

Efficient C–H bond activations *via* O<sub>2</sub> cleavage by a dianionic cobalt(II) complex†Cite this: *Chem. Sci.*, 2014, 5, 2874Andy I. Nguyen,<sup>a</sup> Ryan G. Hadt,<sup>b</sup> Edward I. Solomon<sup>b</sup> and T. Don Tilley<sup>\*a</sup>

A dianionic, square planar cobalt(II) complex reacts with O<sub>2</sub> in the presence of acetonitrile to give a cyanomethylcobalt(III) complex formed by C–H bond cleavage. Interestingly, PhIO and *p*-tolyl azide react similarly to give the same cyanomethylcobalt(III) complex. Competition studies with various hydrocarbon substrates indicate that the rate of C–H bond cleavage greatly depends on the pK<sub>a</sub> of the C–H bond, rather than on the C–H bond dissociation energy. Kinetic isotope experiments reveal a moderate KIE value of ca. 3.5 using either O<sub>2</sub> or PhIO. The possible involvement of a cobalt(IV) oxo species in this chemistry is discussed.

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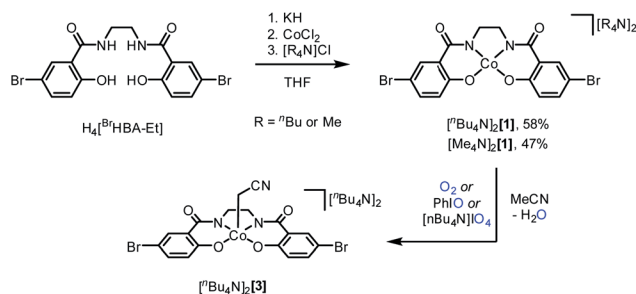
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## Introduction

An important challenge for the development of new catalytic oxidations is the utilization of O<sub>2</sub> from the air, as this reactant should enable the most atom-economical, cost effective and environmentally benign oxidations. In this context, the development of cobalt-based catalysts is particularly promising, since several types of homogeneous and heterogeneous cobalt catalysts are already known to utilize oxygen in oxidations of organic compounds.<sup>1</sup> Much of this chemistry is thought to proceed *via* peroxy intermediates that initiate the generation of organic radicals.<sup>2</sup> However, high-valent cobalt oxo intermediates have been postulated for certain oxidations, such as benzylic alcohol oxidation, amine oxidation, and epoxidation.<sup>1</sup> Despite abundant circumstantial evidence for cobalt-mediated O<sub>2</sub> cleavage, there has been no observation of a cobalt oxo species as the direct product of this type of O<sub>2</sub> activation. Notably, the generation of a cobalt(IV) oxo intermediate *via* O<sub>2</sub> cleavage would seem to be difficult given ligand field arguments,<sup>3</sup> and the fact that numerous cobalt(II) complexes have been shown to reversibly bind O<sub>2</sub> to give superoxo or  $\mu$ -peroxo complexes without O<sub>2</sub> cleavage.<sup>6</sup>

This contribution describes attempts to promote O–O bond cleavage in a  $\mu$ -peroxo intermediate to access a high-valent oxo species, with use of a tetraanionic ligand. The tetraanionic ligand <sup>Br</sup>HBA-Et (Scheme 1) provides a strong ligand field that features hard donor atoms, and ligands of this type have been

Scheme 1 Synthesis of [nBu<sub>4</sub>N]<sub>2</sub>[1], [Me<sub>4</sub>N]<sub>2</sub>[1], and [nBu<sub>4</sub>N]<sub>2</sub>[3].

shown to support a number of metal complexes in high oxidation states.<sup>7</sup> This approach has led to observation of clean C–H bond activations of acetonitrile and other hydrocarbons upon reaction of a dianionic cobalt(II) complex with O<sub>2</sub>. Furthermore, the use of oxo- and imido-transfer agents is shown to produce reactive intermediates with similar characteristics, implying that putative cobalt(IV) oxo and imido complexes<sup>5</sup> may be generated in these cases. Most importantly, this report describes a cobalt system that utilizes O<sub>2</sub> cleavage in promoting unusual C–H bond activations.

## Results and discussion

Deprotonation of (<sup>Br</sup>HBA-Et)<sub>4</sub>H<sub>4</sub>, *N,N'*-(ethane-1,2-diyl)bis(5-bromo-2-hydroxybenzamide), with four equivalents of KH in THF, followed by treatment with CoCl<sub>2</sub> and then salt metathesis with a tetraalkylammonium (<sup>n</sup>Bu<sub>4</sub>N<sup>+</sup> or Me<sub>4</sub>N<sup>+</sup>) chloride gave the dianionic complexes [<sup>n</sup>Bu<sub>4</sub>N]<sub>2</sub>[(<sup>Br</sup>HBA-Et)<sub>2</sub>Co] ([<sup>n</sup>Bu<sub>4</sub>N]<sub>2</sub>[1]) and [Me<sub>4</sub>N]<sub>2</sub>[(<sup>Br</sup>HBA-Et)<sub>2</sub>Co] ([Me<sub>4</sub>N]<sub>2</sub>[1]) as orange, crystalline solids in 58% and 47% yields, respectively (Scheme 1). The complex [<sup>n</sup>Bu<sub>4</sub>N]<sub>2</sub>[1] is a low spin, *S* = 1/2 Co(II) complex, as demonstrated by the solution magnetic moment (1.98  $\mu_B$ , 298 K). A rhombic

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signal in the 77 K X-band EPR spectrum ( $g_1 = 1.956$ ,  $g_2 = 2.29$ ,  $g_3 = 3.15$ ) with hyperfine coupling to the  $I = 7/2$   $^{59}\text{Co}$  nucleus ( $|A_1| = 81$  MHz,  $|A_2| = 285$  MHz,  $|A_3| = 300$  MHz) is consistent with an  $(xy)^2(z^2)^2(yz)^2(xz)^1$  or  $(xy)^2(z^2)^2(xz)^2(yz)^1$  ground state (ESI, Fig. S3†). Single crystal X-ray diffraction revealed that  $[\text{Bu}_4\text{N}]_2\mathbf{1}$  contains a nearly square planar cobalt center (sum of angles about Co =  $360.2(4)^\circ$ ), with Co–N and Co–O bond distances that both average to 1.87 Å (Fig. 1). Cyclic voltammetry reveals a reversible one-electron redox event at  $E_{1/2} = -0.22$  V (vs. NHE) corresponding to the Co(II)/Co(III) couple (ESI, Fig. S6†). This redox couple is more negative than that for cobalt complexes supported by salen<sup>8a</sup> ( $E_{1/2} = +0.25$  V vs. NHE), porphyrin<sup>8b</sup> ( $E_{1/2} = +0.68$  V vs. NHE), corrole<sup>8c</sup> ( $E_{1/2} = +0.03$  V vs. NHE), 1,1'-(ethane-1,2-diyl)bis(3-*tert*-butylurea)<sup>4a</sup> ( $E_{1/2} = -0.086$  V vs. NHE), and 2,2',2'-nitrilo-tris(*N*-isopropylacetamide)<sup>4b</sup> ( $E_{1/2} = +0.44$  V vs. NHE) ligands.

The one-electron oxidation of  $[\text{Bu}_4\text{N}]_2\mathbf{1}$  by AgCl in THF afforded the Co(III) complex  $[\text{Bu}_4\text{N}][\text{BrHBA-EtCo}]$  ( $[\text{Bu}_4\text{N}]\mathbf{2}$ ), which gives a deep purple solution in acetonitrile ( $\lambda_{\text{max}} = 560$  nm,  $\epsilon = 6800$  M<sup>-1</sup> cm<sup>-1</sup>; 98% isolated yield). Solution magnetic moment measurements characterize  $[\text{Bu}_4\text{N}]\mathbf{2}$  as having an  $S = 1$  ( $2.88 \mu_{\text{B}}$ , 298 K) ground state. X-ray crystallography (ESI, Fig. S1†) reveals that Co is in a nearly square planar geometry (sum of angles about Co =  $360.5(2)^\circ$ ). The average Co–N and Co–O bond distances are contracted to 1.84 Å and 1.83 Å, respectively, relative to analogous values for  $[\text{Bu}_4\text{N}]_2\mathbf{1}$ . Presumably, the electron-rich nature of the ligand in  $[\mathbf{2}]^+$  stabilizes the four-coordinate cobalt(III) center and substantially reduces its Lewis acidity. This geometry contrasts with that of

most cobalt(III) compounds which prefer an octahedral coordination environment with a diamagnetic ground state.

Reaction of 0.25 equivalents of dry dioxygen with  $[\text{Bu}_4\text{N}]_2\mathbf{1}$  in acetonitrile- $d_3$  resulted in a rapid color change from orange to dark brown, and generation of  $[\text{Bu}_4\text{N}]_2\mathbf{3}$ - $d_2$  in 88% yield by  $^1\text{H}$  NMR spectroscopy with respect to  $[\text{Bu}_4\text{N}]_2\mathbf{1}$ . Use of excess dry dioxygen (1 atm) in the reaction with  $[\text{Bu}_4\text{N}]_2\mathbf{1}$  in acetonitrile produced  $[\text{Bu}_4\text{N}]\mathbf{2}\mathbf{3}$  in only 50% yield with respect to  $[\text{Bu}_4\text{N}]_2\mathbf{1}$ . This lower yield is probably due to oxidation of the cyanomethyl ligand of  $[\text{Bu}_4\text{N}]\mathbf{2}\mathbf{3}$  by the excess  $\text{O}_2$ , to form  $[\text{Bu}_4\text{N}]\mathbf{2}$  which was isolated from the reaction solution in 12% yield and identified by NMR spectroscopy. The complex  $[\text{Bu}_4\text{N}]\mathbf{2}\mathbf{3}$ , isolated as green crystals, was shown by X-ray crystallography to possess a cyanomethyl ligand (Fig. 1b). Thus, reaction of  $[\text{Bu}_4\text{N}]_2\mathbf{1}$  with  $\text{O}_2$  results in activation of the relatively strong C–H bond of acetonitrile ( $\text{BDE}_{\text{C-H}} = 96$  kcal mol<sup>-1</sup>,  $\text{p}K_{\text{a}} = 31.1$  in DMSO).

Interestingly, reactions of  $[\text{Bu}_4\text{N}]_2\mathbf{1}$  with oxo-transfer reagents also resulted in formation of  $[\text{Bu}_4\text{N}]\mathbf{2}\mathbf{3}$ . Thus, reaction of 0.5 of an equivalent of tetra-*n*-butylammonium periodate,  $[\text{Bu}_4\text{N}]\text{IO}_4$ , with  $[\text{Bu}_4\text{N}]_2\mathbf{1}$  in acetonitrile resulted in quantitative formation of  $[\text{Bu}_4\text{N}]\mathbf{2}\mathbf{3}$  after 30 min (by  $^1\text{H}$  NMR spectroscopy). A control experiment using potassium iodate ( $\text{KIO}_3$ ) and 18-crown-6 with  $[\text{Bu}_4\text{N}]_2\mathbf{1}$  in acetonitrile revealed no reaction over this time, demonstrating that all oxo-transfer reactivity is derived from the periodate anion. Similarly, reaction of 0.5 equivalents of PhIO with  $[\text{Bu}_4\text{N}]_2\mathbf{1}$  gave  $[\text{Bu}_4\text{N}]\mathbf{2}\mathbf{3}$  in 46% yield (by  $^1\text{H}$  NMR spectroscopy). The lower yield for this reaction is attributed to its heterogeneous nature.

Notably, Valentine and co-workers have shown that iodosylbenzene is activated as an oxo-transfer reagent in the presence of both redox-active and non-redox-active metal ions (e.g., Co, and Zn), without the generation of an oxo ligand at the metal center. In these cases, iodosylbenzene undergoes Lewis-acid activation toward oxo-transfer to olefins (epoxidation) in the presence of metal salts in acetonitrile solvent, apparently with no activation of the latter.<sup>9</sup> For comparison, a mixture of iodosylbenzene (1 equivalent),  $[\text{Bu}_4\text{N}]_2\mathbf{1}$ , and cyclohexene in acetonitrile gave no transformation of the olefin during complete conversion of  $[\text{Bu}_4\text{N}]_2\mathbf{1}$ , with formation of  $[\text{Bu}_4\text{N}]\mathbf{2}\mathbf{3}$  in 46% yield, as monitored by  $^1\text{H}$  NMR spectroscopy and gas-chromatography-mass-spectrometry (GC-MS). Thus, any intermediate formed by the interaction of iodosylbenzene with  $[\text{Bu}_4\text{N}]_2\mathbf{1}$  seems to have low electrophilicity and is unreactive toward cyclohexene. This appears to reflect the observed, low Lewis acidity for the cobalt(II) center of  $[\text{Bu}_4\text{N}]_2\mathbf{1}$ , with its strongly donating ligand and dianionic nature. Thus, Lewis acid activation of iodosylbenzene seems unlikely with  $[\text{Bu}_4\text{N}]_2\mathbf{1}$ , and the highly reducing nature of this complex is more consistent with a redox event and oxo-transfer from iodosylbenzene. Thus, the observed reaction chemistry appears to suggest that a cobalt oxo intermediate forms upon reaction with  $\text{O}_2$  or oxo-transfer reagents.

To investigate the nature of the C–H bond activation step, a competition experiment between toluene ( $\text{BDE}_{\text{C-H}} = 86$  kcal mol<sup>-1</sup>,  $\text{p}K_{\text{a}} = 41$  in DMSO) and acetonitrile- $d_3$  as substrates (1 : 1 molar mixture) was performed using PhIO or  $\text{O}_2$  as the

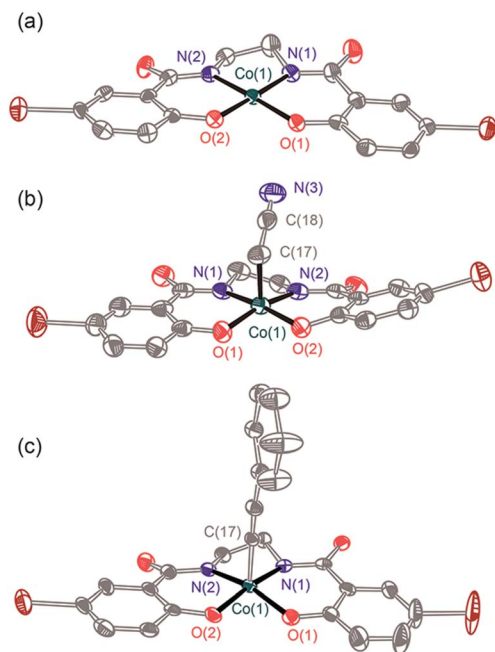


Fig. 1 ORTEP diagrams of (a)  $[\text{Bu}_4\text{N}]_2\mathbf{1}$ , (b)  $[\text{Bu}_4\text{N}]\mathbf{2}\mathbf{3}$ , and (c)  $[\text{Bu}_4\text{N}]\mathbf{2}\mathbf{4}$ . Thermal ellipsoids are drawn at 50%, and the solvent molecule,  $[\text{Bu}_4\text{N}]^+$  cations, and hydrogen atoms are omitted for clarity.



oxidant. Significantly,  $[\text{Bu}_4\text{N}]_2\text{3-d}_2$  was the only organocobalt species observed by  $^1\text{H}$  NMR spectroscopy, and no trace of a toluene-activated product was detected. By  $^2\text{H}$  NMR spectroscopy, the reaction mixture contained no detectable amounts of deuterated toluene products that might form *via* initial toluene activation, followed by metathesis with acetonitrile- $\text{d}_3$ . In addition, a competition experiment involving 10 equivalents of 9,10-dihydroanthracene, a more acidic substrate ( $\text{BDE}_{\text{C-H}} = 78 \text{ kcal mol}^{-1}$ ,  $\text{pK}_a = 30$  in DMSO),<sup>10</sup> in acetonitrile- $\text{d}_3$  solvent produced anthracene (13%) and 9,10-anthraquinone (12%) using PhIO or  $\text{O}_2$ , respectively, as oxidant.<sup>11</sup> The formation of 9,10-anthraquinone with  $\text{O}_2$  as the oxidant may result from reaction of  $^3\text{O}_2$  with the 9-anthracenyl radical formed by initial C-H bond abstraction.<sup>12</sup> Thus, C-H bond activations in this system appear to be promoted by acidic character in the C-H bond. This was further indicated by reactions of  $[\text{Bu}_4\text{N}]_2\text{1}$  in acetonitrile with  $\text{O}_2$  or PhIO in the presence of phenylacetylene (10 equivalents), which contains a very acidic but strong C-H bond ( $\text{BDE}_{\text{C-H}} \approx 133 \text{ kcal mol}^{-1}$ ,  $\text{pK}_a = 28$  in DMSO).<sup>13</sup> This reaction quantitatively (by  $^1\text{H}$  NMR spectroscopy) forms the diamagnetic, green cobalt alkynyl complex  $[\text{Bu}_4\text{N}]_2[(\text{BrHBA-Et})\text{Co-C}\equiv\text{CPh}]$  ( $[\text{Bu}_4\text{N}]_2\text{4}$ ,  $\nu_{\text{C}\equiv\text{C}} = 2106 \text{ cm}^{-1}$ ). The structure of  $[\text{Bu}_4\text{N}]_2\text{4}$  was confirmed by X-ray crystallography (Fig. 1c). The strong preference for more acidic substrates suggests that in the C-H bond activation step, proton transfer may precede electron transfer (*vide infra*).

A kinetic isotope effect (KIE) for reaction of acetonitrile in the presence of  $[\text{Bu}_4\text{N}]_2\text{1}$  and  $\text{O}_2$  was obtained from a competition experiment involving a 1 : 1 mixture of acetonitrile and acetonitrile- $\text{d}_3$ . Quantification of the  $[\text{Bu}_4\text{N}]_2\text{3}/[\text{Bu}_4\text{N}]_2\text{3-d}_2$  ratio by high-resolution electrospray mass spectrometry gave a KIE value of 3.3(2). Interestingly, the analogous reaction with PhIO as the oxidant provided a KIE value that is essentially identical, 3.6(2). This moderate primary KIE value is consistent with an early or late transition state for the C-H bond activation step, and heterolytic C-H bond cleavage. Coupled with the selectivities described above, these results suggest that a common intermediate is formed by reactions of PhIO or  $\text{O}_2$  with  $[\text{Bu}_4\text{N}]_2\text{1}$ , which activates C-H bonds by a heterolytic mechanism involving considerable proton-transfer character. Note that highly basic metal oxo complexes are expected to exhibit a moderate primary KIE in C-H bond activations.<sup>14</sup>

In an attempt to observe an intermediate in the  $\text{O}_2$ -mediated activation of acetonitrile, a 1 : 1 THF-MeCN solution of  $[\text{Bu}_4\text{N}]_2\text{1}$  at  $-63^\circ\text{C}$  was treated with  $\text{O}_2$  (1 atm) and the reaction progress was followed by UV-vis spectroscopy. After 10 min, a new absorbance at *ca.* 400–450 nm, which decayed over the course of 1 h ( $t_{1/2} \approx 35 \text{ min}$ ), was observed (Fig. 2). EPR spectroscopy (X-band, 77 K; ESI, Fig. S4†) was used to characterize this intermediate, generated by addition of dry  $\text{O}_2$  at room temperature to an *n*-butyronitrile solution of  $[\text{Bu}_4\text{N}]_2\text{1}$  in the EPR tube. This experiment allowed observation of a new  $S = 1/2$  signal with hyperfine coupling to  $^{59}\text{Co}$  ( $g_1 = 2.026$ ,  $g_2 = 2.028$ ,  $g_3 = 2.13$ ,  $|A_1| = 57 \text{ MHz}$ ,  $|A_2| = 43 \text{ MHz}$ ,  $|A_3| = 85 \text{ MHz}$ ), the appearance of which after 30 seconds was accompanied by elimination of the signal for  $[\text{Bu}_4\text{N}]_2\text{1}$ . After 10 minutes at room temperature, the intensity of the new signal diminished

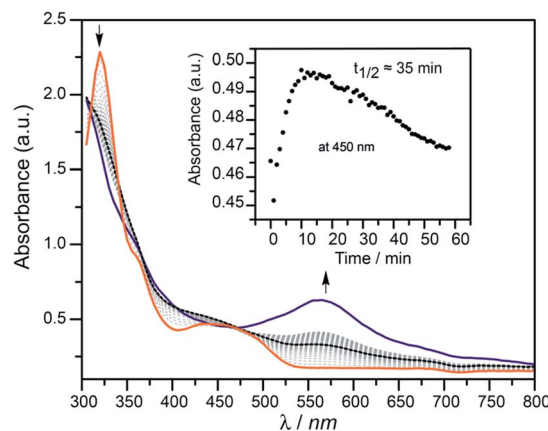
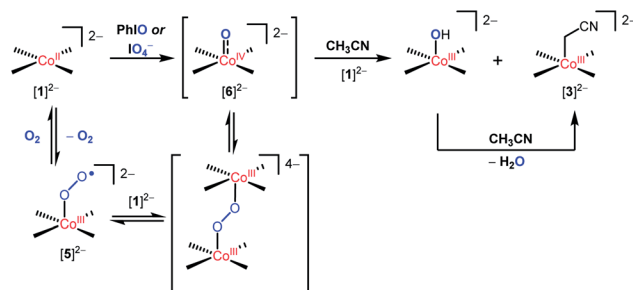


Fig. 2 UV-vis time trace of  $[\text{Bu}_4\text{N}]_2\text{1}$  reaction with 1 atm  $\text{O}_2$  at  $-63^\circ\text{C}$  in 1 : 1 MeCN-THF. Orange trace is  $[\text{Bu}_4\text{N}]_2\text{1}$ ; purple trace is at  $t = 60 \text{ min}$ ; dashed-black trace is  $t = 10 \text{ min}$ .

(to  $\sim 10\%$  of the original intensity, by integration of the EPR signal) with no appearance of new signals, consistent with the formation of EPR-silent products. However, when the solution was degassed by a freeze-pump-thaw cycle after acquisition of the first spectrum, the  $S = 1/2$  signal diminished and the signal for  $[\text{Bu}_4\text{N}]_2\text{1}$  increased (ESI, Fig. S5†). This behavior is consistent with reversible  $\text{O}_2$  coordination to the cobalt(II) center to form the  $\eta^1$ -superoxo complex  $[\text{Bu}_4\text{N}]_2[(\text{BrHBA-Et})\text{Co}(\text{O}_2)]$ ,  $[\text{Bu}_4\text{N}]_2\text{5}$  (Scheme 2).<sup>4</sup> In addition, analysis of the reaction mixture of  $[\text{Me}_4\text{N}]_2\text{1}$  with  $\text{O}_2$  in acetonitrile after approximately 10 seconds at room temperature by high-resolution ESI-MS revealed the presence of a dianion with  $m/z = 264.42$ , and an isotopic distribution consistent with the terminal cobalt(IV) oxo complex  $[\text{Bu}_4\text{N}]_2[(\text{BrHBA-Et})\text{CoO}]$ ,  $[\text{Bu}_4\text{N}]_2\text{6}$  (ESI, Fig. S4†).

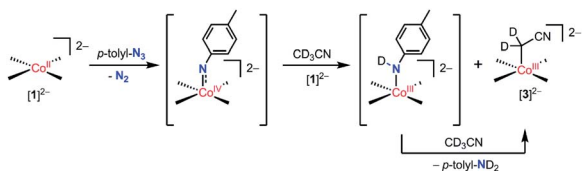
The observations of  $[\text{Bu}_4\text{N}]_2\text{5}$  and  $[\text{Bu}_4\text{N}]_2\text{6}$  implicate these species as potential intermediates that directly engage in C-H bond-cleavage reactions. However, the results described above are most consistent with involvement of the oxo complex  $[\text{6}]^{2-}$  in this chemistry. Firstly, metal superoxo complexes often exhibit much higher  $k_{\text{H}}/k_{\text{D}}$  values in intermolecular C-H bond activations (a range of  $k_{\text{H}}/k_{\text{D}} = 6.3$  to 50 is typical).<sup>15</sup> The substrate competition experiments are consistent with initial proton abstraction from a C-H bond, but the  $\text{pK}_a$  of hydrogen superoxide ( $\text{pK}_a = 12$  in DMF)<sup>16,17</sup> suggests that such species



Scheme 2 Proposed mechanism for the formation of  $[\text{3}]^{2-}$  by the reaction of  $[\text{1}]^{2-}$  with  $\text{O}_2$  or oxo-transfer reagents.







Scheme 3 Proposed mechanism for the formation of  $[3]^{2-}$  by the reaction of  $[1]^{2-}$  with tolyl azide.

should not be basic enough to accomplish such deprotonations. Furthermore, the observed reaction chemistry for  $O_2$  closely parallels that observed with oxo-transfer reagents PhIO and  $IO_4^-$ , suggesting a cobalt(IV) oxo species as a common intermediate. Thus, the reaction with  $O_2$  presumably involves binding of cobalt(II) to the initially formed superoxo complex  $[5]^{2-}$ , followed by O–O bond cleavage to generate the oxo complex  $[6]^{2-}$ . This oxo complex is presumed to react with hydrocarbons *via* proton- and electron-transfers to produce hydroxide and the cobalt(III) complex  $[2]^{2-}$ . This would generate the cyanomethyl radical  $NCCH_2^{\cdot}$ , and rapid trapping of this species by  $[1]^{2-}$  would give  $[3]^{2-}$ . The cobalt(III) hydroxide species, proposed as the direct product of a proton-coupled-electron-transfer to  $[6]^{2-}$ , is expected to provide a second pathway to the  $[3]^{2-}$  product, *via* deprotonation of acetonitrile. This hypothesis is supported by the observed reaction of  $[2]^{2-}$  with (18-crown-6)KOH in acetonitrile over 1 h, to give  $[3]^{2-}$  in quantitative yield.

The reaction of  $[^nBu_4N]_21$  with the oxo-transfer reagents PhIO and  $IO_4^-$  suggest the possibility of a putative cobalt(IV) oxo complex. Consistent with this hypothesis,  $[^nBu_4N]_21$  was observed to react with *p*-tolyl azide, a nitrene transfer reagent, in acetonitrile- $d_3$  to cleanly produce  $[^nBu_4N]_23$  and 1 equiv of toluidine- $d_2$  (by  $^1H$  NMR and  $^2H$  NMR spectroscopy). This reaction is tentatively proposed to proceed *via* a cobalt(IV) imido species and a mechanism analogous to that proposed above for the cobalt(IV) oxo species (Scheme 3).

## Conclusions

In summary, the reaction of  $O_2$  with  $[^nBu_4N]_21$  forms a cyanomethylcobalt(III) complex,  $[^nBu_4N]_23$ , that results from an intermolecular C–H bond activation of acetonitrile. Oxo- and nitrene-transfer reagents are observed to induce the same reactivity, suggesting that cobalt(IV)-oxo and -imido species are key intermediates. Note that Schaefer and coworkers reported that, in the presence of  $O_2$ , a (salen)cobalt(II) species activates acetone to form a Co–C bond. No mechanistic details were provided, but this process may proceed *via* a cobalt-oxo intermediate that abstracts proton from acetone (which is about 7 orders of magnitude more acidic than acetonitrile).<sup>18</sup> The well-behaved system described above is expected to provide opportunities to establish mechanistic details for  $O_2$  activation by cobalt(II), and perhaps the microscopic reverse, O–O bond formation. Along these lines, future efforts will target kinetic and low-temperature spectroscopic studies to better characterize the intermediates resulting from  $O_2$  activation.

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