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MINI REVIEW

Catalyst Carbonylation: A Hidden, but Essential, Step in Reaction Initiation

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The proliferation of increasingly useful reactions for hydrogen transfer in organic synthesis has included the introduction of many new homogeneous catalysts into the organic synthesis lexicon. Unlike the proliferation of palladium-based cross-coupling reactions in which the mechanism is generally conserved, we are learning that these emerging hydrogen transfer catalysts have a rich diversity of mechanisms for catalyst activation, speciation, C-H bond cleavage and formation, and ultimately deactivation. We find that an underappreciated commonality in the catalytic activation for some of these system is the generation of a (carbonyl)metal group, which dominates the downstream speciation of the catalyst system. In this mini-review we highlight a few well-documented cases of this phenomenon as food for thought for those who are designing new catalytic systems to introduce into this dynamic and impactful area.

1 Introduction

Almost like the proliferation of cross-coupling reactions 10 years earlier, we are seeing the emergence of increasingly impactful catalytic dehydrogenation and hydrogen transfer reactions in organic synthesis. Some key examples include alcohol oxidation, hydrogen borrowing amination, asymmetric carbonyl hydrogenation, carbonyl transfer, and many other useful manipulations of oxygenated and aminated functional groups. Wide-spread use of these methods through the organic community has been transformative, enabling displacement of stoichiometric, often metallic, waste streams generated by reactions like chromate oxidation, reductive amination, lithium aluminium hydride reduction, and related pathways, while simultaneously introducing game-changing approaches for carbon-heteroatom bond formation and asymmetric induction in small molecules.

As new catalysts and conditions emerge for these high-value synthetic methods, more, increasingly thought-provoking, mechanistic studies are also emerging that show that in many cases the mechanistic story is much more complicated than the simple template of β-hydride elimination and insertion that were characterized in early examples. We now see that the catalytic precursors for many useful dehydrogenation catalysts are completely transformed by a metal carbonylation. The initial decarbonylation of an alcohol starting material defines the catalyst initiation sequence, first through the active catalyst system, then through catalyst deactivation. While we were initially surprised to find this role of a starting alcohol in some of our recent work, we see that it is one that has been characterized in the mechanisms of several high-value synthetic transformations, yet it is generally omitted from the discussions of hydrogen transfer reactions that proliferate in the synthetic literature.

Catalyst carbonylation is certainly not a necessary feature for hydrogen transfer catalysts. A great many scaffolds show reactivity in this area, with pathways utilizing both inner- and outer-sphere proton- and hydride-transfer mechanisms. We will not endeavour to describe all of them here, but rather we will point out a few case studies in which a CO ligand–anticipated or unanticipated–changed the course of the mechanism of a catalytic hydrogen-transfer reaction.

Catalyst carbonylation has been known to organometallic chemistry since the first metal-carbonyl complex was reported in 1868 by Schutzenberger.[1] Throughout the 20th century, carbonyl-containing metal complexes have been used as catalysts for reactions ranging from Monsanto's acetic acid process[2] to reductive hydrosilylation of amides.[3] The metal carbonyl can be directly involved in catalysis, as in the case of olefin hydroformylations, or as a spectator ligand, as in reactions of Milstein's ruthenium-pincer complexes.[4, 5] Either way, the metal carbonyl group plays an important role in defining the electronic environment of the catalyst and thus governs energetics of the catalytic cycle. Herein, we will show cases where catalyst carbonylation changed the fate of a catalytic reaction sequence and created an active catalyst that is considerably different than its precursor.

2 How do organics decarbonylate?

Rhodium-mediated decarbonylation was first reported by Tsuji and Ohno in the mid-1960s as a stoichiometric reaction to decarbonylate various aldehydes.[6] They found that Wilkinson's catalyst will form carbonylated rhodium complexes in the presence of aldehydes, which they characterized by FTIR spectroscopy. They correctly identified that this reaction is closely related to a similar one in which Vaska found that

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osmium halides tend to hydrocarbonylate by reaction with various alcohols.[7] Tsuji and Ohno also reported palladium-catalysed hydroformylation of olefins in a separate article the same year.[8] Their reactions would be stepping stones for further reaction development over the next 50 years and lead to numerous high utility catalytic carbonylation and decarbonylation systems.

The general mechanism (Scheme 1) for alcohol or aldehyde decarbonylation using an MXL_3 generic pre-catalyst (**1**, centre) begins with oxidative addition of either the hydroxyl bond of the alcohol and the acyl C—H bond of the aldehyde. In the former case, the alcohol then undergoes β-hydride elimination to produce coordinated aldehyde **2**, which subsequently releases H_2 and activates the aldehyde to form **3**. The (acyl)metal group of **3** then undergoes migratory extrusion and reductive elimination of the decarbonylated product to give carbonylated species **4**. The reaction rate and selectivity depend on both the metal and its ligand set. The process is common and facile; in fact, Morton and co-workers published a study of this with Wilkinson's catalyst,[9] in which they discovered that decarbonylation of the intermediate aldehyde is so facile that it is difficult to prevent. Moreover, once the catalyst is carbonylated in this case, the catalytic alcohol oxidation reaction is poisoned. This could be either because the CO ligand is blocking the metal coordination site needed for alkoxide binding or because back-bonding to the CO depletes electron density needed for alcohol oxidative addition. Morton showed that the active catalyst could be regenerated either by photo dissociation of the CO, this worked moderately, or by decarboxylation via hydroxide attack. Strategically, Morton intended to dehydrogenate alcohols with this method, and catalyst poisoning by aldehyde decarbonylation presented a complication. Thus, this was an early case of the dilemma of how to design catalysts selectively to achieve dehydrogenation over decarbonylation. This sort of poisoning by CO is seen in many different types of hydrogenation and dehydrogenation catalysts, including proton-exchange membrane fuel cells, but there are also cases in which catalyst carbonylation is beneficial, or even essential.

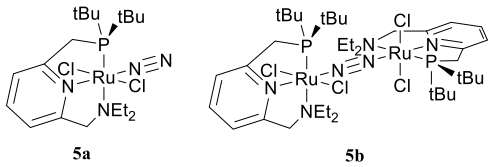
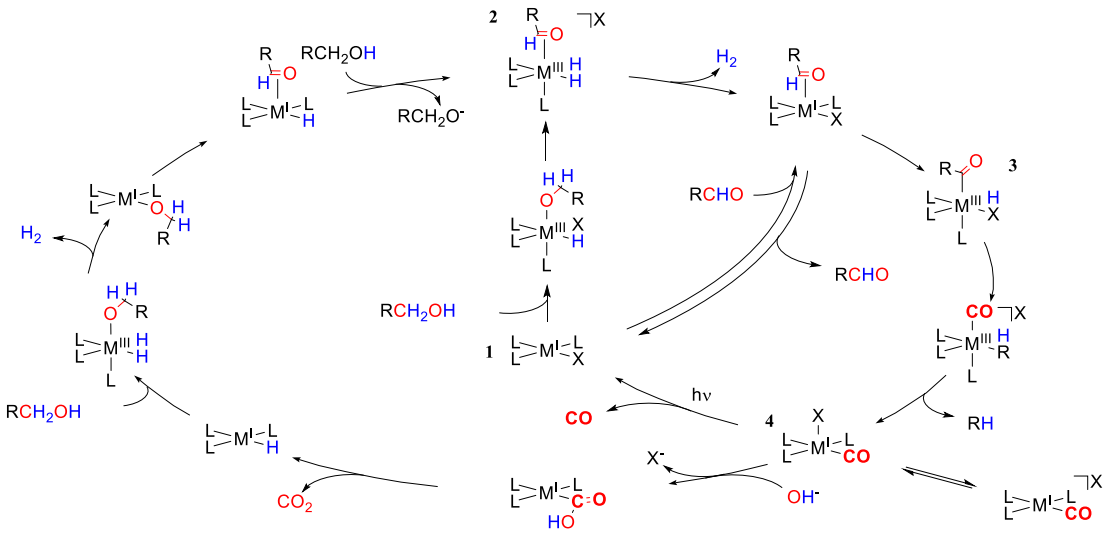


Figure 1. PNN monomer (**5a**) and dimer (**5b**) pre-catalysts for primary and secondary alcohol dehydrogenation.

In a more recent case study, Zhang and co-workers developed electron-rich ruthenium complexes that dehydrogenate secondary alcohols. The pre-catalysts form complexes with terminal (**5a**) or bridging (**5b**) dinitrogen ligands (Fig. 1), allowing facile access by substrate alcohols. The mechanism then follows the same general path in scheme 1, except that since they use secondary alcohols, migratory extrusion cannot occur, so the ketone is released as a product. The authors attempted to use primary alcohols in these experiments, but this resulted in catalyst poisoning by carbonylation. Like Morton's case, these investigators encountered CO poisoning, but this time in a rigidly defined (pincer)ruthenium environment. The resulting CO complex was characterized by X-ray diffraction. Despite these findings, secondary alcohols are not completely safe from decarbonylation. There are a few rare cases of catalyst carbonylation by secondary alcohols, including one that was well-characterized by the Ozerov group. They found that their ruthenium PNP pincer complex could oxidize isopropanol to acetone, then carbonylate to release two equivalents of methane. This is unique, because C—C oxidative addition is much less facile than aldehyde activation.[10]

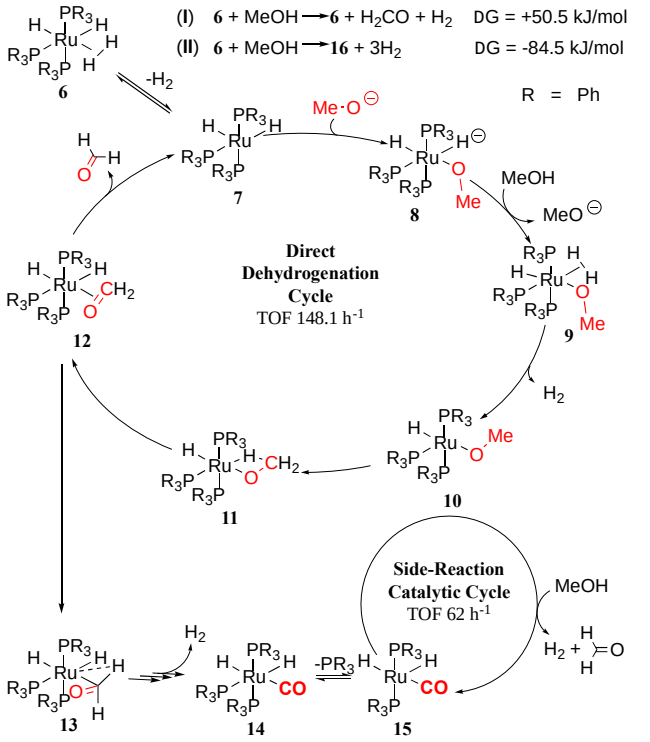
Catalyst poisoning by decarbonylation can be temperature dependent. Koridze and co-workers documented a case of this in which Jensen's (POCOP)iridium scaffold is carbonylates by ethanol. This is a particularly nice example, whereas the authors were able to isolate intermediates in the ethanol decomposition sequence. The POCOP pincer, an iridium bis(phosphine), and a ruthenocene pincer complex were all carbonylated and deactivated only at an elevated temperature, 200 °C.[11]



Scheme 1. General mechanism for primary alcohol dehydrogenation and aldehyde decarbonylation using a generic MXL_3 pre-catalyst.

3 Catalytic alcohol dehydrogenation

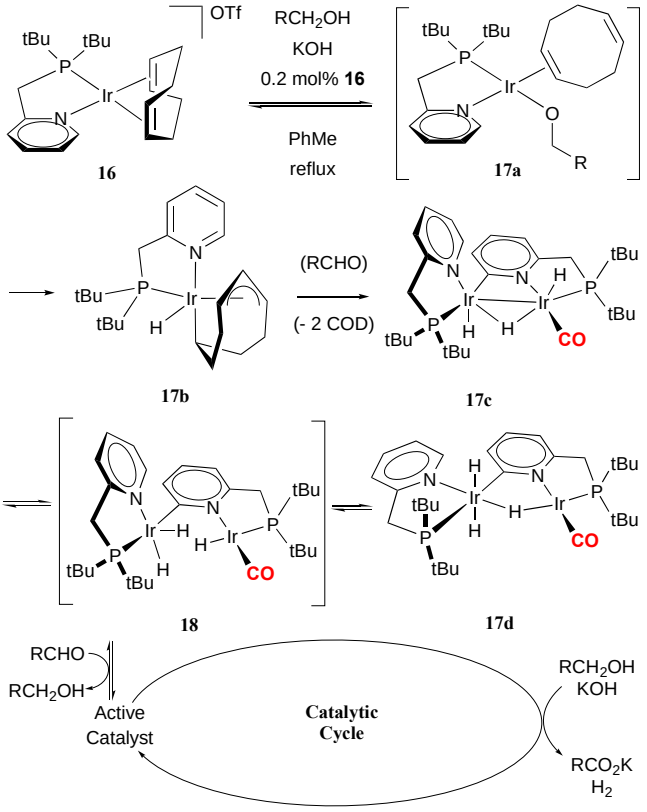
Traditional alcohol oxidation methods usually require the alcohol to be activated as a leaving group (e.g., halide or sulfonate) or that a stoichiometric amount of strong and toxic metal-containing oxidants such as potassium permanganate, chromium (VI) oxide, hypervalent iodine compounds, DMSO (Swern oxidation), peroxide, or pressurized oxygen is used. These produce harmful waste streams. The catalytic community is working to move away from such strategies by introducing transfer and acceptorless dehydrogenation systems that reduce waste and reagent costs.[12] So doing, the community has confronted this catalyst carbonylation issue laid out above, with CO poisoning catalysis in some cases[13, 14] and enabling it in others.[15, 16]



Scheme 2. Catalyst carbonylation side product of methanol dehydrogenation by Morton and Cole-Hamilton.

Morton and co-workers documented a particularly instructive example of CO poisoning (Scheme 2) in which the precursor $[RuH_2(X_2)(PPh_3)_3]$ (X = H_2, N_2, PPh_3) (**6**) has two catalytic cycles originating from the parent and carbonylated metal species: (1) the parent dehydrogenation pathway, TOF = 148.1 h^{-1}, with complex **7** as the active catalyst and (2) the carbonylated pathway, TOF 62 h^{-1}, with complex **15** as the active catalyst.[9, 17] Equations (I) and (II) highlight the driving force for catalyst carbonylation in this system. Further, while dehydrogenation (equation I) is an overall endergonic process which requires an energy input of 50.5 kJ mol^{-1}, catalyst carbonylation (equation II) is highly exergonic at -84.5 kJ mol^{-1}.

Formation of M—CO complex **15** proceeds through activation of aldehyde-complex **12**. Formation of agostic complex **13** favours the acyl activation step, thus facilitating the exergonic pathway to complex **14**. Complex **14** then proceeds to the cycle of the carbonylated catalyst. While this cycle is slow compared to the parent, CO ligand dissociation is enthalpically prohibitive, so a re-activation step would be required to return to the parent cycle.



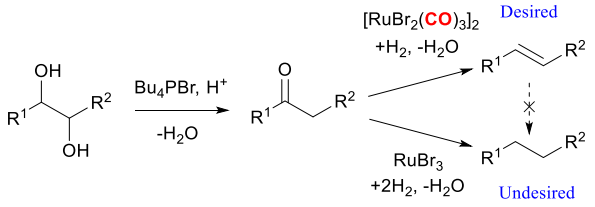
Scheme 3. Catalyst speciation pathway to initiation and termination via carbonylation.

While examples of carbonylation of rhodium[8,13,18] and iridium[19] dehydrogenation catalysts span 1974 to the present day, we were the first to characterize initiation of iridium- or ruthenium-catalysed dehydrogenation systems that require metal carbonylation for activation. In these two systems, [Ir(2-PyCH$_2$P^{t}Bu$_2$)(COD)]OTf[16] and [(η^6-cymene)RuCl(2-PyCH$_2$P^{t}Bu$_2$)]OTf,[12, 15] the active catalysts are carbonylated dinuclear complexes **18** (Scheme 3) and **21** (vide infra, Scheme 6), respectively. Species **18** contains a (chelate)MH(CO) structural fragment, a common substructure in the alcohol dehydrogenation literature. This arrives through two initiating steps in which initial carbonylation leads to dimerization.[16] A singly-carbonylated dimer is the active dehydrogenation catalyst. Our observation of the carbonylation event is consistent with the observed facility of carbonylation of late metal complexes: this sits well with conventional wisdom about the energetics of late metal back bonding. Our situation is different than the earlier ones, though, because the CO does not inhibit catalysis: in fact, it is necessary. While it is uncertain which iridium centre is the locus of reactivity, we have not been able to see catalytic activity of iridium alkoxides like **17a** without first generating a carbonylated dimer.

Alcohol decarbonylation can be used as an efficient tandem reaction to convert primary alcohols to alkanes. Andersson and Madsen have shown a productive (BINAP)iridium system for

such defunctionalization of benylic alcohols.[19] In this case, it is the same (BINAP)Ir^{I}Cl(CO) species that mediates both the dehydrogenation and decarbonylation pathways. The same process introduced a hiccup in a very nice glycol upgrading reaction reported by Heinekey and Goldberg.[20] In this case, we see the POCOP pincer again, as (POCOP)IrH_2 carbonylates to give (POCOP)Ir(CO), which appears to be the active catalyst for conversion of propylene glycol to 1-propanol.

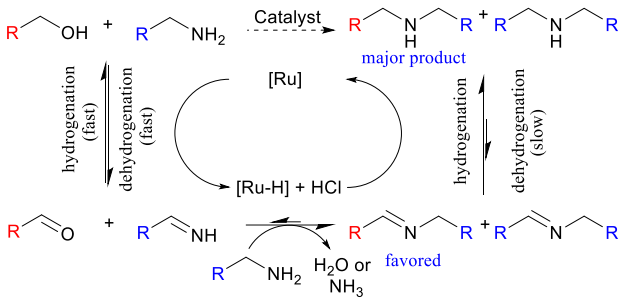
Another example, a recent study from De Vos and co-workers showed that a CO ligand is essential in a Ru-mediated dehydroxylation of biomass alcohols (Scheme 4).[21] This particular process is a tandem combination of alcohol dehydration and ketone reduction, ultimately to give alkene products in high selectivity. The homogenous ruthenium catalyst is required for the ketone reduction step. In this case, the active catalyst contains a BrRu—CO fragment. The authors show that the CO ligand plays the essential role of preventing overreduction of the product alkene. Thus, CO acts as a catalyst poison in this system, but it serves the very important purpose of poisoning a value-decreasing side reaction in which the product alkene could have been downgraded to an alkane.



Scheme 4. Carbonylation of a bromoruthenium pre-catalyst enables selectivity for alkene, rather than alkane, products in biomass dehydroxylation.

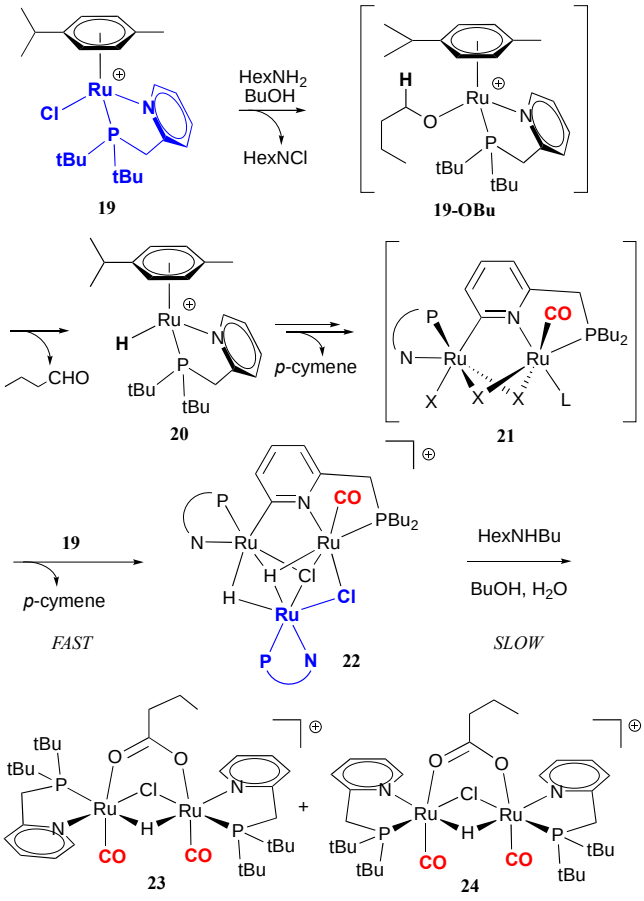
4 Hydrogen borrowing amination

Amination by hydrogen borrowing has been one of the most synthetically attractive reactions that has come out of the literature of catalytic hydrogen-transfer.[22-25] Conceptually, this is a way to do reductive amination without pre-forming an aldehyde, supplying a hydride reagent, or generating a waste stream other than water. Like the parent oxidation pathway, we have seen the importance of catalytic carbonylation in catalyst speciation. The mechanism of hydrogen borrowing amination involves alcohol dehydrogenation, followed by condensation of the intermediate carbonyl with an amine to form an imine. This imine is then hydrogenated to form the amine product (Scheme 5). Our P-N chelated ruthenium catalyst (**19**) is one of a great number of catalysts for this reaction. It is special for 2 reasons: first, the reversible alcohol dehydrogenation step is faster than the condensation step, which changes the reaction's selectivity pattern and enables incredible functional group tolerance, e.g. it will couple alkyl amines in the present of anilines.[26] Second, its speciation, lifecycle, and deactivation are known (Scheme 6).[15]



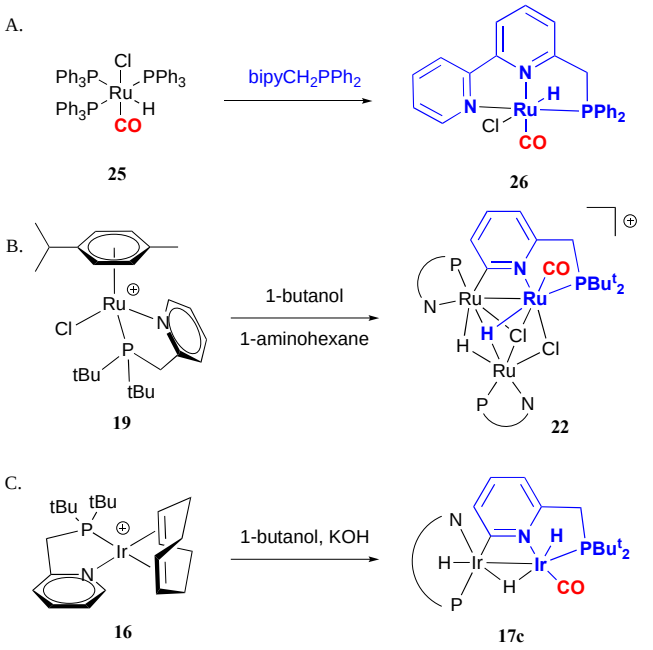
Scheme 5. Mechanism for hydrogen borrowing amination.

In this system, catalyst initiation commences with *n*-butoxide displacement of chloride. The butoxide complex (**19-OBu**) undergoes β-hydride elimination to form butyraldehyde and hydride **20** (Scheme 6). While we showed that the **19-OBu** can effect alcohol oxidation and that **20** can regenerate **19-OBu** under the conditions, this path is much slower than our catalytic reaction. Rather, in the catalytic conditions, **20** converts on to a carbonylated species, which takes up another metal to generate singly-carbonylated ruthenium dimer **21**, itself an intermediate seen only by MALDI-MS and NMR spectroscopy, that we suspect to be the active catalyst. An additional equivalent of **19** reacts quickly with **21** to generate dormant species **22**, from which the active species can regenerate. The catalyst slowly deactivates by carbonylating a second time to form **23** and **24** over the course of about 24-72 hours, depending on the ruthenium loading. Like iridium species **18**, **21** contains the shared (chelate)MH(CO) fragment (X = H for at least one X in **21**), which is derived through metal carbonylation and dimerization. Further, and analogous to Morton's observation of Wilkinson's catalysis, we see here that CO can shut down catalysis: some CO is necessary, too much CO is a poison. We still do not understand why iridium system **18** is inert to this sort of deactivation.



Scheme 6. Activation, evolution, and deactivation of amination catalyst **21**.

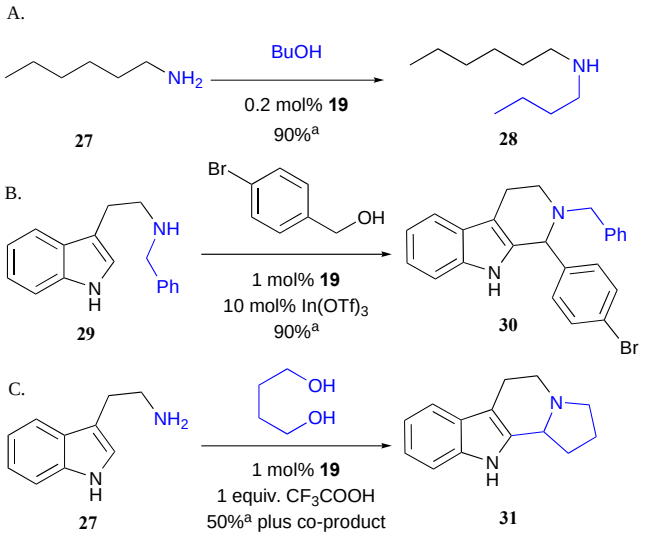
Our original report of our amination system featured only the more reactive benzylic alcohols as electrophiles, because we were unable to access less reactive aliphatic alcohols.[26] We were able to expand this reaction scope once we understood the non-intuitive conclusion of our mechanistic study: less catalyst is more. An initial catalyst carbonylation activates the catalyst, but formation of a resting trimer (**22**) sets up a second carbonylation that was killing the system (as **23**/**24**). Applying the conventional wisdom of adding more catalyst only increased [**21**] and accelerated catalyst deactivation. By lowering ruthenium loading, we were able to utilize simple primary alcohols (e.g., butanol), and general amines (e.g., aminohexane) to give useful amination yields (e.g. 90%).[15]



Scheme 7. Different catalytic carbonylation pathways leading to different speciation scopes. **26** Pre-catalyst for alcohol amine coupling; **22** Deactivated amination catalyst; **17c** Resting state for alcohol oxidation catalyst.

From a fascination with the recurrence of this (chelate)MH(CO) fragment in our active species, we observe an analogy to other (pincer)metal hydrogen transfer systems:[16, 27, 28] we seem to have come in to a special case of the Milstein pincer system, where a second metal is serving as a very special hemi-labile arm on the pincer.[15, 16, 27] While Milstein has carefully designed pincers that feature a labile arm (e.g. **26**), we're forming analogous structures in situ (Scheme 7)**.** We have not yet established, though, which metal of our systems is responsible for bond cleavage and formation or if both centres are acting cooperatively.

Understanding our catalyst deactivation mechanism, we were able to extend the reaction first to aliphatic alcohols, then to tandem reactions. For example, we took up the application of hydrogen borrowing amination to the synthesis of indole alkaloids. This required conditions to execute an acid-mediated Pictet-Spengler reaction in situ with the base-promoted amination sequence. This conundrum was resolved with the use of $In(OTf)_3$ as a co-catalyst. These conditions were developed first for the efficient construction of tetrahydro-β-carbolines from tryptamine (Scheme 8).[28] Further optimization of this strategy enabled the one-step total synthesis of the indole alkaloid Harmicine.[29]



Scheme 8. A. Amination of a simple alcohol. B. High-yielding synthesis of tetrahydro-β-carbolines from *N*-benzyltryptamine. C. One-pot synthesis of harmicine. [a]NMR yield with mesitylene as internal standard. [b]Isolated yield.

5 Carbonylation reactions

Among reagents for organic synthesis, CO gas itself is, to our tastes, a very useful and generally underutilized building block. Still, the carbonylation of organic molecules has been widely applied in the industrial-scale production of commodity chemicals from designer surfactants and lubricants to acetic acid. To understand the difficulties in reaction selectivity and rate that are intrinsic to such a simple and reactive building block, many modern studies have been conducted in the stoichiometric CO insertion with organometallic catalysts, avoiding the direct involvement of CO gas.[30, 31] The dehydrogenation reactions above feature examples of a CO ligand appearing in the catalyst's lifecycle in cases where no CO is intrinsic to the reaction. Of course, there are numerous catalytic processes that engage CO as a reagent, and in such cases, CO must necessarily interact with the catalyst. The flagship example of these is olefin hydroformylation, a process originally reported in pre-war Germany and practiced at scale today.[32]

Just last year, George Stanley and co-workers contributed "the first major discovery in hydroformylation in 50 year"[33] by designing a catalyst carbonylation equilibrium that lowers the key kinetic barrier intrinsic to the process' seminal $HCo(CO)_4$ catalyst.[34] These workers reported that a (chelate)Co(II) complex (Fig. 2) can form a unique 19 e^- triply-carbonylated complex that exploits the antibonding of the 19th electron to labilise CO and enable alkene access to the metal: thus, this third CO ligand makes an enabling modification to the mechanism by opening alkene access to the metal centre. The new catalyst can achieve reaction rates similar to $HCo(CO)_4$ at half the CO pressure. The key to the new system is the ability to coordinate bulky olefins with an open equatorial position.

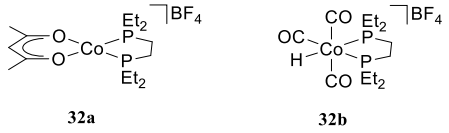
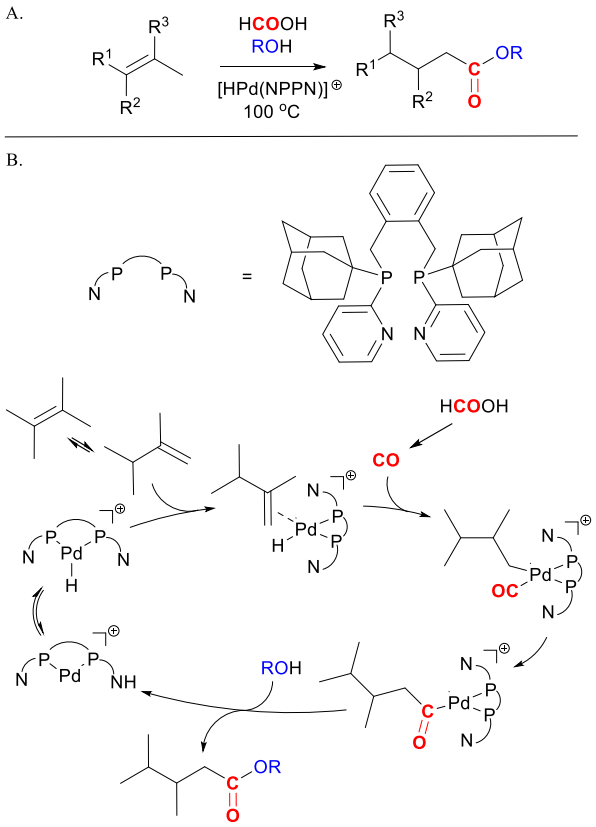


Figure 2. Cobalt (II) pre-catalyst **32a** for hydroformylation of bulky olefins. Catalyst **32b** is a 19 e^- complex that forms from **32a** under reaction with syngas.



Scheme 9. A. Hydroformylation of substituted olefins. B. One proposed mechanism where CO was involved in carbonylation on the metal centre.

Another series of synthetically useful carbonylation reactions is CO insertion into palladium coupling reactions, as in the conversion of aryl halides to carboxylic acid derivatives.[35] Beller recently reported a related reaction, carboxylation of allylic systems, in which catalyst carbonylation by formic acid played a critical, but anticipated role.[36] The overall reaction in this case is hydrocarboxylation of an allylic system with tandem allylic transposition (Scheme 9A).[13] The overall scheme utilizes CO to carbonylate the allylic substrate and an appropriate alcohol converts the intermediate (formyl)palladium to a product ester. This case is a logical complement to those that we found in our group's dehydrogenation systems: the reaction scheme necessarily involves catalyst carbonylation, but the CO must be displaced from palladium for the allylic functionalization to proceed; e.g., CO must be formed by the catalyst, then must somehow leave the catalyst to enable the process (Scheme 9B). Thereby, with the formation of the desired product, the catalyst can be converted back to its active form for the new catalytic cycle. Our cases differ in that CO must

be formed by the catalyst, then must remain bound to enable the catalytic process.

6 Conclusions and outlook

The metal-CO bond is one of the most versatile and well-studied functionalities in organometallic chemistry. Despite this, its appearance in the mechanisms of many hydrogen-transfer systems appears to us to be underappreciated. Catalyst carbonylation has long been known as an unproductive or poisoning mechanism to be avoided in catalyst design. We have shown that unanticipated catalyst carbonylation can also be productive, or even essential, in several cases of catalytic hydrogen transfer, whether as a beneficial poison or essential activating group. We hope that this analysis provides useful food for thought for the numerous groups introducing transformative, new technology in the hydrogen transfer space.

Conflicts of interest

T.J.W. is a founder of a start-up company, Catapower Inc., which is working to commercialize complex **16** for lactate synthesis.

Acknowledgements

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