

Efficient C–H bond activations *via* O₂ cleavage by a dianionic cobalt(II) complex†

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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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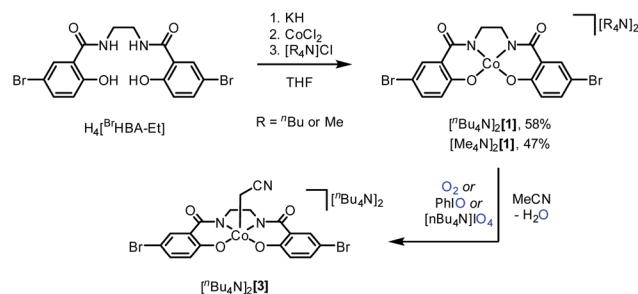
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Introduction

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]₂1, [^{Me}₄N]₂1, and [ⁿBu₄N]₂3.

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]₂1) and [Me₄N]₂[(^{Br}HBA-Et)₂Co] ([Me₄N]₂1) as orange, crystalline solids in 58% and 47% yields, respectively (Scheme 1). The complex [ⁿBu₄N]₂1 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)^{8d} ($E_{1/2} = -0.086$ V vs. NHE), and 2,2',2'-nitriolo-tris(*N*-isopropylacetamide)^{8e} ($E_{1/2} = +0.44$ 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 μ_{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 $[\text{Bu}_4\text{N}]_2\mathbf{3}$ 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 $[\text{Bu}_4\text{N}]_2\mathbf{3}$ by the excess O₂, 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 $[\text{Bu}_4\text{N}]_2\mathbf{3}$, 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 O₂ 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 $[\text{Bu}_4\text{N}]_2\mathbf{3}$. 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 $[\text{Bu}_4\text{N}]_2\mathbf{3}$ after 30 min (by ¹H NMR spectroscopy). A control experiment using potassium iodate (KIO₃) 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 $[\text{Bu}_4\text{N}]_2\mathbf{3}$ 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 $[\text{Bu}_4\text{N}]_2\mathbf{3}$ 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 O₂ 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 O₂ as the

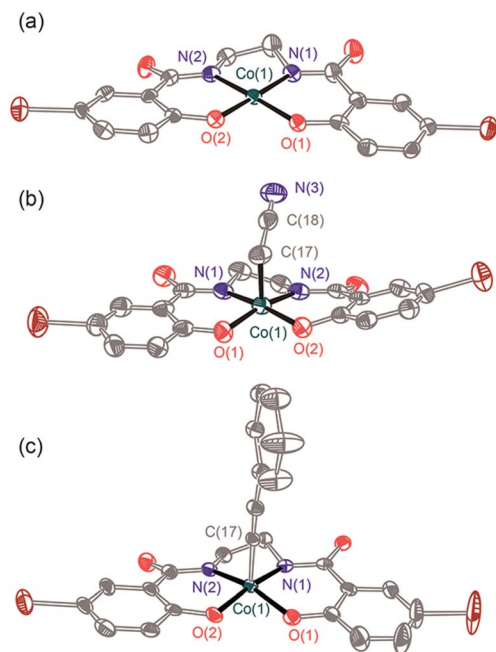


Fig. 1 ORTEP diagrams of (a) $[\text{Bu}_4\text{N}]_2\mathbf{1}$, (b) $[\text{Bu}_4\text{N}]_2\mathbf{3}$, and (c) $[\text{Bu}_4\text{N}]_2\mathbf{4}$. Thermal ellipsoids are drawn at 50%, and the solvent molecule, $[\text{Bu}_4\text{N}]^+$ cations, and hydrogen atoms are omitted for clarity.



oxidant. Significantly, $[^n\text{Bu}_4\text{N}]_2\text{3-d}_2$ 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 ($\text{BDE}_{\text{C-H}} = 78 \text{ kcal mol}^{-1}$, $\text{p}K_{\text{a}} = 30$ 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 $[^n\text{Bu}_4\text{N}]_2\text{1}$ in acetonitrile with O_2 or PhIO in the presence of phenylacetylene (10 equivalents), which contains a very acidic but strong C-H bond ($\text{BDE}_{\text{C-H}} \sim 133 \text{ kcal mol}^{-1}$, $\text{p}K_{\text{a}} = 28$ in DMSO).¹³ This reaction quantitatively (by ^1H NMR spectroscopy) forms the diamagnetic, green cobalt alkynyl complex $[^n\text{Bu}_4\text{N}]_2[(^{\text{Br}}\text{HBA-Et})\text{Co-C}\equiv\text{CPh}]$ ($[^n\text{Bu}_4\text{N}]_2\text{4}$, $\nu_{\text{C}\equiv\text{C}} = 2106 \text{ cm}^{-1}$). The structure of $[^n\text{Bu}_4\text{N}]_2\text{4}$ 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 $[^n\text{Bu}_4\text{N}]_2\text{1}$ and O_2 was obtained from a competition experiment involving a 1 : 1 mixture of acetonitrile and acetonitrile- d_3 . Quantification of the $[^n\text{Bu}_4\text{N}]_2\text{3}/[^n\text{Bu}_4\text{N}]_2\text{3-d}_2$ 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 $[^n\text{Bu}_4\text{N}]_2\text{1}$, 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 $[^n\text{Bu}_4\text{N}]_2\text{1}$ 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 $[^n\text{Bu}_4\text{N}]_2\text{1}$ 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 $[^n\text{Bu}_4\text{N}]_2\text{1}$. After 10 minutes at room temperature, the intensity of the new signal diminished

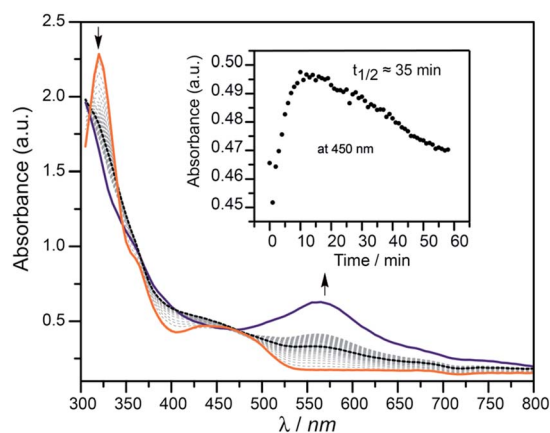
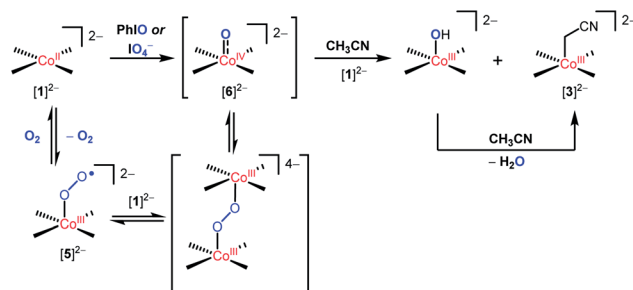


Fig. 2 UV-vis time trace of $[^n\text{Bu}_4\text{N}]_2\text{1}$ reaction with 1 atm O_2 at -63°C in 1 : 1 MeCN-THF. Orange trace is $[^n\text{Bu}_4\text{N}]_2\text{1}$; purple trace is at $t = 60 \text{ min}$; dashed-black trace is $t = 10 \text{ min}$.

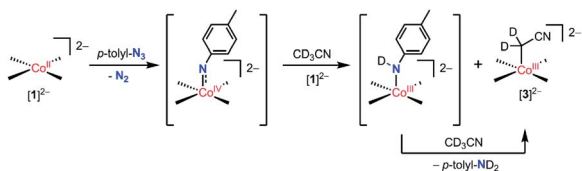
(to $\sim 10\%$ of the original intensity, by integration of the EPR signal) with no appearance of new signals, consistent with the formation of EPR-silent products. However, when the solution was degassed by a freeze-pump-thaw cycle after acquisition of the first spectrum, the $S = 1/2$ signal diminished and the signal for $[^n\text{Bu}_4\text{N}]_2\text{1}$ 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 $[^n\text{Bu}_4\text{N}]_2[(^{\text{Br}}\text{HBA-Et})\text{Co}(\text{O}_2)]$, $[^n\text{Bu}_4\text{N}]_2\text{5}$ (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 $[^n\text{Bu}_4\text{N}]_2[(^{\text{Br}}\text{HBA-Et})\text{CoO}]$, $[^n\text{Bu}_4\text{N}]_2\text{6}$ (ESI, Fig. S4†).

The observations of $[^n\text{Bu}_4\text{N}]_2\text{5}$ and $[^n\text{Bu}_4\text{N}]_2\text{6}$ 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 $[6]^{2-}$ 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 $\text{p}K_{\text{a}}$ of hydrogen superoxide ($\text{p}K_{\text{a}} = 12$ in DMF)^{16,17} suggests that such species



Scheme 2 Proposed mechanism for the formation of $[3]^{2-}$ by the reaction of $[1]^{2-}$ 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 $[^nBu_4N]_2\mathbf{1}$ with the oxo-transfer reagents PhIO and IO_4^- suggest the possibility of a putative cobalt(IV) oxo complex. Consistent with this hypothesis, $[^nBu_4N]_2\mathbf{1}$ was observed to react with *p*-tolyl azide, a nitrene transfer reagent, in acetonitrile- d_3 to cleanly produce $[^nBu_4N]_2\mathbf{3}$ 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 $[^nBu_4N]_2\mathbf{1}$ forms a cyanomethylcobalt(III) complex, $[^nBu_4N]_2\mathbf{3}$, 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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Notes and references

- (a) R. Chakrabarty, P. Sarmah, B. Saha, S. Chakravorty and B. K. Das, *Inorg. Chem.*, 2009, **48**, 6371–6379; (b) R. Chakrabarty, S. J. Bora and B. K. Das, *Inorg. Chem.*, 2007, **46**, 9450–9462; (c) S. L. Jain and D. Sain, *Angew. Chem., Int. Ed.*, 2003, **42**, 1265–1267; (d) B. L. Caetano, L. A. Rocha, E. Molina, Z. N. Rocha, G. Ricci, P. S. Calefi, O. J. de Lima, C. Mello, E. J. Nassar and K. J. Ciuffi, *Appl. Catal., A*, 2006, **311**, 122–134; (e) Y. J. Song, M. Y. Hyun, J. H. Lee, H. G. Lee, J. H. Kim, S. P. Jang, J. Y. Noh, Y. Kim, S. Kim, S. J. Lee and C. Kim, *Chem.–Eur. J.*, 2012, **18**, 6094–6101; (f) J. D. Koola and J. K. Kochi, *J. Org. Chem.*, 1987, **52**, 4545–4553; (g) F. A. Chavez, J. M. Rowland, M. M. Olmstead and P. K. Mascharak, *J. Am. Chem. Soc.*, 1998, **120**, 9015–9027; (h) R. P. Hanzlik and D. Williamson, *J. Am. Chem. Soc.*, 1976, **98**, 6570–6573; (i) A. Sobkowiak and D. T. Sawyer, *J. Am. Chem. Soc.*, 1991, **113**, 9520–9523; (j) T. Penniyamurthy, B. Bhatia, M. M. Reddy, G. C. Maikap and J. Iqbal, *Tetrahedron*, 1997, **53**, 7649–7670; (k) S. Fukuzumi, K. Okamoto, Y. Tokuda, C. P. Gros and R. Guilard, *J. Am. Chem. Soc.*, 2004, **126**, 17059–17066.
- (a) R. A. Sheldon and J. K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, 1981; (b) F. A. Chavez and P. K. Mascharak, *Acc. Chem. Res.*, 2000, **33**, 539–545.
- J. R. Winkler and H. B. Gray, *Struct. Bonding*, 2012, **142**, 17–28.
- (a) P. L. Larsen, T. J. Parolin, D. R. Powell, M. P. Hendrich and A. S. Borovik, *Angew. Chem., Int. Ed.*, 2003, **42**, 85–89; (b) R. L. Lucas, M. K. Zart, J. Murkerjee, T. N. Sorrell, D. R. Powell and A. S. Borovik, *J. Am. Chem. Soc.*, 2006, **128**, 15476–15489.
- (a) K. H. Hopmann and A. Ghosh, *ACS Catal.*, 2011, **1**, 597–600; (b) V. Lyakovskyy, A. I. Olivios Suarez, H. Lu, H. Jiang, P. X. Zhang and B. de Bruin, *J. Am. Chem. Soc.*, 2011, **133**, 12264–12273.
- (a) J. R. Fritch, G. G. Christoph and W. P. Schaefer, *Inorg. Chem.*, 1973, **12**, 2170–2175; (b) W. P. Schaefer and R. E. Marsh, *J. Am. Chem. Soc.*, 1966, **88**, 178–179; (c) R. S. Gall, J. F. Rogers, W. P. Schaefer and G. G. Christoph, *J. Am. Chem. Soc.*, 1976, 5135–5144; (d) C. Floriani and



- F. Calderazzo, *J. Chem. Soc. A*, 1969, 946; (e) J. P. Collman, R. R. Gagne, J. Kouba and H. Ljusberg-Wahren, *J. Am. Chem. Soc.*, 1974, **96**, 6800–6802.
- 7 (a) T. J. Collins, R. D. Powell, C. Slebodnick and E. S. Uffelman, *J. Am. Chem. Soc.*, 1990, **112**, 899–901; (b) F. Tiago de Oliveira, A. Chanda, D. Banerjee, X. Shan, S. Mondal, L. Que, Jr, E. L. Bominaar, E. Münck and T. J. Collins, *Science*, 2007, **315**, 835–838; (c) F. C. Anson, T. J. Collins, R. J. Coots, S. L. Gipson and T. G. Richmond, *J. Am. Chem. Soc.*, 1984, **106**, 5037–5038; (d) F. C. Anson, T. J. Collins, T. G. Richmond, B. D. Santarsiero, J. E. Toth and B. G. R. T. Treco, *J. Am. Chem. Soc.*, 1987, 2974–2979; (e) T. J. Collins, T. R. Nichols and E. S. Uffelman, *J. Am. Chem. Soc.*, 1991, **113**, 4708–4709.
- 8 (a) B. Ortiz and S.-M. Park, *Bull. Korean Chem. Soc.*, 2000, **21**, 405–411; (b) C. Shi and F. C. Anson, *Inorg. Chem.*, 1998, **37**, 1037–1043; (c) K. M. Kadish, J. Shen, L. Frémond, P. Chen, M. El Ojaimi, M. Chkounda, C. P. Gros, J.-M. Barbe, K. Ohkubo, S. Fukuzumi and R. Guilard, *Inorg. Chem.*, 2008, **47**, 6726–6737.
- 9 (a) R. B. VanAtta, C. C. Franklin and J. S. Valentine, *Inorg. Chem.*, 1984, **23**, 4121–4123; (b) W. Nam and J. S. Valentine, *J. Am. Chem. Soc.*, 1990, **112**, 4977–4979; (c) Y. Yang, F. Diederich and J. S. Valentine, *J. Am. Chem. Soc.*, 1991, **113**, 7195–7205.
- 10 F. G. Bordwell, J.-P. Cheng, G.-Z. Ji, A. V. Satish and X. Zhang, *J. Am. Chem. Soc.*, 1991, **113**, 9790–9795.
- 11 The remaining products were $[^n\text{Bu}_4\text{N}]_2\text{3}$ and $[^n\text{Bu}_4\text{N}]_2$ formed by the activation of acetonitrile.
- 12 J. O. Hawthorne, K. A. Schowalter, A. W. Simon, M. H. Wilt and M. S. Morgan, *Oxidation of Organic Compounds*, American Chemical Society, 1968, vol. 75, pp. 203–215.
- 13 Y.-R. Luo, *Comprehensive Handbook of Chemical Bond Energies*, Taylor & Francis, 2006.
- 14 T. H. Parsell, M.-Y. Yang and A. S. Borovik, *J. Am. Chem. Soc.*, 2009, **131**, 2762–2763.
- 15 (a) J. Cho, J. Woo and W. Nam, *J. Am. Chem. Soc.*, 2010, **132**, 5958–5959; (b) R. L. Peterson, R. A. Himes, H. Kotani, T. Suenobu, L. Tian, M. A. Siegler, E. I. Solomon, S. Fukuzumi and K. D. Karlin, *J. Am. Chem. Soc.*, 2011, **133**, 1702–1705; (c) J. P. Klinman, *Chem. Rev.*, 1996, 2541–2561; (d) S. R. Prigge, B. A. Eipper, R. E. Mains and L. M. Amzel, *Science*, 2004, **304**, 864–867; (e) Y.-M. Lee, S. Hong, Y. Morimoto, W. Shin, S. Fukuzumi and W. Nam, *J. Am. Chem. Soc.*, 2010, **132**, 10668–10670; (f) K.-B. Cho, H. Kang, J. Woo, J. P. Park, M. S. Seo, J. Cho and W. Nam, *Inorg. Chem.*, 2014, **53**, 645–652.
- 16 D.-H. Chin, G. Chiericato, E. J. Nanni Jr. and D. T. Sawyer, *J. Am. Chem. Soc.*, 1982, **104**, 1296–1299.
- 17 The $\text{p}K_{\text{a}}$ values in DMF are comparable to values in DMSO. F. Maran, D. Celadon, M. G. Severin and E. Vianello, *J. Am. Chem. Soc.*, 1991, **113**, 9320–9329.
- 18 W. P. Schaefer, R. Waltzman and B. T. Huie, *J. Am. Chem. Soc.*, 1978, **100**, 5063–5067.

