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Tripodal Phenylamine-Based Ligands and Their Co^{II} Complexes

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The syntheses of two phenylamine-based ligand systems, N(*o*-PhNH$_2$)$_3$ and N(*o*-PhNHC(O)^{i}Pr)$_3$, are reported. These ligands readily coordinate to Co^{II} to form monomeric complexes. X-ray diffraction studies establish that the [N(*o*-PhNC(O)^{i}Pr)$_3$]$^{3-}$ ligand stabilizes the Co^{II} ion in a trigonal-monopyramidal coordination environment. The axial coordination site in this complex is accessible and, upon cyanide coordination, generates an electrochemically active species.

Tetraamine, tripodal ligand systems have been widely employed in many areas of inorganic chemistry.[1] Tripodal, trianionic triamidoamines[2] derived from tetraamine precursors have received particular attention because of the ability of this ligand type to support metal complexes with uncommon coordination geometries,[3] unique inorganic functionalities,[4] and diverse catalytic capabilities.[5] The most common building block for these types of triamidoamine systems are tripodal tetraamine fragments that contain a tertiary amine substituted by three alkylamine moieties, such as tris(2-aminoethyl)amine (tren).[1] We have been interested in exploring alternative building blocks for this type of ligand as a means of varying the electronic features of the resulting transition-metal centers.

In this context, we were particularly interested in investigating a tripodal tetraamine ligand in which the three ligand arms are comprised of *o*-phenylamine moieties. The incorporation of *o*-phenylamine groups into this ligand backbone is intriguing for several reasons: (1) The *o*-phenylamine ligand backbone should be less flexible upon metal ion chelation than its alkylamine counterparts.[6] (2) Chelating *o*-phenylenediamine units[7] and *o*-phenylenediamine derivatives[8] have the potential to act as noninnocent or redox-active ligands. (3) The tetradentate tripodal ligands of the general form [N(*o*-PhL)$_3$], where L = OH[9] or PR$_2$,[10] have been known for some time, but the coordination chemistry of [N(*o*-PhNH$_2$)$_3$] and its derivatives has, to the best of our knowledge, yet to be investigated with first-row late-transition-metal ions.[11]

In this work, we present the syntheses of the tetraamine ligand tris(2-aminophenyl)amine, N(*o*-PhNH$_2$)$_3$, and its triamidoamine derivative, 2,2′,2″-tris(isobutylamido)triphenylamine [N(*o*-PhNHC(O)^{i}Pr)$_3$]. The Co^{II} complexes of both of these ligands have been prepared and characterized.

The tetraamine ligand N(*o*-PhNH$_2$)$_3$ was synthesized in multigram quantities by first preparing tris(2-nitrophenyl)amine via an S$_N$Ar reaction.[12] The Pd-catalyzed reduction of this species afforded N(*o*-PhNH$_2$)$_3$ in high yield (Scheme 1). The triamidoamine analogue was readily prepared by acylation of a N(*o*-PhNH$_2$)$_3$ unit with isobutyryl chloride

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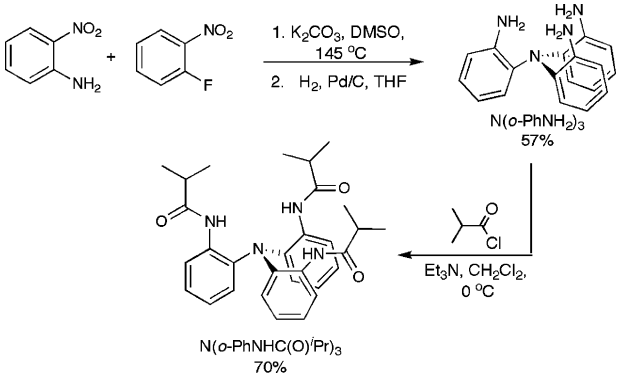
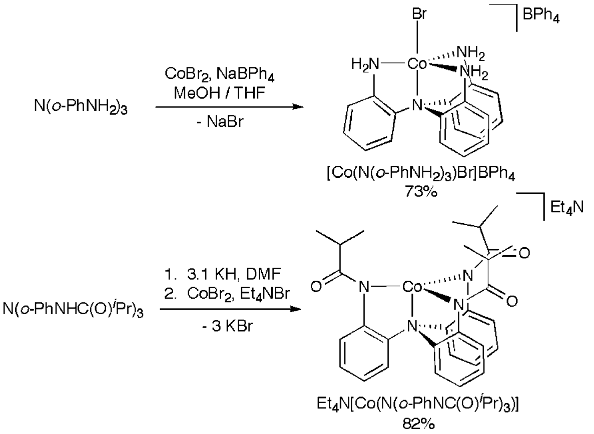
Scheme 1. Syntheses of N(o-PhNH$_2$)$_3$ and N(o-PhNHC(O)^{i}Pr)$_3$



Scheme 2. Syntheses of [Co(N(o-PhNH$_2$)$_3$)Br]BPh$_4$ and Et$_4$N[Co(N(o-PhNC(O)^{i}Pr)$_3$]



(Scheme 1) to afford (N(o-PhNHC(O)^{i}Pr)$_3$ in good yield (70%) as a white microcrystalline solid.

We evaluated the structural features of [N(o-PhNH$_2$)$_3$] by preparing its Co^{II} complex as outlined in Scheme 2. The cationic complex [Co(N(o-PhNH$_2$)$_3$)Br]BPh$_4$ was prepared by metalation of the neutral tetraamine ligand with CoBr$_2$ in a MeOH/THF mixture followed by in situ salt metathesis with 1 equiv of NaBPh$_4$. The resulting indigo complex was purified by recrystallization by slow diffusion of diethyl ether into a THF solution of the metal salt to give the analytically pure [Co(N(o-PhNH$_2$)$_3$)Br]BPh$_4$ in good yield (73%). Crystals suitable for X-ray diffraction measurements were grown by vapor diffusion of diethyl ether into a concentrated acetonitrile solution of the complex. The solid-state molecular structure of [Co(N(o-PhNH$_2$)$_3$)Br]BPh$_4$ was determined and is depicted in Figure 1A.[14] The Co^{II} ion is five-coordinate and displays a trigonal-bipyramidal coordination environment with a τ value of 1.0.[13] The equatorial plane is composed of the three primary amine N donors, and the axial coordination sites are occupied by the tertiary amine of the ligand and a Br$^-$ ion. The Co^{II} center is distorted 0.5 Å out of the trigonal plane toward the Br$^-$ ion. [Co(N(o-PhNH$_2$)$_3$)Br]BPh$_4$ is paramagnetic and displays a high-spin $S = {}^3/_2$ ground state in solution ($\mu_{\text{eff}} = 4.37$, THF-d_8) at 25 °C. The complex is stable for several months under dry anaerobic environments as a crystalline solid or in solution (THF).

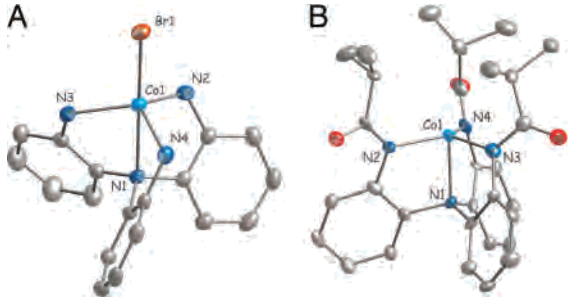


Figure 1. Thermal ellipsoid diagrams of [Co(N(o-PhNH$_2$)$_3$)Br]BPh$_4$ (A) and Et$_4$N[Co(N(o-PhNC(O)^{i}Pr)$_3$)] (B) drawn at 35% probability. Counterions and H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for [Co(N(o-PhNH$_2$)$_3$Br]BPh$_4$: Co1−Br1 2.3875(5), Co1−N1 2.338(2), Co−N2 2.056(3), Co−N3 2.069(3), Co−N4 2.073(3), Br1−Co1−N1 178.42(6), N3−Co1−N4 113.87(10), N2−Co1−N3 117.49, N2−Co1−N4 111.60(10). Selected bond lengths (Å) and angles (deg) for Et$_4$N[Co(N(o-PhNC(O)^{i}Pr)$_3$]: Co1−N1 2.115(8), Co1−N2 1.946(7), Co1−N3 1.965(9), Co1−N4 1.966(4), N2−Co1−N3 115.5(4), N2−Co1−N4 121.4(3), N3−Co−N4 120.5(3), N1−Co1−N2 84.7(3), N1−Co1−N3 85.1(3), N1−Co1−N4 84.1(3).

To evaluate the coordination properties of the triamidoamine N(o-PhNHC(O)^{i}Pr)$_3$ ligand, its Co^{II} complex was prepared. N(o-PhNHC(O)^{i}Pr)$_3$ was reacted with 3 equiv of potassium hydride in N,N-dimethylformamide (DMF) and then transmetalated with CoBr$_2$ to yield a deep-blue solution. Salt metathesis with tetraethylammonium bromide (Et$_4$NBr) yielded Et$_4$N[Co(N(o-PhNC(O)^{i}Pr)$_3$)] in 83% yield with concomitant formation of 3 equiv of potassium bromide (Scheme 2). X-ray-quality teal crystals of Et$_4$N[Co(N(o-PhNC(O)^{i}Pr)$_3$)] were obtained by vapor diffusion of diethyl ether into a DMF solution of the Co complex. The crystal structure of Et$_4$N[Co(N(o-PhNC(O)^{i}Pr)$_3$)] contains two crystallographically independent molecules in the unit cell. The geometrical properties of these two complexes are indistinguishable within experimental error. The solid-state structure of one of the molecules of Et$_4$N[Co(N(o-PhNC(O)^{i}Pr)$_3$)] is depicted in Figure 1B.[15] The complex displays a trigonal-monopyramidal coordination geometry about the Co ion. The trigonal coordination plane is composed of the three anionic N-amidate donors. The average Co−N$_{\text{eq}}$ distance in this plane is 1.959(9) Å. The Co ion is slightly distorted (0.182 Å) out of the trigonal plane toward the vacant axial coordination site. The opposite axial site is occupied by the tertiary amine donor and exhibits a Co−N$_1$ bond distance of 2.115(8) Å. The vacant coordination site on the Co^{II} ion is surrounded by the three amidate isopropyl groups of the ligand. The

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(13) τ is a structural index parameter used to measure trigonality in five-coordinate complexes ($\tau = 0$ for perfect square-pyramidal geometry; $\tau = 1$ for perfect trigonal-bipyramidal geometry). Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349−1356.

(14) Crystal data for [Co(N(o-PhNH$_2$)$_3$)Br]BPh$_4$: C$_{42}$H$_{38}$BBrCoN$_4$, M = 748.41, tetragonal, space group $I4(I)/a$, a = 34.5691(18) Å, b = 34.5691(18) Å, c = 13.4536(10) Å, α = 90°, V = 16077.4(17) Å^3, Z = 16, ρ_{calcd} = 1.237 Mg/m^3, F(000) = 6160, λ(Mo Kα) = 0.710 73 Å, μ(Mo Kα) = 1.453 mm^{-1}, crystal dimensions 0.29 × 0.28 × 0.18 mm^3. The final R is 0.0600 (wR2 = 0.1274). 11 742 total reflections, 10 021 independent (R_{int} = 10.92%) with $I > 2\sigma(I)$.

(15) Crystal data for Et$_4$N[Co(N(o-PhNC(O)^{i}Pr)$_3$)]: C$_{38}$H$_{53}$CoN$_5$O$_3$, M = 686.78, monoclinic, space group $P2(1)$, a = 14.609(11) Å, b = 15.421(12) Å, c = 15.668(12) Å, β = 90.116(16)°, V = 3530(5) Å^3, Z = 4, ρ_{calcd} = 1.292 Mg/m^3, F(000) = 1468, λ(Mo Kα) = 0.710 73 Å, μ(Mo Kα) = 0.530 mm^{-1}, crystal dimensions 0.14 × 0.11 × 0.04 mm^3. The final R is 0.0855 (wR2 = 0.1905). 34 250 total reflections, 10 133 independent (R_{int} = 17.79%) with $I > 2\sigma(I)$.

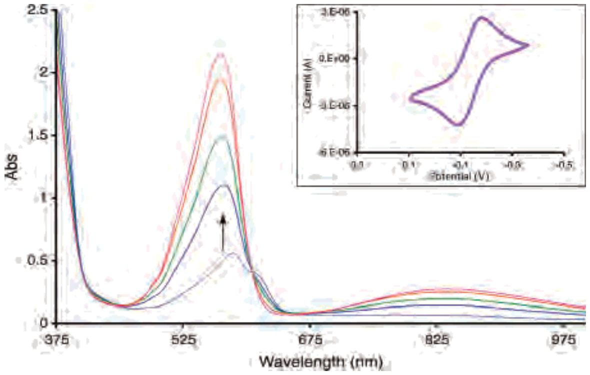

Figure 2. UV−visible absorption data for the titration of $Et_4N[Co(N(o\text{-}PhNC(O)^iPr)_3)]$ with 0.00, 0.25, 0.50, 0.75, and 1.0 equiv of Et_4NCN. (Inset) Cyclic voltammogram of $[Et_4N]_2[Co(N(o\text{-}PhNC(O)^iPr)_3)(CN)]$ recorded in DMF with 0.10 M $[TBA]PF_6$ recorded at 10 mV/s.

groups forming this cavity are oriented so that the methine protons of the isopropyl groups are positioned inside the protective pocket above the Co ion. The trigonal-monopyramidal coordination environment observed in $Et_4N[Co(N(o\text{-}PhNC(O)^iPr)_3)]$ is relatively rare for Co ions but has been observed with other tetradentate, face-capping ligand systems on both Co^I [16] and Co^{II} [17] centers.

$Et_4N[Co(N(o\text{-}PhNC(O)^iPr)_3)]$ displays a high-spin electronic configuration ($S = {}^3/_2$) at 25 °C in DMSO-d_6 with $\mu_{eff} = 4.69\ \mu_B$. The electrochemical properties of the complex were investigated utilizing cyclic voltammetry, but the complex did not display any significant or reversible electrochemical events at 25 °C in DMF with *n*-tetrabutylammonium hexafluorophosphate ($[TBA]PF_6$) as the supporting electrolyte.

We speculated that $Et_4N[Co(N(o\text{-}PhNC(O)^iPr)_3)]$ should have an open and accessible axial coordination site given the geometry it displayed in the solid state. This assumption was supported by the observation that $Et_4N[Co(N(o\text{-}PhNC(O)^iPr)_3)]$ exhibited a dramatic color change, from blue to magenta, upon dissolution in acetonitrile. Acetonitrile binding to the complex is reversible, however, because the complex reverts to its original blue color and displays its original solution-state (DMF) optical properties after it is dried under reduced pressure.

In an attempt to generate an isolable five-coordinate metal complex, $Et_4N[Co(N(o\text{-}PhNC(O)^iPr)_3)]$ was dissolved in DMF and treated with increasing quantities of tetraethylammonium cyanide ($[Et_4N]CN$). The UV−visible absorption data from the titration experiment are shown in Figure 2. The visible absorption spectrum changes after each addition until exactly 1 equiv of $[Et_4N]CN$ has been added. The addition of more than 1 equiv of $[Et_4N]CN$ causes no additional change in the visible absorption spectrum. These data are consistent with the formation of a 1:1 $CN^-/[Co(N(o\text{-}PhNC(O)^iPr)_3)]^-$ complex, which we formulate as $[Et_4N]_2[Co(N(o\text{-}PhNC(O)^iPr)_3)(CN)]$. This formulation is supported by a Job's plot (Figure S1 in the Supporting Information) and Fourier transfer infrared (FTIR) spectroscopy of the magenta complex, which displays a transition at 2112 cm^{-1} consistent with the formation of a terminal cyano complex.[18] The binding constant of the CN^- ligand to ${}^-[Co(N(o\text{-}PhNC(O)^iPr)_3)]^-$ was determined to be ca. 6×10^2 from the titration data (see Figure S2 in the Supporting Information).

$[Et_4N]_2[Co(N(o\text{-}PhNC(O)^iPr)_3)(CN)]$ was also examined by cyclic voltammetry (Figure 2, inset). $[Et_4N]_2[Co(N(o\text{-}PhNC(O)^iPr)_3)(CN)]$ displays a single, reversible electrochemical event at −0.145 V ($\Delta E_p = 0.095$ V; $i_{pc}i_{pa}^{-1} = 0.95$) vs Fc^0/Fc^+. We tentatively assign this one-electron redox process to the Co^{II}/Co^{III} couple. The observation that both CN^- and acetonitrile bind to the Co center in $[Co(N(o\text{-}PhNC(O)^iPr)_3)]$ but DMF and Br^- do not indicates that the cavity surrounding the Co ion is limiting exogenous ligand binding to small or linear donors. Additional characterization studies of $[Et_4N]_2[Co(N(o\text{-}PhNC(O)^iPr)_3)(CN)]$ and its one-electron oxidation product are in progress in our laboratories.

In summary, we have reported the syntheses of a new type of tetradentate tripodal ligand system and its triamidoamine derivative. The neutral tetraamine ligand, $N(o\text{-}PhNH_2)_3$, forms a monocationic five-coordinate Co complex, while the trianionic $[(N(o\text{-}PhNC(O)^iPr)_3]^{3-}$ derivative stabilizes the Co^{II} ion in an uncommon trigonal-monopyramidal geometry. Exogenous ligand binding in the unoccupied axial site of this complex may be controlled by the cavity surrounding the vacant coordination site. Efforts to understand these effects and investigate the coordination chemistry of these ligands with other transition metals are ongoing in our laboratories.

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Supporting Information Available: Details for all ligand and complex syntheses, spectroscopic experiments, and X-ray crystallographic details for $Et_4N[Co(N(o\text{-}PhNC(O)^iPr)_3)]$ and $[Co(N(o\text{-}PhNH_2)_3)Br]BPh_4$ (CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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