Rapid and ordered carbonylation and oxygenation of a cobalt(II) methyl

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Recommended Citation  
Reinig, Regina R.; Fought, Ellie L.; Ellern, Arkady; Windus, Theresa Lynn; and Sadow, Aaron D., "Rapid and ordered carbonylation and oxygenation of a cobalt(II) methyl" (2017). *Ames Laboratory Accepted Manuscripts*. 44.  
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Abstract
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Rapid and ordered carbonylation and oxygenation of a cobalt(II) methyl

Regina R. Reinig, Ellie L. Fought, Arkady Ellern, Theresa L. Windus, and Aaron D. Sadow

The oxidative carbonylation of $\text{To}^\text{M} \text{CoMe}$ (1; $\text{To}^\text{M} = \text{tris}(4,4$-dimethyl-2-oxazolyl)phenylborate) involves its rapid, reversible reaction with CO to form $\text{To}^\text{M} \text{Co(C(O)Me)CO}$ (2) followed by rapid reaction with $\text{O}_2$ yielding $\text{To}^\text{M} \text{CoOAc}$ (3), in contrast to the slow direct carboxylation of $\text{To}^\text{M} \text{CoMe}$ by CO$_2$.

Catalytic oxidative carbonylation reactions are generally proposed to involve metal-based oxidations. Consider, for example, catalytic production of benzoic acid from benzene, CO, and an oxidant. Palladium(II) mediates the combination of the arene, CO and water to afford benzoic acid, with palladium(0) generated as a byproduct. Then, the suggested catalytic cycle is completed by metal-based oxidation, rather than oxygenation of an acylpalladium intermediate. Interestingly, the proposed biosynthesis of the energy-carriers acetate or acetyl-CoA follows a conceptually similar outline, involving insertion of CO into a metal-methyl bond followed by metal-based oxidation and thiolysis (reductive elimination of the C–S bond) to form acetyl-CoA.

Oxidation of metal-carbon bonds (or the reductive coupling followed by oxidation pathway) is key to many hydrocarbon functionalization schemes. On the other hand, acetate may be derived directly from CO$_2$ and methyl transition metal compounds. Although CO$_2$ is a substrate for acetogenesis, it is reduced by carbon monoxide dehydrogenase (CODH) to CO prior to its interaction with the metal-methyl. Likewise, oxidative carbonylation yields are sometimes improved under CO$_2$, yet CO is the ultimate source of carbonyl in the transformation. The distinction between CO/[O] in oxidative carbonylation versus CO$_2$ in carboxylation, in terms of their kinetic and thermodynamic parameters, is critical for the development of sustainable processes that utilize C$_1$ starting materials, such as methane, carbon monoxide, or carbon dioxide, because the processes must balance atom and energy economy with rate, yield, and selectivity to be viable.

Four-coordinate organocobalt(II) species are expected to be reactive toward CO, O$_2$ and CO$_2$ based on studies of bulky $\text{Tp}^\text{R,HR}$, $\text{Tp}^\text{Pr}$, $\text{Tp}^\text{Bu}$, and $\text{PhTt}^\text{Bu}$ ($\text{Tp}^\text{R,R} = \text{HB(3R,5R',N}_2\text{C}_2\text{H}_4\text{R}_2)\text{C}_6$; $\text{PhTt}^\text{Bu} = \text{PhB(CH}_3\text{S}_2\text{Bu})_3$). These reactions give either reduction or carbonylation products, oxidation or oxygenation, or carboxylation, respectively. CO affects one-electron reductions to give $\text{Tp}^\text{R,HR} \text{CoCO}$ or $\text{Tp}^\text{Pr,Me} \text{CoCO}$; and while carboxylation to cobalt(II) acyl species is also reported.

Oxidation of organocobalt(II) to a cobalt alkyl peroxyxide could follow our observations for related zinc compounds, where kinetics of zinc alkyl oxygenation to alkylperoxides or alkoxides are consistent with a turnover-limiting bimolecular substitution of zinc alkyl with alkylperoxo radical ($\text{S}_\text{I} \text{II}$). This oxygenation pathway avoids metal-centered oxidation. Indeed, alkylperoxy and acetylperoxy metal compounds are intermediates in oxygenation reactions. In the present work, a comparison of oxygenation, carbonylation and oxygenation, and carboxylation of $\text{To}^\text{M} \text{CoMe}$ (1; $\text{To}^\text{M} = \text{tris}(4,4$-dimethyl-2-oxazolyl)phenylborate) reveals that the kinetically favored pathway selectively produces acetate through an ordered, multistep sequence.

The reaction of $\text{To}^\text{M} \text{CoCl}$ and MeLi at room temperature affords $\text{To}^\text{M} \text{CoMe}$ as a deep aquamarine solid (equation (1)).

\[
\text{Ph-B} + \text{CoCl} + \text{MeLi} \xrightarrow{\text{Et}_2\text{O}} \text{Ph-B} \text{CoMe}
\]

The $^1$H NMR spectrum of 1 showed signals at 15.44 and –12.05 ppm assigned to the oxazoline’s methylene and methyl groups, respectively, on the basis of integration. These signals were shifted downfield compared to $\text{To}^\text{CoCl}$ (24.88 and 8.38 ppm, respectively). A resonance for the methyl ligand was not detected. The $^1$B signal at 100 ppm was significantly shifted in comparison to the peak of $\text{To}^\text{CoCl}$ (~29 ppm). A single $\nu_{\text{C=O}}$ band at 1594 cm$^{-1}$ in the IR spectrum suggested tridentate $\text{To}^\text{Co}$ coordination. The UV-Vis spectrum of 1 (in Et$_2$O)
revealed intense absorptions at 346 (ε: 1412 M⁻¹ cm⁻¹) and 697 (ε: 1078 M⁻¹ cm⁻¹) assigned to charge transfer transitions associated with the alkyl ligand on the basis of their large molar absorptivities (>1000 M⁻¹ cm⁻¹) and the lack of similar signals in To⁴CoCl. Weaker absorptions at 581 (ε: 388 M⁻¹ cm⁻¹) and 617 (ε: 424 M⁻¹ cm⁻¹) were attributed to d←d transitions. The effective magnetic moment of 1 (4.2(2) μB), determined by Evans method, is consistent with a high-spin cobalt(II) (S = 3/2). The EPR spectrum of 1, acquired at 5 K in glassed toluene, showed a rhombic spectrum with hyperfine coupling to the ⁵⁹Co center (I = 7/2) in a characteristic eight-line pattern.

The identity of 1 as the cobalt(II) methyl is unambiguously established by X-ray diffraction (Figure 1). The compound is slightly distorted from the C₃v symmetry suggested by solution-phase spectroscopy, with the C22 (methyl) displaced from the B–Co–Me: 172.83°. The Co1–C22 distance in To⁴CoMe (1.994(2) Å) is within the range of similar pseudotetrahedral methylcobalt(II) species, which vary from 1.9 to 2.1 Å.⁵,₆,₈,₁₆,₁₀,₁⁷

![Figure 1. Rendered thermal ellipsoid diagram of To⁴CoMe (1) with ellipsoids plotted at 50% probability. H atoms are omitted for clarity.](image-url)

DFT calculations show that the quartet state (S = 3/2) is lowest energy and 49 kcal/mol lower than the doublet state. A TDDFT-calculated electronic transition at 310 nm (using implicit solvation) allows the experiment band at 346 nm to classified as LMCT. This transition involves occupied orbitals mostly on the methyl carbon to unoccupied orbitals delocalized over Co, B, and the unsaturated C in the To⁴ ligand. Additional peaks at 602 nm, 740 nm and 743 nm, found both in To⁴CoMe and To⁴CoCl calculations, support the assignment of the weaker signals in the experimental spectra as d←d transitions. The strong, experimentally observed band at 697 nm was not evident, which may be due to the single configuration approach of TDDFT.

To⁴CoMe and CO (1 atm) rapidly react in benzene-d₆ or THF at room temperature, as evidenced by an immediate color change from blue to orange. The possible products of To⁴CoMe and CO include reduced To⁴Co or To⁴Co(CO)₂ species, To⁴Co(Me)CO or its inserted isomer To⁴Co(CO)Me, To⁴Co(CO)Me(CO), or To⁴Co(CO)Me(CO)₂. A single ¹¹B NMR signal at ~4 ppm, shifted upfield by 104 ppm from the value for 1, suggested the formation of a single To⁴Co-containing product (2). The ¹H and ¹¹B NMR spectra did not vary from room temperature to ~80 °C.

Evaporation of a solution of 2 to dryness overnight gives 1 as the only detectable To⁴Co-containing species, indicating that the reaction of 1 and CO is reversible. This reversibility hampers the isolation of 2. Compound 2 persists in partially degassed solutions, while evaporation of all solvent and immediate redissolution affords a mixture of 1 and 2. The reversible interaction of 1 and CO rules out formation of To⁴CoCO because the byproducts of 1 e⁻ reduction of 1 are unlikely to persist in a form that could re-methylate 2.

An in situ IR spectrum of the orange THF solution, collected on a ZnSe ATR crystal, revealed bands at 1984, 1886, 1687, and 1655 cm⁻¹. The two higher energy peaks were assigned to coordinated CO ligands, with the higher energy peak at 1984 cm⁻¹ significantly more intense. The lower energy absorptions were assigned to rotamers of the cobalt acyl group, and the signal at 1655 cm⁻¹ was notably non-Gaussian shaped with a shoulder tailing toward the red. On the basis of DFT calculations (see below), we assign this shoulder to the ν̂CoC of a weakly or non-coordinated oxazoline, which typically appears at 1630 cm⁻¹.¹⁵ In addition, a peak at 1590 cm⁻¹, corresponding to the ν̂CoC of cobalt-coordinated oxazoline, was red-shifted by ~4 cm⁻¹ in comparison to the To⁴CoMe starting material. For comparison, the IR spectrum of isolated Tp⁵⁹Co(C(O)Et)CO contained a single CO band at 1999 cm⁻¹ and an acyl peak at 1636 cm⁻¹.⁷ The IR spectrum of Ph₅⁵⁹Co(C(O)Me)CO contained carboxyl ν̂CO at 1993 cm⁻¹ and acyl ν̂CO at 1684 and 1663 cm⁻¹ (assigned to rotamers).¹⁰ Thus, the interaction of To⁴CoMe and CO affords a mixture of To⁴Co(C(O)Me)CO (2; major, 1984, 1687, and 1655 cm⁻¹) and To⁴Co(Me)CO (minor, 1886 cm⁻¹; Scheme 1).

![Scheme 1. Reversible reaction of To⁴CoMe ([1] and CO.](image-url)

The effective magnetic moment of 2 is 2.7(1) μB (determined by Evans method). This value is reduced with respect to high spin To⁴CoMe and is distinct from that of low-spin acyls Ph₅⁵⁹Co(C(O)R)CO (R = Me, Et, Ph; μeff = 1.9 – 2.1 μB).¹⁰ The result for 2 does not fit the spin-only μB for low spin Co(II) (S = ½ is 1.73 μB). While high spin Co(I) (S = 1) would give a spin-only value of 2.83 μB (e.g., for Tp⁵⁹CoCO and Tp⁵⁹Co(CO)CO), this type of product is ruled out above.¹¹,¹⁸ Instead, the effective magnetic moment of 2 is rationalized by a square pyramidal structure with a long axial Co–N interaction on the basis of the typical moments for square planar cobalt(II) complexes.¹⁹,²¹ While a trigonal bipyramidal structure is also consistent with the magnetic moment, DFT calculations (described below) are more consistent with the square pyramidal geometry. A room temperature isotropic signal (giso ≈ 2.1) in the EPR spectrum of 2 further supported the low spin assignment.²²,²³ The UV-vis spectrum of 2 was

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DOI: 10.1039/C7CC06339C

ChemComm Accepted Manuscript

Published on 15 September 2017. Downloaded by Iowa State University on 21/09/2017 15:51:10.
distinct from 1 and contained a broad, weak band from 760 to 1100 nm with $\lambda_{\text{max}}$ at 885 nm ($\varepsilon$: 305 M$^{-1}$cm$^{-1}$). In addition, a strong absorption tail from 200 to 600 nm.

DFT calculations of $\text{To}^{\text{III}}\text{CoO}_2\text{(C(O)Me)_2}$ suggest a square pyramidal geometry for the optimized structure. The low spin state is 33 kcal/mol lower in energy than the high spin state. A TDDFT calculation with implicit solvation finds strong electronic transitions at 448 and 462 nm, with multiple smaller contributing transitions between 300 nm and 400 nm, consistent with experimental findings. In a DFT Hessian calculation, the frequency corresponding to the acyl carbonyl stretching mode is found at 1731 cm$^{-1}$ and the terminal carbonyl stretching is located at 2117 cm$^{-1}$. In addition, the calculated $v_{\text{CN}}$ stretches occur at 1636, 1667, and 1693 cm$^{-1}$ with the highest energy $v_{\text{CN}}$ being associated with the non-coordinated oxalozine. DFT calculations also suggest a square pyramidal geometry for the optimized structure of $\text{To}^{\text{III}}\text{Co(Me)}_2\text{CO}$. The low spin state is found to be 30 kcal/mol lower in energy than the high spin state. TDDFT calculations identify electronic transitions at 386 nm and 395 nm, which could be obscured by the multiple excitations found with the $\text{To}^{\text{III}}\text{CoO}_2\text{(C(O)Me)_2}$CO species. The calculated frequency for the CO stretch at 2030 cm$^{-1}$ is lower energy than in $\text{To}^{\text{III}}\text{CoO}_2\text{(C(O)Me)_2}$CO providing support for the assignment of the experimental spectrum.

The orange carbonylated cobalt 2 rapidly reacts with $\text{O}_2$ to give purple $\text{To}^{\text{III}}\text{CoO}_2\text{Ac}$ (3, equation (2)), identified by comparison with an authentic sample’s electronic spectrum ($\lambda_{\text{max}}$ = 486 and 585 nm), $^1\text{H}$ and $^1\text{B}$ NMR spectra, and X-ray diffraction pattern. This reaction is sufficiently rapid and selective (and $\text{To}^{\text{III}}\text{CoO}_2\text{Ac}$ is easily crystallized) that this product is typically isolated from attempted crystallizations of the monocarbonyl acyl complex at $\sim$ 80 °C due to trace $\text{O}_2$ impurities. In situ-generated 2 reacts with $\text{O}_2$ to afford 3 under a range of conditions, including 1 atm of $\text{O}_2$ at room temperature (analyzed by $^1\text{H}$ and $^1\text{B}$ NMR spectroscopy) or addition of $\text{O}_2$ as a THF solution (5 – 20 equiv. $\text{O}_2$, with or without excess CO, analyzed by UV-vis spectroscopy) at room temperature. Also, addition of a solution of $\text{O}_2$ (10-20 equiv.) to 2 at $\sim$ 100 °C provides an intermediate ($\lambda_{\text{max}}$ = 511, 550, and 585 nm) that converts into 3 upon warming to room temperature. That is, the transformation of equation (2) is fairly robust.

The reverse order of reaction of $\text{To}^{\text{III}}\text{CoMe}$, oxidation followed by carbonylation, is not nearly so robust, selective or efficient. Reactions of 1 and $\text{O}_2$ at room temperature in THF or toluene-$d_8$ give a mixture of unidentified species that are unreactive toward CO. At $\sim$ 100 °C, a new, single $^1\text{B}$ NMR signal at $\sim$ 25 ppm suggested one species is formed from addition of $\text{To}^{\text{III}}\text{CoMe}$ and $\text{O}_2$ (1 atm). This species persists (based on unchanged $^1\text{B}$ NMR and EPR spectra) and is unreactive toward CO until the mixture is warmed to $\sim$ 20 °C.

At that point, the solution becomes purple and $\text{To}^{\text{III}}\text{CoO}_2\text{Ac}$ forms as a minor component in a mixture of $\text{To}^{\text{III}}\text{Co}$-containing species.

The direct carbonylation reaction of 1 with $\text{CO}_2$ (1 atm or 85 psi) to form 3 requires 2 weeks (equation (3)), as monitored by $^1\text{H}$ NMR spectroscopy and a gradual blue to purple color change. The rate of this conversion is significantly slower than the rapid carbonylation/oxidation chemistry described above. A related reaction of 2 and $\text{CO}_2$ also sluggishly provides $\text{To}^{\text{III}}\text{CoO}_2\text{Ac}$ at room temperature over ~2 weeks. Thus, while $\text{CO}_2$ insertion is possible, carbonylation and oxygenation by $\text{O}_2$ is the kinetically favored pathway.

These three sets of experiments provide considerable insight into the oxidative carbonylation sequence. First, a pathway from 2 to 3 involving 1 as an intermediate via initial decarbonylation steps is unlikely because decarbonylation appears to be slow as indicated by the long drying times needed to fully convert 2 to 1. Second, catalytic oxidation of CO to $\text{CO}_2$ by $\text{To}^{\text{III}}\text{CoO}_2\text{O}_2$ followed by carbonylation is ruled out as kinetically unfeasible by the experiment of equation (3).

We conclude that the sequence involving carbonylation of 1 to produce 2 followed by oxygenation to form 3 is kinetically favored. These results suggest that strategies for utilization of $\text{CO}_2$ involving carbonylation of organic compounds could benefit from an enzyme-inspired approach involving initial reduction to CO, CO migratory insertion, and finally oxidation rather than a direct, one-step carbonylation. At least in this case, a multistep compulsory-ordered pathway is considerably faster (and more selective) than random addition or direct insertion. Because acetate is important as a privileged ligand in oxidation catalysis and in CH activation pathways, the oxidative carbonylation studied here may be useful as part of selective hydrocarbon functionalization schemes. We are currently investigating related cobalt(II) alkyl and aryl compounds in pursuit of catalytic conversions.

This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences. The Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. DE-AC02-07CH11358.

Notes and references
† X-ray data for $\text{To}^{\text{III}}\text{CoMe}$ (CCDC 1564301): $\text{C}_8\text{H}_8\text{BCoNiO}_2$; FW 456.24; monoclinic; a: 10.917(2), b: 13.444(2), c: 16.223(3), $\beta$: 97.171(2), volume: 2362.3(6); P121/c1; Z = 4; temp. 173 K; reflections: collected, 24315; independent, 5916; $R_w$: 0.0386; 4634 data I>2σ(I): $R$: 0.0337, $wR$: 0.0794; $R_w$: 0.0505, $wR$: 0.0880.
$^{10}$M$^2$CoMe reacts rapidly with CO to give a low spin $^{10}$M$^2$Co{C(O)Me}CO species, which is selectively oxygenated to form $^{10}$M$^2$CoOAc.