

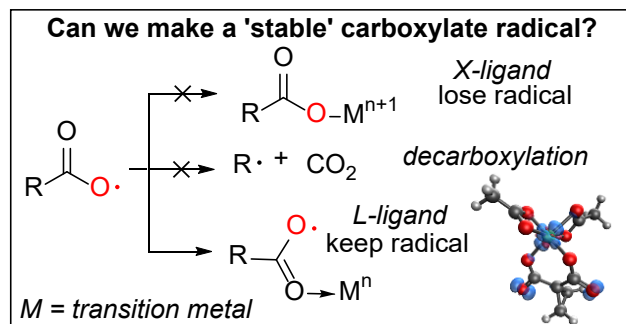
Carboxylate as a non-innocent L-ligand – computational and experimental search for metal-bound carboxylate radicals

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Supporting Information Placeholder

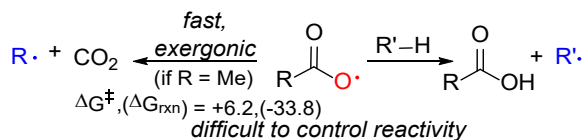


ABSTRACT: We show that the carboxylate radical acts as a L-ligand with certain high-spin transition metal centers. Such coordination preserves the O-radical character needed for C-H activation *via* HAT. Capture of the new C-radical by the metal and subsequent reductive elimination leads to formal C-H acyloxylation. Decarboxylation of the RCO_2 radical is minimized through hybridization effects introduced by spiro-cyclopropyl moiety.

Metals have the ability to stabilize a variety of transient species through coordination.¹ A particularly interesting situation arises when the metal-bound species adjusts its oxidation state to match the electronic demands of the metal and the reaction, i.e., behave as a “non-innocent ligand” (NIL).²

Oxygen radicals are non-innocent because they have both the filled and half-empty p-orbitals and, hence, are capable of interacting with the metal as either a one-electron X-ligand or a two-electron L-ligand. Such interesting duality is known for redox-non-innocent phenoxyl ligands.¹ On the other hand, such behavior, to our knowledge, is not documented for RCO_2 , a reactive, electrophilic, O-centered carboxylate radical which has a tendency to undergo fast decarboxylation (especially when $R = \text{alkyl}$, Scheme 1).³⁻⁷

Scheme 1. Instability of the carboxyl radical. Thermodynamic values from ref. 3 in kcal/mol.

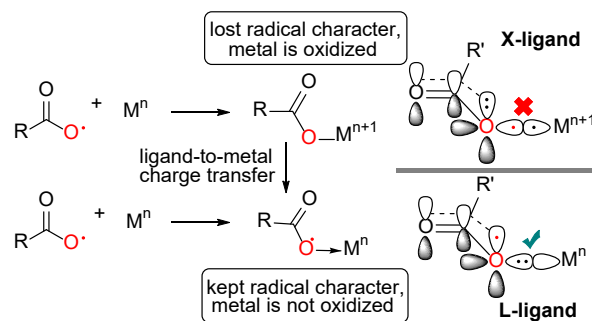


Although carboxylates are ubiquitous organic ligands, capable of forming complexes with a wide range of transition metals,^{8,9} they generally behave as one-electron X-ligands

and form a covalent M-O bond with the loss of radical character.¹⁰⁻¹²

Considering the untapped synthetic potential of metal-bound carboxylate radicals, we were interested in learning how to encourage carboxylate to be a monodentate two-electron L-ligand and to preserve radical character (Scheme 2).

Scheme 2. Two ways to use carboxylate as a ligand for the formation of M-O bonds. Top: Carboxylate acts as an X-ligand and loses radical character. Bottom: Carboxylate maintains radical character when forming a ligand-metal bond as an L-ligand. Only one lobe of oxygen p-orbitals are shown for clarity.

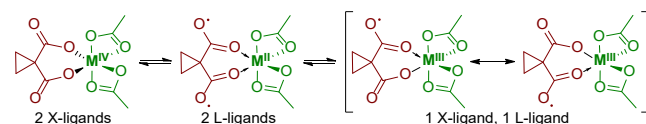


How would a metal “choose” between L- over X-ligand behavior? When a radical behaves as an X-ligand, the metal provides one electron for the M-O bond and, hence, is formally oxidized. One can envision that if a metal is reluctant to be oxidized further, then the payoff of forming a covalent M-O bond may not be enough to compensate for the cost of going from M^n to M^{n+1} . Instead, an empty orbital of the metal may form a dative M-O bond with a lone pair of the oxygen.

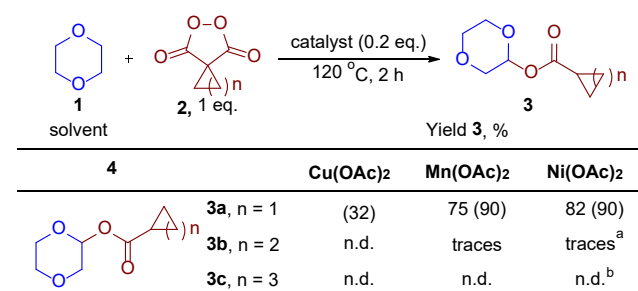
To find the right window of reactivity, we explored transition metals with a variety of redox potentials. Our search focused on first row transition metals due to their relative abundance and general cost-effectiveness.¹³ Additionally, several of these metals (Cu,¹⁴⁻¹⁷ Co,^{18,19} Fe²⁰) have been successfully utilized in C-H activation with peroxides previously.²¹

Cyclic malonoyl peroxides²²⁻²⁶ are convenient precursors for carboxyl radicals and have relatively low reduction potentials for the peroxide (~ -0.75 and -1.2 V vs. Ag/Ag⁺ for the 1st and 2nd reduction, respectively). Oxidative addition of the bis-peroxide to the metal can potentially result in a variety of bonding modes and oxidation states (Scheme 3). If both carboxylates of the malonoyl peroxide were to act as X-ligands, the metal would have a formal +4 charge. This high oxidation state has been shown to be accessible for Pd^{27,28}, Mn²⁹, and even Ni³⁰⁻³², however, it is less common for Co and Cu³³. Whether the high oxidation state can be reached will be dependent on the redox potentials of the metal and the peroxide.

Scheme 3. Potential oxidation states of $M(OAc)_2$ after oxidative insertion into the malonoyl peroxide.



We explored the possibility of forming metal-bound carboxylate radicals experimentally in reactions of cyclic malonoyl peroxides with 1,4-dioxane, **1**, in the presence of several transition metal complexes. In order to test for the involvement of radical species we have used bicyclic spiro diacyl peroxides with the spiro-cycle of varying size. Remarkably, only the cyclopropyl malonoyl peroxide was found to lead to efficient C-H functionalization, i.e., acyloxylation of dioxane (Figure 1). Such difference between cyclopropyl and the larger cyclic substituents is very interesting as it provides indirect evidence for the radical mechanism (vide infra).³⁴



conversion of peroxide: ^a 60%; ^b 35%

yields on the isolated product (yields according to ¹H NMR)

Figure 1. Cu-, Mn-, or Ni-catalyzed oxidative acyloxylation of

1,4-dioxane with cyclic diacyl peroxides. For catalyst preparation, see SI, pg S3.

Considering the above results, we selected cyclopropyl malonoyl peroxide as the bis-carboxylate precursor and expanded the selection of transition metals to include Cu, Co, Mn, Ni, Fe, and Pd due to their range of reduction potentials (SI).

Exploratory computations for the complexes formed from transition metal acetates *via* formal insertion into the peroxide O-O bond illustrate the diversity of bonding patterns (Figure 2).

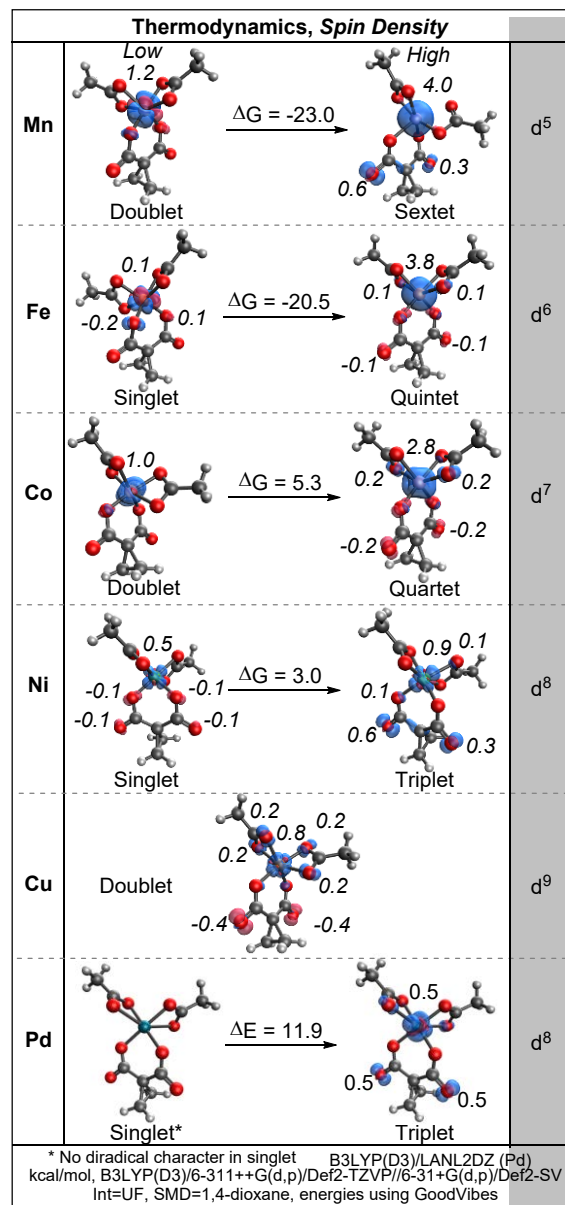


Figure 2. The stability of high vs. low spin states for the product of oxidative addition of the metal acetate into the peroxide O-O bond with selected metals. Additionally, the spin density at both the high and low spin state is shown.

For all metals in the low spin state (singlet or doublet), the spin density is primarily located on the metal. In the high spin state, the radical character becomes delocalized

between the metal and carboxyl-oxygens (Figure 2). Therefore, for compounds where the high spin state is assessable one would expect the carboxylate radical to be able to act as an L-ligand.

Cu(II) is a unique case, not only is it the hardest to oxidize of the first row transition metals, but it is also a d^9 -complex where only the doublet spin state is available. Unlike Co and Mn, which have no carboxylate radical character in the low spin doublet state, Cu does.

Intrigued by this rich palette of reactive patterns, we have expanded experimental studies to explore the catalytic activity of various metal salts in the oxidative acyloxylation of 1,4-dioxane (**1**) (Table 1).

Table 1. Oxidation of **1** with **2a** in the presence of various catalysts.

Entry	Catalyst	¹ H NMR yield 3a , % ^a
1	-	n.d.
2	Cu(OAc) ₂ •H ₂ O	32
3	Co(OAc) ₂ •4H ₂ O	48
4	Fe(OAc) ₂ •9H ₂ O	60
5	Mn(OAc) ₂ •4H ₂ O	78 (73)
6	Ni(OAc) ₂ •4H ₂ O	88 (75)
7	Pd(OAc) ₂	n.d.

^a Yields of the isolated product are indicated in parentheses

Peroxide **2a** doesn't react with 1,4-dioxane without a catalyst (Table 1, entry 1). The Cu(OAc)₂, Co(OAc)₂ and Fe(OAc)₂ catalyzed reactions led to product **3a** in 32%, 48%, and 60% yield, respectively (entries 2-4). The highest yields were achieved using Mn(OAc)₂ (73% isolated yield) and Ni(OAc)₂ (75% isolated yield) (entries 5 and 6). Pd(OAc)₂, the Ni analog, did not provide any product (entry 7). The importance of hard acetate co-ligands was illustrated by lack of reactivity for the metal halides (Table S1).

Note that the C-H activation product **3a** was obtained for Fe, Cu, Co, Mn, and Ni which all had an accessible high spin state. No product was obtained for Pd which, according to calculations, favors a closed-shell singlet state by a larger margin.

The correlation between the M^{3+}/M^{2+} reduction potential of the metal and the experimental yield (Ni→Cu, Figure 3) suggests that the reaction requires a metal that is electron rich to assist in opening the peroxide O-O bond (*vide infra*) but also be able to resist oxidation by the peroxide radical. Fe seems to be just outside the optimal window whereas Ni achieves the delicate balance between these opposing requirements.

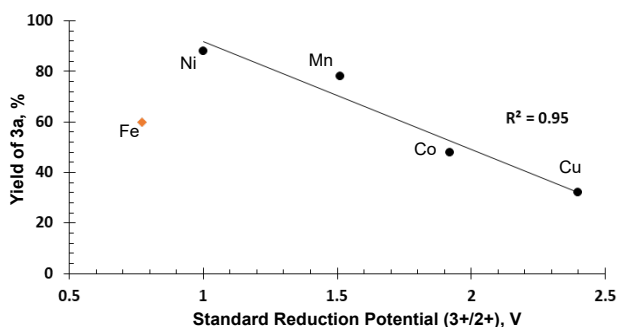


Figure 3. A plot of the standard reduction potential of the metal catalyst versus the experimental yield. Standard reduction potential from ref. ³⁵.

Considering the experimental results, we have explored computationally the reaction of 1,4-dioxane with Ni(OAc)₂, the most promising catalyst. According to computational analysis, the catalyst exists in several forms ("a cocktail of catalysts")^{36, 37} differing in the nature of coordinating ligands and spin states. The most favorable oxidative addition occurs in the triplet state between an oxygen lone pair in the O-O bond and the two half-empty d-orbitals on Ni, leading to one of two interconverting Ni-intermediates, intermediate **C** and **D** (Figure 4A). The spin density of both of these triplet intermediates clearly identifies a radical carboxylate moiety (Figure 4B). The TS for Ni-assisted O-O bond activation is ~27 kcal/mol relative to the most stable of the Ni-species in the catalytic cocktail and is readily accessible at the reaction conditions.

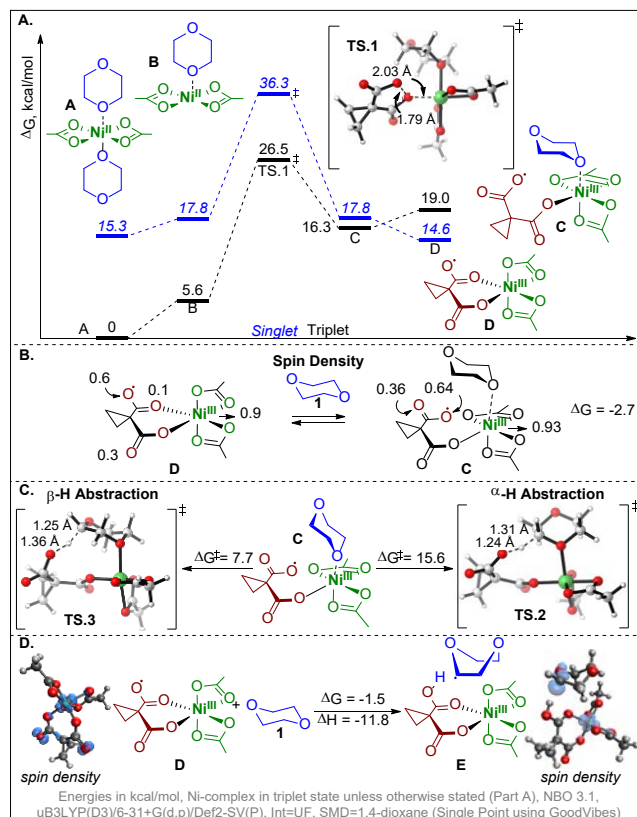


Figure 4. A) Oxidative addition pathway resulting in the formation of the key Ni-intermediates. B) Spin density of the two key Ni-intermediates **C** and **D**. C) The activation barriers for α-

and β -H abstraction from the Ni(III)-complex, **C**. **D**) The thermodynamics for H-abstraction from the Ni(III)-complex, **D**.

According to spin density, the product of the formal insertion of Ni(OAc)₂ into the peroxide O-O bond, i.e., the intermediate **D**, has one radical located on the metal center and the other delocalized on the non-coordinating oxygens of the two malonate carbonyls (Figure 4B). Since the spin density of **D** suggests the carboxylate is behaving non-innocently, oxidation states (OS) of the carboxylate ligand were examined using intrinsic atomic orbitals (IAO). IAOs are capable of assigning OS in non-innocent ligands by determining the occupancies of the individual d-orbitals (Table S4).³⁸ The OS of Ni in high-spin **D** was determined to be +3 which is consistent with one carboxylate acting as an X-ligand while the other acts as an L-ligand (Scheme 3, 1 X-ligand, 1 L-ligand). Furthermore, IAOs show that there is only one unpaired d-electron on the metal-center in the triplet and, hence, the other unpaired electron is localized on the ligands, in agreement with the calculated spin density (Table S3).

Presence of the Ni-complex **C** provides a potential explanation for the decrease in yields when moving from a spiro-cyclopropyl to spiro-cyclopentane substrate (Figure 1). In this Ni-complex, where only one coordination site is available for the peroxide, one carboxylate group is left as a free radical (Figure 4B). Typically, a free carboxylate radical will rapidly decompose producing CO₂ and a carbon radical. The cyclopropyl group slows decarboxylation by increasing s-character in the C-CO₂* bond and making this bond stronger (Scheme S2).³⁹

Both of the Ni-complexes, **C** and **D**, were found to be capable of hydrogen atom transfer (HAT). If dioxane is coordinated to the metal-center, i.e., in the intermediate **C**, the free carboxylate radical is capable of abstracting a remote hydrogen with an activation barrier of 16 and 8 kcal/mol for the α - and β -C-H bonds, respectively (Figure 4C).

Importantly, H-abstraction from a dioxane molecule by the bound carboxylate L-ligand in Ni-complex **D** is both exergonic (-11.8 kcal/mol) (Figure 4D) and barrierless (Figure S1). All attempts to locate a transition state for the complex of intermediate **D** with 1,4-dioxane in the boat conformer prior to HAT optimized directly to the H-abstraction product, **E**. The absence of barrier can be attributed to several factors. Not only is the O-radical in close proximity to a Lewis acid very electrophilic, but the target σ_{C-H} bond is electron rich due to the anomeric $n_O \rightarrow \sigma^*_{C-H}$ donation. In agreement with the literature precedents, the boat conformer of 1,4-dioxane is a more favorable reaction partner than the chair conformer due to the better array of stereoelectronic interactions involved in the "radical homoanomeric effect".^{40, 41} The spin density evolution in the reaction is consistent with radical H-transfer. In reactant **D**, the non-coordinated oxygen has substantial spin density, while in **E** there is no spin density on the oxygen after the O-H bond is formed, suggesting a HAT mechanism (Figure 4D).

Based on the above results, we propose that the reaction starts from oxidative addition of malonoyl peroxide **2a** to Ni(II) with the formation of a Ni-dioxane complex **C**, which can interconvert to a nearly isoenergetic L-ligand Ni-complex **D** (Scheme 4). Activation of the C-H bond in dioxane can

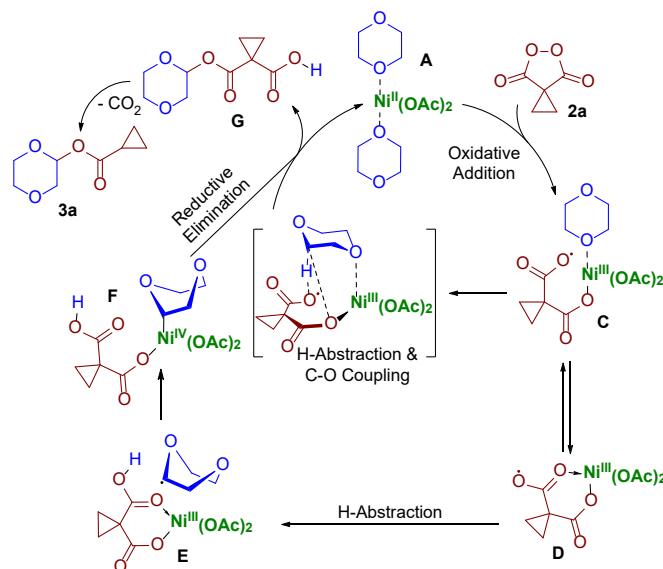
occur with either one of these reactive Ni-complexes. For the Ni-dioxane complex **C**, H-abstraction appears to be followed by barrierless C-O coupling, potentially facilitated by the metal-center. On the other hand, a step-wise process is likely for the L-ligand Ni-complex, **D**, where H-abstraction forms carbon radical intermediate **E** stabilized by the radical anomeric effect.⁴⁰⁻⁴² Reductive elimination leads to C-O coupling forming intermediate **G** (a point where the two mechanistic paths converge). Decarboxylation of **G** affords the final product **3a**.

In summary, the potential for a metal-bound carboxylate radical was explored both experimentally and computationally. It was determined that the carboxylate ligand can maintain radical character upon coordination to a variety of transition metals. Several factors seem to contribute to the success of this process:

1. The use of a metal that is nucleophilic enough to open the malonoyl peroxide O...O bond, but reluctant to be oxidized further.
2. The use of metals that favor a high spin state.
3. Introduction of a spiro-cyclopropyl moiety disfavors the decarboxylation pathway.

This work uncovered the metal-catalyzed oxidative acyloxylation of C(sp³)-H bonds in ethers through the generation of carboxylate radicals which are capable of avoiding decarboxylation while remaining reactive O-centered radicals. Further explorations of scope, limitations, and stereoelectronic aspects of this potentially rich chemistry are in progress.

Scheme 4. Proposed mechanism for the oxidative acyloxylation of ethers using two Ni(III)-complexes.



ASSOCIATED CONTENT

Supporting Information

Experimental procedures, CV data, characterization data of synthesized compounds, NMR spectra, computational data including coordinates and additional reactions explored (PDF).

The Supporting Information is available free of charge on the ACS Publications website.

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Author Contributions

All authors have given approval to the final version of the manuscript.

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