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Catalytic dioxygen activation by Co(II) complexes employing a coordinatively versatile ligand scaffold†

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The ligand bis(2-isobutyrylamidophenyl)amine has been prepared and used to stabilize both mononuclear and dinuclear cobalt(II) complexes. The nuclearity of the cobalt product is regulated by the deprotonation state of the ligand. Both complexes catalytically oxidize triphenylphosphine to triphenylphosphine oxide in the presence of O$_2$.

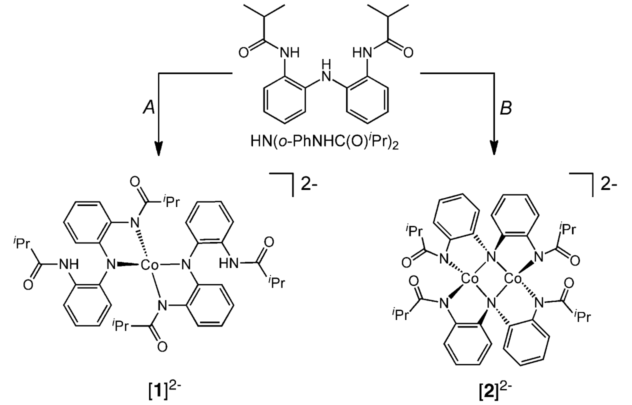
Molecular oxygen is often viewed as the consummate oxidant for catalytic oxidation reactions because it is abundant, relatively inexpensive, and environmentally benign.[1] Cobalt(II) complexes, because of their tendency to bind molecular oxygen,[2] have been widely studied as potential catalysts for these reactions.[3,4] Examples of homogeneous catalytic oxidation reactions that employ Co(II) species, dioxygen, and additive co-reductants (*e.g.*, aldehydes) include olefin epoxidation,[5] sulfide oxidation,[6] and the formation of oxaziridines from imines.[7] Catalytic oxygen-atom transfer reactions that utilize Co(II) and dioxygen and do not require a co-reductant, however, are less common.[3] Sain and Jain reported using Co(II) Schiff base complexes and dioxygen to catalytically oxygenate tertiary nitrogen compounds to their corresponding *N*-oxides.[8] Examples of catalytic triphenylphosphine oxidation reactions that use Co(II) complexes and dioxygen under ambient conditions are also limited. Cobalt(II) Schiff base[9] and dimethylglyoximato complexes[10] have been shown to catalytically oxidize triphenylphosphine in the presence of dioxygen, but their turnover frequencies (TOF = mol of product/mol of catalyst·hour) are low (less than 1 h^{-1}).

Ligands that incorporate *N*-amidate donors are appealing candidates for oxidation catalysts because of their ability to stabilize high oxidation states due to their strong σ-donor capacity.[11] With the goal of developing a ligand system that would incorporate two *N*-amidate donors and one amido donor and support coordinatively unsaturated metal centres with open coordination sites available for small molecule binding, the bis(2-isobutyrylamidophenyl)amine (HN(o-PhNHC(O)^{iPr})$_2$) fragment was targeted. Herein, we describe the coordination chemistry of this scaffold with Co(II) and demonstrate that it can stabilize both mononuclear and dinuclear complexes. Furthermore, we demonstrate that these complexes are capable of catalytic oxidation reactions using dioxygen.

The ligand HN(o-PhNHC(O)^{i}Pr)$_2$ was synthesized in high yield (85%) by acylating bis(2-aminophenyl)amine[12] with isobutyryl chloride.

The resulting white microcrystalline powder is air stable. When HN(o-PhNHC(O)^{i}Pr)$_2$ was treated with two equivalents of base and 0.5 equivalents CoBr$_2$, a dark red product, K$_2$[**1**] (where [**1**]$^{2-}$ = [Co$^{\rm II}$(N-κN(o-PhNC(O)^{i}Pr-κN)-(o-PhNHC(O)^{i}Pr))$_2$]$^{2-}$), was isolated in good yield (70%). Conversely, treating HN(o-PhNHC(O)^{i}Pr)$_2$ with three equivalents of potassium hydride and one equivalent of CoBr$_2$ resulted in the formation of an emerald green product, K$_2$[**2**] (where [**2**]$^{2-}$ = [{Co$^{\rm II}$(μ_2-N(o-PhNC(O)^{i}Pr-κN)$_2$)}$_2$]$^{2-}$). Both products can be isolated as either dipotassium salts or bis(tetraethylammonium) salts, as shown in Scheme 1.

The molecular structures of (Et$_4$N)$_2$[**1**] and (Et$_4$N)$_2$[**2**] were determined by X-ray crystallography, and the results are shown in Fig. 1. The monomeric species (Et$_4$N)$_2$[**1**] crystallizes in the *Pca*2$_1$ space group and confirms the ligand to cobalt ion ratio to be 2 : 1 (Fig. 1A)‡. The cobalt ion is coordinated in a distorted trigonal pyramidal environment (τ_4 = 0.74)[13] by one



Scheme 1 Synthesis of (Et$_4$N)$_2$[**1**] (route *A*) and (Et$_4$N)$_2$[**2**] (route *B*). *Conditions*: (*A*) DMF, 2 KH, 0.5CoBr$_2$, Et$_4$NBr; (*B*) DMF, 3KH, CoBr$_2$, Et$_4$NBr.

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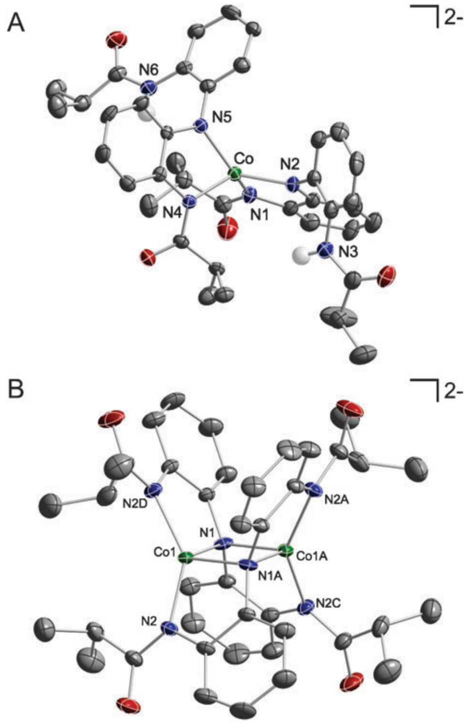

Fig. 1 Displacement ellipsoid plots (drawn at the 50% probability level) of (Et$_4$N)$_2$[**1**] (A) and (Et$_4$N)$_2$[**2**] (B). All H atoms (except the amide hydrogens in [**1**]$^{2-}$) and counter ions are omitted for clarity. Selected bond lengths (Å) and angles (°) for [**1**]$^{2-}$: Co–N1 2.029(3), Co–N2 1.996(3), Co–N4 2.035(3), Co–N5 1.996(3), N1–Co–N5 123.50(13), N1–Co–N2 83.05(13), N1–Co–N4 117.14(13), N2–Co–N5 132.03(13), N2–Co–N4 123.38(13), N4–Co–N5 82.33(5). For [**2**]$^{2-}$: Co1–Co1A 2.6807(9), Co1–N1 2.040(2), Co–N2 1.975(2), N1–Co–N2 120.01(7), N1A–Co–N2 86.08(7), N1–Co–N1A 97.84(11), N2–Co–N2D 141.63(13).

amido and one *N*-amidate donor from each ligand. The Co–N1 and Co–N4 (*N*-amidate) bond lengths of 2.029(3) and 2.035(3) Å, respectively, are slightly longer than the Co–N2/N5 (amido) bond lengths of 1.996(3) Å. The dinuclear complex (Et$_4$N)$_2$[**2**] crystallizes with two crystallographically independent but geometrically similar molecules in the asymmetric unit. The molecular structure of one of these units is shown in Fig. 1B and shows that two deprotonated amido donors and two cobalt ions make up a Co$_2$N$_2$ diamond core assembly in which the atoms are related by inversion. The Co1–N1 (bridging amido) bond lengths of 2.040(2) Å in [**2**]$^{2-}$ are longer than the Co1–N2 (*N*-amidate) bonds (1.975(2) Å) but comparable to the distances observed in other known Co$^{II}_2$N$_2$ (bridging amido) structures.[14] The Co1–Co1A separation of 2.6807(9) Å found in [**2**]$^{2-}$ is slightly longer than the Co–Co separations found in similar Co$^{II}_2$N$_2$ structures but does not preclude the existence of metal–metal interactions.[14]

Both (Et$_4$N)$_2$[**1**] and (Et$_4$N)$_2$[**2**] are soluble in a variety of solvents (*e.g.*, CH$_2$Cl$_2$, THF, and CH$_3$CN) and give rise to paramagnetically shifted ^{1}H NMR spectra. Magnetic susceptibility studies of (Et$_4$N)$_2$[**1**] (CD$_2$Cl$_2$, 298 K) indicate a μ_{eff} of 4.39(2) μ_{B} that is consistent with an S = 3/2 ground state. The ^{1}H NMR spectrum of (Et$_4$N)$_2$[**2**] is solvent independent, suggesting that the dimeric species does not dissociate in coordinating solvents. In solution, the magnetic moment, μ_{eff}, of (Et$_4$N)$_2$[**2**] (CD$_2$Cl$_2$, 298K) was measured to be 4.73(2) μ_{B}.

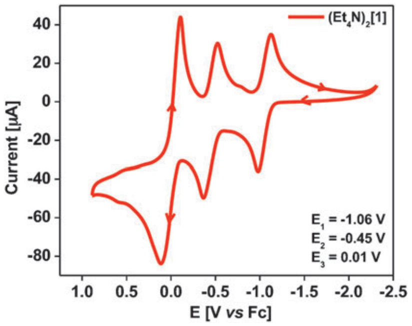

Fig. 2 Cyclic voltammogram of (Et$_4$N)$_2$[**1**] recorded at 25 °C in CH$_2$Cl$_2$ (0.10 M ^{n}BuN$_4$PF$_6$) with a glassy carbon working electrode, Ag/AgNO$_3$ reference electrode, and scan rate of 100 mV s^{-1}.

The cyclic voltammograms of both (Et$_4$N)$_2$[**1**] and (Et$_4$N)$_2$[**2**] were recorded in CH$_2$Cl$_2$. The dinuclear species, (Et$_4$N)$_2$[**2**], gives rise to a number of irreversible responses in its cyclic voltammogram that we cannot assign (Fig. S3, ESI†). The monomeric species, (Et$_4$N)$_2$[**1**], however, displays several reversible electrochemical events in its cyclic voltammogram, Fig. 2. To probe the nature of these responses, controlled potential coulometry experiments were conducted (Fig. S5 and S6, ESI†), and based upon these studies we assign all three of these events ($E^1_{\frac{1}{2}}$ = −1.06 V, $E^2_{\frac{1}{2}}$ = −0.45 V, and $E^3_{\frac{1}{2}}$ = + 0.01 V) as oxidations. The first two events ($E^1_{\frac{1}{2}}$ = −1.06 V, $E^2_{\frac{1}{2}}$ = −0.45 V) are both one-electron processes, whereas the third event ($E^3_{\frac{1}{2}}$ = +0.01 V) is a two-electron process. Bulk electrolysis experiments were initially used to determine the stability of the one-electron oxidized product. A 1.0 mM solution (CH$_2$Cl$_2$, 0.1 M ^{n}Bu$_4$NPF$_6$) of (Et$_4$N)$_2$[**1**] was subjected to bulk electrolysis at −0.86 V (*vs.* Fc/Fc$^+$), over the course of which the solution changed from deep red to navy blue. The blue species proved to be stable in electrolyte solution, as evidenced by time-dependent UV-visible absorption spectroscopy and cyclic voltammetry experiments. The apparent stability of this blue species prompted us to attempt a one-electron chemical oxidation of (Et$_4$N)$_2$[**1**] using one equivalent of FcBF$_4$ in CH$_3$CN. This reaction proceeded smoothly to afford the one-electron oxidized product, (Et$_4$N)[**1**].

Recrystallization of (Et$_4$N)[**1**] produces small, dark blue crystals. However, the structural data obtained from these are of poor quality (Fig. S9, ESI†). This structure does allow us to confirm structural connectivity and the charge on the metal-containing fragment. These data show that the cobalt ion remains four-coordinate and that overall charge on the metal complex has been reduced to −1. Further experimentation is needed to confirm the formal oxidation state of the cobalt ion in the one-electron and two-electron oxidized products.[15] We speculate that some of the oxidation events observed in the cyclic voltammogram of (Et$_4$N)$_2$[**1**] could be ligand-based as recent work has shown that a tris(amido) ligand derived from a substituted bis(2-aminophenyl)amine backbone is redox-active.[16]

As expected from the electrochemistry experiments (*i.e.*, adequately negative first oxidation potentials),[17] both (Et$_4$N)$_2$[**1**] and (Et$_4$N)$_2$[**2**] react rapidly with dioxygen. Upon

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exposure to dioxygen, acetonitrile solutions of $(Et_4N)_2$[**1**] and $(Et_4N)_2$[**2**] form deep purple and burgundy solutions, respectively. To test the ability of $(Et_4N)_2$[**1**] and $(Et_4N)_2$[**2**] to act as oxidation catalysts, both complexes were exposed to dioxygen in the presence of an excess of triphenylphosphine. An acetonitrile solution containing $(Et_4N)_2$[**1**] (0.02 mmol) and PPh_3 (2.0 mmol) was exposed to dioxygen (1 atm) and monitored using gas chromatography. After fifteen minutes, 44% of the PPh_3 had been converted to triphenylphosphine oxide ($OPPh_3$). After two hours, the reaction mixture yielded 69% (1.38 mmol) of the oxidized product. In a separate experiment, an acetonitrile solution containing $(Et_4N)_2$[**2**] (0.019 mmol) and PPh_3 (1.9 mmol) was exposed to dioxygen (1 atm). After fifteen minutes, 78% of the PPh_3 was converted to $OPPh_3$, and after two hours, 95% of the PPh_3 had been converted to $OPPh_3$ (1.81 mmol). Performing these reactions with large substrate to catalyst loading ratios (500 : 1) gives maximum turnover numbers (TON = mol product/mol cat) of 185 and 345 for $(Et_4N)_2$[**1**] and $(Et_4N)_2$[**2**], respectively. Labeling studies with $^{18}O_2(g)$ were conducted to confirm that the oxygen atom incorporated into the products ($OPPh_3$) of these reactions is derived from dioxygen. At this point, we cannot rule out the possibility that both $(Et_4N)_2$[**1**] and $(Et_4N)_2$[**2**] react with dioxygen to form similar reactive intermediates. While triphenylphosphine is a relatively easy substrate to oxidize, few transition metal catalysts are capable of carrying out this transformation with good efficiency (TOF $> 60\ h^{-1}$).[18]

In summary, the HN(*o*-PhNHC(O)^{i}Pr)$_2$ ligand has been used to stabilize both mononuclear ([**1**]$^{2-}$) and dinuclear ([**2**]$^{2-}$) cobalt(II) complexes. Under ambient conditions in the presence of excess dioxygen, both species catalytically oxidize triphenylphosphine to triphenylphosphine oxide with much better catalytic efficiencies than those previously observed for cobalt(II) complexes. Studies addressing the mechanism of these reactions are ongoing to further our understanding of the role of supporting ligands in dioxygen activation by transition metal complexes.

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Notes and references

‡ Crystal data. $(Et_4N)_2$[**1**]: $C_{56}H_{86}N_8O_4Co$, $M = 994.26$, $0.17 \times 0.11 \times 0.07\ mm^3$, orthorombic, space group $Pca2_1$, $a = 17.364(4)$ Å, $b = 16.539(4)$ Å, $c = 19.385(5)$, $V = 5567(2)$, $R_{int} = 0.1821$, $Z = 4$, $\rho_{cald} = 1.186\ g\ cm^{-3}$, $\mu = 0.359\ mm^{-1}$, $F(000) = 2148$, $T = 172(2)$ K, $R(F^2 > 2\sigma) = 0.0662$, $wR_2 = 0.1229$, 16 016 independent reflections [$\theta = 30.63°$] and 622 parameters, GOF of $F^2 = 1.006$. For $(Et_4N)_2$[**2**]: $C_{56}H_{84}Co_2N_8O_4$, $M = 1051.18$, $0.44 \times 0.40 \times 0.37\ mm^3$, tetragonal, space group $I4_122$, $a = 18.7790(8)$ Å, $b = 18.7790(8)$ Å, $c = 35.798(3)$, $V = 12624.1(1)$, $R_{int} = 0.0500$, $Z = 8$, $\rho_{cald} = 1.106\ g\ cm^{-3}$, $\mu = 0.571\ mm^{-1}$, $F(000) = 4496$, $T = 172(2)$ K, $R(F^2 > 2\sigma) = 0.0506$, $wR_2 = 0.1505$, 9495 independent reflections [$\theta = 30.71°$] and 320 parameters, GOF on $F^2 = 1.063$.

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