

Efficient C–H bond activations *via* O₂ cleavage by a dianionic cobalt(II) complex†Cite this: *Chem. Sci.*, 2014, 5, 2874Andy I. Nguyen,^a Ryan G. Hadt,^b Edward I. Solomon^b and T. Don Tilley^{*a}

A dianionic, square planar cobalt(II) complex reacts with O₂ 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_a 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 O₂ or PhIO. The possible involvement of a cobalt(IV) oxo species in this chemistry is discussed.

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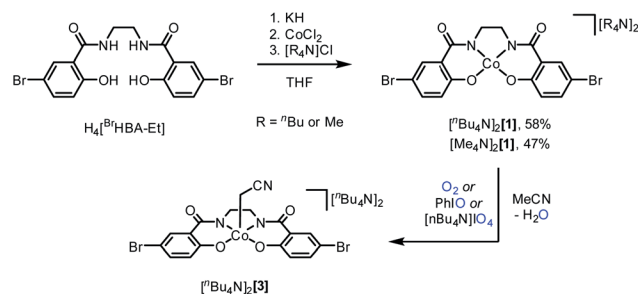
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Introduction

An important challenge for the development of new catalytic oxidations is the utilization of O₂ 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.¹ Much of this chemistry is thought to proceed *via* peroxy intermediates that initiate the generation of organic radicals.² However, high-valent cobalt oxo intermediates have been postulated for certain oxidations, such as benzylic alcohol oxidation, amine oxidation, and epoxidation.¹ Despite abundant circumstantial evidence for cobalt-mediated O₂ cleavage, there has been no observation of a cobalt oxo species as the direct product of this type of O₂ activation. Notably, the generation of a cobalt(IV) oxo intermediate *via* O₂ cleavage would seem to be difficult given ligand field arguments,³ and the fact that numerous cobalt(II) complexes have been shown to reversibly bind O₂ to give superoxo or μ -peroxo complexes without O₂ cleavage.⁶

This contribution describes attempts to promote O–O bond cleavage in a μ -peroxo intermediate to access a high-valent oxo species, with use of a tetraanionic ligand. The tetraanionic ligand ^{Br}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 [nBu₄N]₂[1], [Me₄N]₂[1], and [nBu₄N]₂[3].

shown to support a number of metal complexes in high oxidation states.⁷ 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 O₂. 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 complexes⁵ may be generated in these cases. Most importantly, this report describes a cobalt system that utilizes O₂ cleavage in promoting unusual C–H bond activations.

Results and discussion

Deprotonation of (^{Br}HBA-Et)₄H₄, *N,N'*-(ethane-1,2-diyl)bis(5-bromo-2-hydroxybenzamide), with four equivalents of KH in THF, followed by treatment with CoCl₂ and then salt metathesis with a tetraalkylammonium (ⁿBu₄N⁺ or Me₄N⁺) chloride gave the dianionic complexes [ⁿBu₄N]₂[(^{Br}HBA-Et)₂Co] ([ⁿBu₄N]₂[1]) and [Me₄N]₂[(^{Br}HBA-Et)₂Co] ([Me₄N]₂[1]) as orange, crystalline solids in 58% and 47% yields, respectively (Scheme 1). The complex [ⁿBu₄N]₂[1] is a low spin, *S* = 1/2 Co(II) complex, as demonstrated by the solution magnetic moment (1.98 μ_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}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^{8a} ($E_{1/2} = +0.25$ V vs. NHE), porphyrin^{8b} ($E_{1/2} = +0.68$ V vs. NHE), corrole^{8c} ($E_{1/2} = +0.03$ V vs. NHE), 1,1'-(ethane-1,2-diyl)bis(3-*tert*-butylurea)^{4a} ($E_{1/2} = -0.086$ V vs. NHE), and 2,2',2'-nitrilo-tris(*N*-isopropylacetamide)^{4b} ($E_{1/2} = +0.44$ 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⁻¹ cm⁻¹; 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 $[\text{Bu}_4\text{N}]_2\mathbf{3}$ in 88% yield by ^1H 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 $[\text{Bu}_4\text{N}]\mathbf{2}$ 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 $[\text{Bu}_4\text{N}]\mathbf{2}$ by the excess 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 $[\text{Bu}_4\text{N}]\mathbf{2}$, 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 O_2 results in activation of the relatively strong C–H bond of acetonitrile ($\text{BDE}_{\text{C-H}} = 96$ kcal mol⁻¹, $\text{p}K_{\text{a}} = 31.1$ in DMSO).

Interestingly, reactions of $[\text{Bu}_4\text{N}]_2\mathbf{1}$ with oxo-transfer reagents also resulted in formation of $[\text{Bu}_4\text{N}]\mathbf{2}$. 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 $[\text{Bu}_4\text{N}]\mathbf{2}$ after 30 min (by ^1H NMR spectroscopy). A control experiment using potassium iodate (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 $[\text{Bu}_4\text{N}]\mathbf{2}$ in 46% yield (by ^1H 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.⁹ 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 $[\text{Bu}_4\text{N}]\mathbf{2}$ in 46% yield, as monitored by ^1H 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 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⁻¹, $\text{p}K_{\text{a}} = 41$ in DMSO) and acetonitrile- d_3 as substrates (1 : 1 molar mixture) was performed using PhIO or O_2 as the

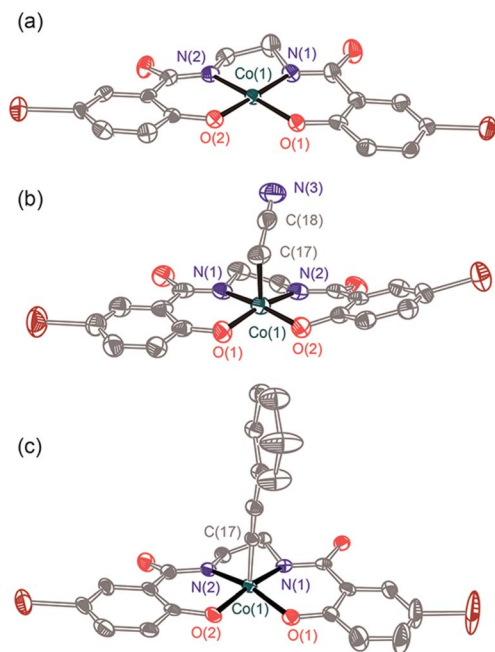


Fig. 1 ORTEP diagrams of (a) $[\text{Bu}_4\text{N}]_2\mathbf{1}$, (b) $[\text{Bu}_4\text{N}]\mathbf{2}$, and (c) $[\text{Bu}_4\text{N}]\mathbf{2}$. Thermal ellipsoids are drawn at 50%, and the solvent molecule, $[\text{Bu}_4\text{N}]^+$ cations, and hydrogen atoms are omitted for clarity.



oxidant. Significantly, $[\text{Bu}_4\text{N}]_2\text{3-d}_2$ was the only organocobalt species observed by ^1H NMR spectroscopy, and no trace of a toluene-activated product was detected. By ^2H 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- 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),¹⁰ in acetonitrile- d_3 solvent produced anthracene (13%) and 9,10-anthraquinone (12%) using PhIO or O_2 , respectively, as oxidant.¹¹ The formation of 9,10-anthraquinone with 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.¹² 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 O_2 or PhIO in the presence of phenylacetylene (10 equivalents), which contains a very acidic but strong C-H bond ($\text{BDE}_{\text{C-H}} = \sim 133 \text{ kcal mol}^{-1}$, $\text{pK}_a = 28$ in DMSO).¹³ This reaction quantitatively (by ^1H 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 O_2 was obtained from a competition experiment involving a 1 : 1 mixture of acetonitrile and acetonitrile- 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 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.¹⁴

In an attempt to observe an intermediate in the O_2 -mediated activation of acetonitrile, a 1 : 1 THF-MeCN solution of $[\text{Bu}_4\text{N}]_2\text{1}$ at -63°C was treated with 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 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}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

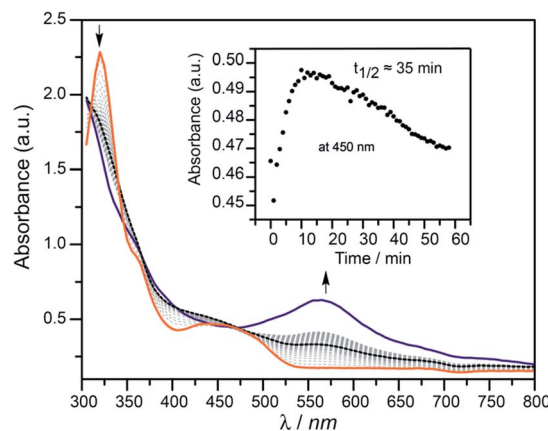
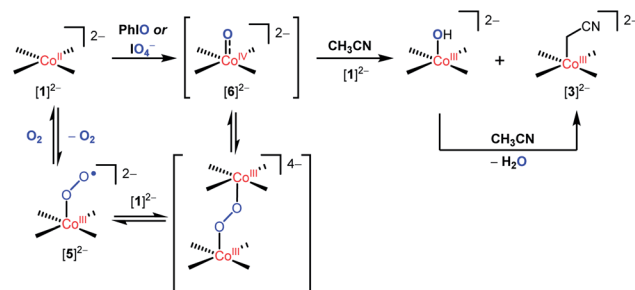


Fig. 2 UV-vis time trace of $[\text{Bu}_4\text{N}]_2\text{1}$ reaction with 1 atm O_2 at -63°C in 1 : 1 MeCN-THF. Orange trace is $[\text{Bu}_4\text{N}]_2\text{1}$; purple trace is at $t = 60 \text{ min}$; dashed-black trace is $t = 10 \text{ min}$.

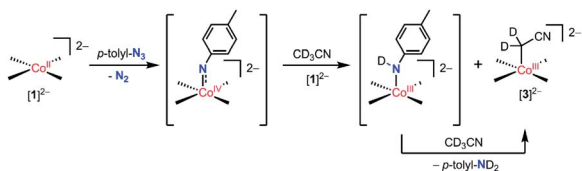
(to $\sim 10\%$ of the original intensity, by integration of the EPR signal) with no appearance of new signals, consistent with the formation of EPR-silent products. However, when the solution was degassed by a freeze-pump-thaw cycle after acquisition of the first spectrum, the $S = 1/2$ signal diminished and the signal for $[\text{Bu}_4\text{N}]_2\text{1}$ increased (ESI, Fig. S5†). This behavior is consistent with reversible O_2 coordination to the cobalt(II) center to form the η^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).⁴ In addition, analysis of the reaction mixture of $[\text{Me}_4\text{N}]_2\text{1}$ with 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).¹⁵ The substrate competition experiments are consistent with initial proton abstraction from a C-H bond, but the pK_a of hydrogen superoxide ($\text{pK}_a = 12$ in DMF)^{16,17} suggests that such species



Scheme 2 Proposed mechanism for the formation of $[\text{3}]^{2-}$ by the reaction of $[\text{1}]^{2-}$ with 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).¹⁸ 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.

Acknowledgements

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