98
H(2CC)	1071	8818	3359	98
H(3CA)	845	11221	2189	103
H(3CB)	358	10771	1607	103
H(4CA)	-438	11585	2266	125
H(4CB)	-195	11109	2951	125
H(4CC)	-683	10660	2366	125
H(5CA)	1675	9265	1986	98
H(5CB)	1356	9857	1402	98
H(6CA)	2600	10210	1703	138
H(6CB)	2340	10341	2488	138
H(6CC)	2025	10931	1897	138
H(7CA)	492	8778	2320	97
H(7CB)	-209	9348	2535	97
H(8CA)	-448	8754	1491	161
H(8CB)	323	9138	1178	161
H(8CC)	-378	9712	1394	161

H(9CA)	9369	4290	3671	54
H(9CB)	8616	4150	3212	54
H(10B)	8443	5289	3929	74
H(10C)	8429	5571	3139	74
H(10D)	9184	5713	3597	74
H(11B)	9042	5454	2078	58
H(11C)	9407	4773	1596	58
H(12A)	8076	4763	1491	106
H(12B)	7983	4616	2302	106
H(12C)	8351	3927	1825	106
H(13A)	9318	3326	2421	54
H(13B)	10058	3656	2022	54
H(14B)	10427	2697	2848	88
H(14C)	10049	3230	3448	88
H(14D)	10790	3556	3045	88
H(15D)	11298	5390	2349	84
H(15E)	10644	5235	1783	84
H(15F)	11050	4486	2158	84
H(16D)	10086	5628	2835	50
H(16E)	10501	4890	3215	50

Table 6. Torsion angles [°] for PSM16B.

N(1)-C(1)-C(2)-C(3)	172.4(4)
C(6)-C(1)-C(2)-C(3)	0.5(6)
C(1)-C(2)-C(3)-C(4)	-0.7(7)
C(2)-C(3)-C(4)-C(5)	-0.2(7)
C(3)-C(4)-C(5)-C(6)	1.5(7)
C(4)-C(5)-C(6)-N(2)	-177.9(4)
C(4)-C(5)-C(6)-C(1)	-1.7(6)
C(2)-C(1)-C(6)-N(2)	177.2(4)
N(1)-C(1)-C(6)-N(2)	4.3(5)
C(2)-C(1)-C(6)-C(5)	0.7(6)
N(1)-C(1)-C(6)-C(5)	-172.3(4)
C(12)-C(7)-C(8)-C(9)	2.3(6)
N(2)-C(7)-C(8)-C(9)	-179.7(4)
C(7)-C(8)-C(9)-C(10)	-1.1(7)
C(8)-C(9)-C(10)-C(11)	-1.0(8)
C(9)-C(10)-C(11)-C(12)	1.7(7)
C(10)-C(11)-C(12)-C(7)	-0.4(7)
C(10)-C(11)-C(12)-N(3)	-177.8(4)
C(8)-C(7)-C(12)-C(11)	-1.5(6)
N(2)-C(7)-C(12)-C(11)	-179.5(4)
C(8)-C(7)-C(12)-N(3)	175.9(4)
N(2)-C(7)-C(12)-N(3)	-2.1(6)
O(2)-C(13)-C(14)-C(16)	-103.7(6)
N(3)-C(13)-C(14)-C(16)	75.8(7)
O(2)-C(13)-C(14)-C(15)	22.5(7)
N(3)-C(13)-C(14)-C(15)	-158.1(4)
O(1)-C(17)-C(18)-C(20)	-48.0(6)
N(1)-C(17)-C(18)-C(20)	130.4(4)
O(1)-C(17)-C(18)-C(19)	75.7(5)
N(1)-C(17)-C(18)-C(19)	-106.0(5)
N(4)-C(21)-C(22)-C(23)	174.4(4)
C(26)-C(21)-C(22)-C(23)	-0.2(6)
C(21)-C(22)-C(23)-C(24)	1.1(7)
C(22)-C(23)-C(24)-C(25)	-1.7(7)

C(23)-C(24)-C(25)-C(26)	1.4(6)
C(24)-C(25)-C(26)-N(5)	-178.4(4)
C(24)-C(25)-C(26)-C(21)	-0.5(6)
C(22)-C(21)-C(26)-N(5)	178.0(3)
N(4)-C(21)-C(26)-N(5)	2.8(5)
C(22)-C(21)-C(26)-C(25)	-0.1(5)
N(4)-C(21)-C(26)-C(25)	-175.3(3)
C(32)-C(27)-C(28)-C(29)	-2.1(6)
N(5)-C(27)-C(28)-C(29)	171.5(4)
C(27)-C(28)-C(29)-C(30)	-1.3(7)
C(28)-C(29)-C(30)-C(31)	3.3(7)
C(29)-C(30)-C(31)-C(32)	-1.8(7)
C(30)-C(31)-C(32)-C(27)	-1.8(6)
C(30)-C(31)-C(32)-N(6)	178.9(4)
C(28)-C(27)-C(32)-C(31)	3.7(6)
N(5)-C(27)-C(32)-C(31)	-169.8(4)
C(28)-C(27)-C(32)-N(6)	-177.0(4)
N(5)-C(27)-C(32)-N(6)	9.6(6)
O(4)-C(33)-C(34)-C(35)	20.4(6)
N(6)-C(33)-C(34)-C(35)	-162.4(4)
O(4)-C(33)-C(34)-C(36)	-102.6(5)
N(6)-C(33)-C(34)-C(36)	74.6(5)
O(3)-C(37)-C(38)-C(40)	-65.6(5)
N(4)-C(37)-C(38)-C(40)	111.9(4)
O(3)-C(37)-C(38)-C(39)	55.3(5)
N(4)-C(37)-C(38)-C(39)	-127.3(4)
O(1)-C(17)-N(1)-C(1)	13.3(7)
C(18)-C(17)-N(1)-C(1)	-164.9(3)
O(1)-C(17)-N(1)-Co(1)	-152.2(4)
C(18)-C(17)-N(1)-Co(1)	29.6(5)
C(2)-C(1)-N(1)-C(17)	15.6(6)
C(6)-C(1)-N(1)-C(17)	-172.0(4)
C(2)-C(1)-N(1)-Co(1)	-177.1(3)
C(6)-C(1)-N(1)-Co(1)	-4.8(4)
N(5)-Co(1)-N(1)-C(17)	-53.6(4)
N(2)-Co(1)-N(1)-C(17)	169.7(3)

N(4)-Co(1)-N(1)-C(17)	45.6(4)
N(5)-Co(1)-N(1)-C(1)	139.9(2)
N(2)-Co(1)-N(1)-C(1)	3.2(3)
N(4)-Co(1)-N(1)-C(1)	-120.9(3)
C(5)-C(6)-N(2)-C(7)	-6.0(6)
C(1)-C(6)-N(2)-C(7)	177.7(3)
C(5)-C(6)-N(2)-Co(1)	174.6(3)
C(1)-C(6)-N(2)-Co(1)	-1.6(4)
C(8)-C(7)-N(2)-C(6)	118.3(4)
C(12)-C(7)-N(2)-C(6)	-63.8(5)
C(8)-C(7)-N(2)-Co(1)	-62.4(5)
C(12)-C(7)-N(2)-Co(1)	115.4(4)
N(5)-Co(1)-N(2)-C(6)	-130.6(3)
N(1)-Co(1)-N(2)-C(6)	-0.9(3)
N(4)-Co(1)-N(2)-C(6)	117.1(3)
N(5)-Co(1)-N(2)-C(7)	50.1(4)
N(1)-Co(1)-N(2)-C(7)	179.8(3)
N(4)-Co(1)-N(2)-C(7)	-62.1(4)
O(2)-C(13)-N(3)-C(12)	3.1(7)
C(14)-C(13)-N(3)-C(12)	-176.4(4)
C(11)-C(12)-N(3)-C(13)	-41.9(6)
C(7)-C(12)-N(3)-C(13)	140.6(4)
O(3)-C(37)-N(4)-C(21)	7.6(6)
C(38)-C(37)-N(4)-C(21)	-169.6(3)
O(3)-C(37)-N(4)-Co(1)	-153.3(3)
C(38)-C(37)-N(4)-Co(1)	29.6(4)
C(22)-C(21)-N(4)-C(37)	25.3(6)
C(26)-C(21)-N(4)-C(37)	-159.9(3)
C(22)-C(21)-N(4)-Co(1)	-171.9(3)
C(26)-C(21)-N(4)-Co(1)	2.9(4)
N(5)-Co(1)-N(4)-C(37)	157.0(3)
N(2)-Co(1)-N(4)-C(37)	-66.9(3)
N(1)-Co(1)-N(4)-C(37)	33.2(3)
N(5)-Co(1)-N(4)-C(21)	-5.3(2)
N(2)-Co(1)-N(4)-C(21)	130.8(2)
N(1)-Co(1)-N(4)-C(21)	-129.1(2)

C(25)-C(26)-N(5)-C(27)	-6.4(6)
C(21)-C(26)-N(5)-C(27)	175.7(3)
C(25)-C(26)-N(5)-Co(1)	170.7(3)
C(21)-C(26)-N(5)-Co(1)	-7.2(4)
C(32)-C(27)-N(5)-C(26)	-72.7(5)
C(28)-C(27)-N(5)-C(26)	114.0(4)
C(32)-C(27)-N(5)-Co(1)	110.7(4)
C(28)-C(27)-N(5)-Co(1)	-62.6(5)
N(2)-Co(1)-N(5)-C(26)	-121.9(3)
N(1)-Co(1)-N(5)-C(26)	124.4(3)
N(4)-Co(1)-N(5)-C(26)	6.8(2)
N(2)-Co(1)-N(5)-C(27)	54.8(4)
N(1)-Co(1)-N(5)-C(27)	-58.8(3)
N(4)-Co(1)-N(5)-C(27)	-176.4(3)
O(4)-C(33)-N(6)-C(32)	0.8(7)
C(34)-C(33)-N(6)-C(32)	-176.4(4)
C(31)-C(32)-N(6)-C(33)	-13.6(7)
C(27)-C(32)-N(6)-C(33)	167.0(4)
C(3C)-N(1C)-C(1C)-C(2C)	-175.2(5)
C(5C)-N(1C)-C(1C)-C(2C)	-54.0(7)
C(7C)-N(1C)-C(1C)-C(2C)	62.5(7)
C(1C)-N(1C)-C(3C)-C(4C)	-60.4(7)
C(5C)-N(1C)-C(3C)-C(4C)	177.0(5)
C(7C)-N(1C)-C(3C)-C(4C)	59.4(7)
C(1C)-N(1C)-C(5C)-C(6C)	-55.5(6)
C(3C)-N(1C)-C(5C)-C(6C)	67.4(6)
C(7C)-N(1C)-C(5C)-C(6C)	-172.2(5)
C(1C)-N(1C)-C(7C)-C(8C)	175.1(6)
C(3C)-N(1C)-C(7C)-C(8C)	52.8(7)
C(5C)-N(1C)-C(7C)-C(8C)	-65.8(7)
C(13C)-N(2C)-C(9C)-C(10C)	-178.2(4)
C(11C)-N(2C)-C(9C)-C(10C)	-59.1(5)
C(16C)-N(2C)-C(9C)-C(10C)	61.3(5)
C(9C)-N(2C)-C(11C)-C(12C)	-48.8(5)
C(13C)-N(2C)-C(11C)-C(12C)	70.4(5)
C(16C)-N(2C)-C(11C)-C(12C)	-168.4(4)

C(9C)-N(2C)-C(13C)-C(14C)	-64.6(5)
C(11C)-N(2C)-C(13C)-C(14C)	174.4(4)
C(16C)-N(2C)-C(13C)-C(14C)	54.2(5)
C(9C)-N(2C)-C(16C)-C(15C)	171.7(4)
C(13C)-N(2C)-C(16C)-C(15C)	52.7(5)
C(11C)-N(2C)-C(16C)-C(15C)	-66.8(5)

Symmetry transformations used to generate equivalent atoms: