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ARTICLE

Activation of Robust Bonds by Carbonyl Complexes of Mn, Fe and Co

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Metal carbonyl complexes possess among the most storied histories of any compound class in organometallic chemistry. Nonetheless, these old dogs continue to be taught new tricks. In this Feature, we review the historic discoveries and recent advances in cleaving robust bonds (e.g., C-H, C-O, C-F) using carbonyl complexes of three metals: Mn, Fe, and Co. The use of Mn, Fe, and Co carbonyl catalysts in controlling selectivity during hydrofunctionalization reactions is also discussed. The chemistry of these earth-abundant metals in the field of robust bond functionalization is particularly relevant in the context of sustainability. We expect that an up-to-date perspective on these seemingly simple organometallic species will emphasize the wellspring of reactivity that continues to be available for discovery.

Introduction

Metal carbonyls are organometallic compounds consisting of a transition metal bonded to one or more carbonyl (CO) ligands.[1] They have significant importance in various areas of chemistry and industry. Metal carbonyls feature a metal center bonded to carbon monoxide ligands through a synergistic interaction, characterized by both σ-bonding and π-backbonding, resulting in a complex electronic structure.[1–3] This unique bonding imparts strong ligand fields, and, as such, metal carbonyls have distinctive properties characteristic for low-spin complexes.[2,4]

Strong-field environments also make metal carbonyls highly effective catalysts in numerous chemical reactions.[4] They can activate and transform small molecules, such as carbon monoxide and hydrogen, through coordination and activation of robust bonds.[1] Metal carbonyl catalysts find applications in hydrogenation,[5,6] hydroformylation,[7,8] carbonylation,[9] and many other organic transformations.[10,11] As a consequence, metal carbonyls have industrial and medical significance in various processes.[12,13] For example, the Fischer-Tropsch process employs iron or cobalt carbonyls to produce hydrocarbons from carbon monoxide and hydrogen,[14] and hydroformylation utilizes cobalt and rhodium carbonyls to produce aldehydes from alkenes and carbon monoxide.[15,16] These processes have crucial implications in the production of fuels and chemicals.

Moreover, metal carbonyls are often used as precursors for generating other organometallic complexes. The carbonyl ligands can be readily displaced by other ligands, allowing for the synthesis of a wide range of metal complexes with different properties and reactivities.[2] Metal carbonyls can also serve as model systems for understanding fundamental concepts in organometallic chemistry, such as ligand interactions, metal-ligand bonding, and electronic structure. Metal carbonyls also provide insights into reaction mechanisms and catalysis.[2]

This article will focus on the chemistry of manganese, iron and cobalt carbonyls. Unlike traditionally used 4d and 5d noble metals (like Ir, Pd, Ru, Rh and Pt), first-row transition metals are significantly less cost-prohibitive[17] and toxic.[18] Naturally, as a consequence, there is a growing demand for developing the chemistry of earth-abundant 3d transition metals, with a global research focus shifting towards developing "green" synthetic protocols to avoid using noble metals.[19] Development of new, catalytic "green" methods would help with lowering the cost of syntheses and decrease overall environmental impact.[20]

Manganese is the 12th most abundant of the crust's elements and the 3rd most abundant transition metal after Fe and Ti.[21] Mn has relatively low toxicity, as it is an indispensable dietary element for humans and is found as a co-factor in different enzymes.[22] Manganese complexes adopt various geometries and oxidation states, providing a wide range of reactivity modes.[23,24] In particular, manganese carbonyls are widely used as reagents in organometallic chemistry for polymerization,[25] carbonylation, reduction, and activation of different robust bonds.[26]

Iron is the 4th most abundant element in the Earth's crust, and also the most abundant element in Earth as a whole, ahead of oxygen and silicon.[27] This metal has been crucial for development of tools and weapons since prehistorical times, and to this day plays major role in modern industries and technology.[28] As an element, iron is pivotal for maintaining a healthy metabolism,[28] with iron deficiency being the most common nutritional deficiency in the world.[29] From a chemistry standpoint, abundance and low toxicity of Fe make this element an attractive choice for catalysis, given that low-valent (nucleophilic) Fe complexes catalyze many important organic reactions, such as hydrofunctionalization and cross-coupling.[20,30] As for iron carbonyls, they find application both in

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industry (similar to the Mond process) and academic research, being precursors for many other low-valent Fe complexes and being catalysts themselves.[31,32]

Cobalt is an element encountered somewhat less frequently, compared to Fe and Mn, as it is only the 30th most abundant element in the Earth's crust and is widely and unevenly dispersed.[33] Despite this, it is still more abundant than noble metals, and is the active core of many biologically active molecules like cobalamins (vitamin B_{12}).[33] In industry, cobalt is widely used for production of lithium-ion batteries and as a catalyst for many important reactions.[33,34] A good example is cobalt tetracarbonyl hydride $HCo(CO)_4$, the original catalyst used for industrial hydroformylation.[33] Other cobalt carbonyls found use as catalysts for such transformations as Pauson-Khand reaction, hydroformylation, hydrofunctionalization and even carbonylative cross-coupling.[35–37] Even though cobalt carbonyls have been known for more than 70 years, research of their properties continues to this day.[5,38]

This article is organized by different type of bond activation reactions that can be mediated by carbonyl complexes of Mn, Fe, and Co and includes sections on C-F, C-O, and C-H cleavage. Additionally, a section is included on recent advances in hydrofunctionalization reactions of unsaturated substrates (e.g., alkenes, alkynes). In each section, both historical and recent advances enabled by metal carbonyls of each of the three metals are incorporated.

Table 1. Relative nucleophilicities of some metal carbonyl anions[a]

Anion	Relative nucleophilicity	Anion	Relative nucleophilicity
$C_5H_5Fe(CO)_2^-$ (Fp^-)	70,000,000	$Mn(CO)_5^-$ (Mc^-)	77
$C_5H_5Ru(CO)_2^-$ (Rp^-)	7,500,000	$C_5H_5Mo(CO)_3^-$ (Mop^-)	67
$C_5H_5NiCO^-$ (Np^-)	5,500,000	$C_5H_5Cr(CO)_3^-$ (Crp^-)	4
$Re(CO)_5^-$ (Rc^-)	25,000	$Co(CO)_4^-$ (Cc^-)	1
$C_5H_5W(CO)_3^-$ (Wp^-)	~500		

[a]Data as reported by R. E. Dessy, R. L. Pohl, and R. B. King, *J. Am. Chem. Soc.* **1966**, *88*, 5121.

Metal carbonyls (Mn, Fe, Co) in C-F activation

C-F activation is a process of breaking the carbon-fluorine bond in organofluorine compounds, enabling the introduction of new functional groups or the formation of new carbon-carbon bonds. It is a challenging transformation due to the strength and stability of the C-F bond.[39,40] Recent advances in catalysis have led to significant progress in C-F activation reactions.[41–45] The development of efficient and selective C-F activation reactions has important implications in various areas, including pharmaceutical synthesis, agrochemical development, and materials science.[46–51] It allows for the synthesis of fluorinated compounds with unique properties and the incorporation of fluorine atoms into complex molecular structures.[49] This article, however, will focus specifically on C-F activation reactions mediated by Mn, Fe and Co carbonyls.

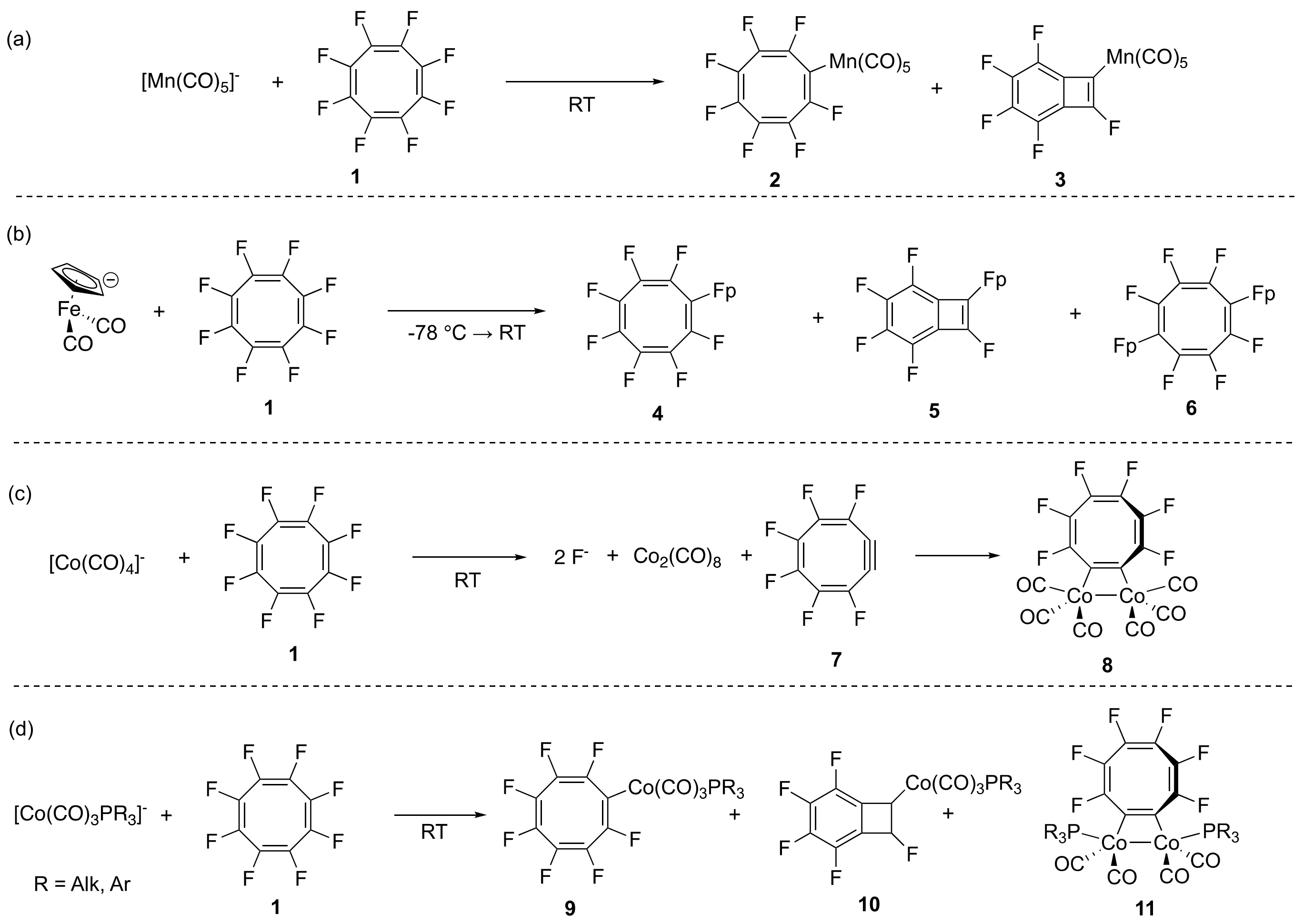
In general, metal carbonyl chemistry has been extensively investigated since the beginning of the 20th century. Among them, metal carbonyl anions, generally good nucleophiles, have been used for preparative purposes as synthetic intermediates towards unusual organometallic complexes.[52] Additionally, metal carbonyl anions' nucleophilicity correlates with their strength as reducing agents, opening nucleophilic substitution by electron-rich metal carbonyl anions as a strategy for activation of C-F bonds to complement oxidative addition.[43,52–54]

Included among the reaction chemistry of metal carbonyl anions is nucleophilic substitution of generally inert alkyl and aryl fluorides due to fluorine being most susceptible to nucleophilic attack via either S_N2 or S_NAr substitution mechanisms.[52] In that regard, polyfluorinated fluorocarbons are especially prone to nucleophilic attack because of electron density being pulled towards highly electronegative fluorine atoms.[43]

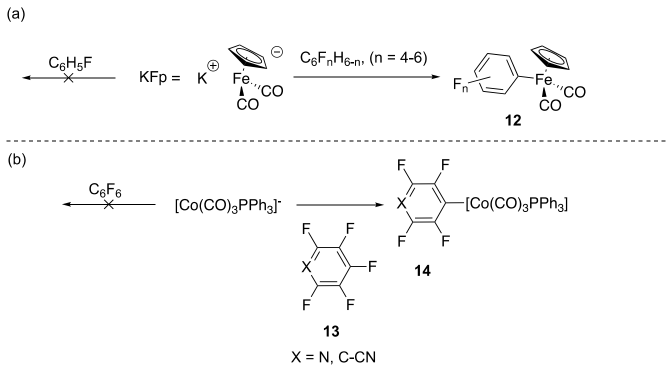
This is verified by numerous studies, where reactivity of metal carbonyl anions generally correlates with their nucleophilicity (Table 1).[55] In that respect, octafluorocyclooctatetraene (OFCOT, **1**) can serve as a benchmark of sorts for nucleophilic C(sp^2)-F bond cleavage with metal carbonyl anions. In 1990, Hughes and coworkers showed that $NaMn(CO)_5$ reacts with **1** at room temperature (Scheme 1a) to yield two products: η^1-heptafluorocyclooctatetraene complex **2** and its valence isomer complex **3**.[56] A significantly stronger nucleophile, Fe complex KFp [Fp = $CpFe(CO)_2$], not only gives similar corresponding Fe h^1-heptafluorocyclooctatetraene complex **4**, but also its Fe valence isomer **5** (Scheme 1b). Moreover, in reaction with KFp a disubstituted complex **6** is also formed, due to a higher nucleophilicity of KFp.[56]

As for cobalt carbonyls, weakly nucleophilic $Co(CO)_4^-$ does not substitute fluoride in OFCOT **1**, but instead forms complex **8** via reduction of OFCOT to hexafluorocycloocta-3,5,7-trien-1-yne **7**, formation of $Co_2(CO)_8$ and subsequent trapping of the alkyne by the latter (Scheme 1c).[57] However, when nucleophilicity of $Co(CO)_4^-$ is enhanced by addition of s-donating trialkyl or triaryl phosphines, corresponding Co-h^1-heptafluorocyclooctatetraene **9** is observed, along with its valence isomer **10** and alkyne complex **11** (Scheme 1d).[58,59]

This trend was also confirmed by similar studies conducted by Bruce and coworkers, who treated perfluoro-olefines, namely perfluorocyclohexene and perfluorocyclobutene, with a series of metal carbonyl anions. Based on the obtained results, the authors reported the following order of increase in nucleophilicity for carbonyl anions of Mn, Fe and Co: $[Fe(CO)_4]^{2-}$ < $[Co(CO)_4]^-$ < $[Mn(CO)_5]^-$ < $[Mn(CO)_4PPh_3]^-$ < $[CpFe(CO)_2]^-$.[60–62] Therefore, as seen from this series of studies, the reactivity of metal carbonyl anion highly depends on its nucleophilicity, which can be enhanced with more electron-rich, basic coordinating ligands such as phosphines or a cyclopentadienyl group.[43]



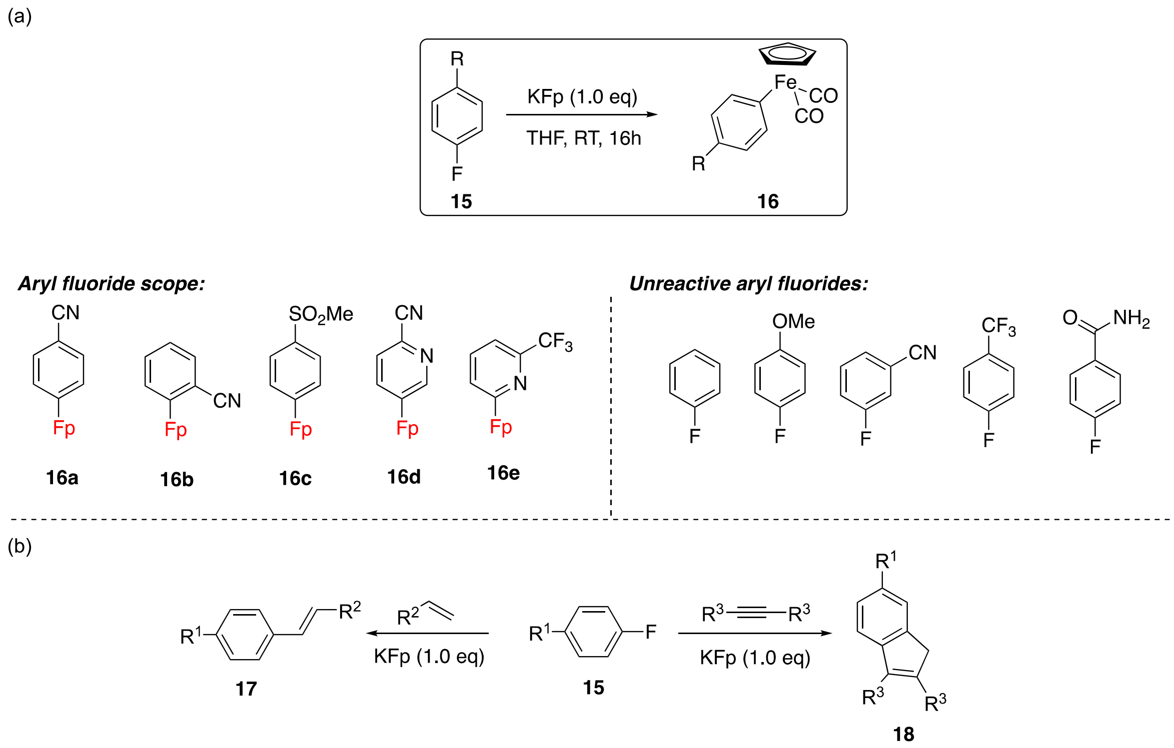
Scheme 1. Reactions of OFCOT **1** with (a) Mn, (b) Fe and (c, d) Co carbonyl anions.



Scheme 2. Reactions of (a) Fe and (b) Co carbonyl anions with (poly)fluoroarenes.

When it comes to aryl fluorides, the outcome is determined by overall balance between nucleophilicity of a metal carbonyl anion in question and the targeted (poly)fluoroarene. For instance, it is known that $[CpFe(CO)_2]^-$ easily reacts with extremely electron-deficient hexa-, penta- and tetrafluorobenzenes (Scheme 2a), giving corresponding substitution products $CpFe(CO)_2(C_6F_nH_{6-n})$ **12**.[63,64] However, no reaction was observed between KFp and more electron-rich fluorobenzene.[43] Many other metal carbonyl anions, being weaker nucleophiles (including Mn and Co carbonyls), are not capable of reacting even with hexafluorobenzene.[63] For example, only by boosting nucleophilicity of cobalt carbonyl by addition of a phosphine ligand and increasing electrophilicity of the arene further (by switching to pentafluoropyridine or adding another strong electron-withdrawing group, **13**) it is possible to get a substitution product **14** (Scheme 2b).[61]

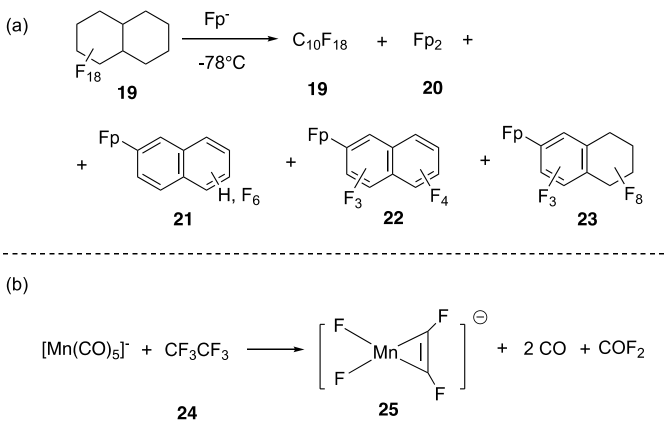
Earlier this year, in 2023, in line with data shown above, our study featured a new method for the synthesis of aryliron(II) carbonyls **16** via reaction of KFp with monofluorobenzenes **15** with (-M)-electron-withdrawing groups and electron-poor monofluoropyridines.[65] Still, electron-rich monofluorides remained unreactive under studied conditions (Scheme 3a). It is interesting to note that previously this reaction was considered impossible by some based on preliminary studies of reduction of electron-deficient bromo and iodobenzenes with KFp.[66,67] In our study bromo- and iodobenzenes were indeed reduced, but chloro- and fluorobenzenes reacted successfully. Moreover, *in-situ* generation of aryliron(II) carbonyls **16** allowed for coupling with alkenes and alkynes, which yielded vinylstyrenes **17** and indene derivatives **18**, respectively (Scheme 3b).



Scheme 3. (a) Reaction of KFp with aryl fluorides; (b) Coupling of aryl fluroides with alkenes and alkynes.

While nucleophilic substitution may work for vinyl and aryl fluorides, it is much harder to substitute C(sp^3)-F bonds by nucleophilic addition. This is where the dual nature of metal carbonyl anions, both nucleophilic and reducing, comes into play. Harrison and Richmond in 1993 showed that Fp$^-$ anion can reduce perfluorodecalin **19** in a reaction that yields Fp$_2$ dimer **20** and a mixture of Fe-substituted (poly)fluorinated naphthalenes **21**, **22** and **23** with a combined yield of 90% (Scheme 4a).[68] A similar reaction of Fp$^-$ is observed with perfluoromethylcyclohexane, which affords (poly)fluoroaryl-Fp substitution products, along with Fp$_2$ dimer. For both cases the authors propose a single electron transfer mechanism to organofluoride happening first.

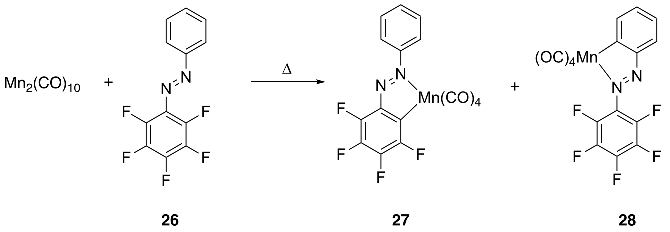
Such outcomes are not surprising given that Fp$^-$ anion is known not only as a very strong nucleophile, but also as a strong reducing agent. It is more surprising that some less reducing and nucleophilic complexes are also capable of C(sp^3)-F activation. This way, C(sp^3)-F in hexafluoroethane CF$_3$-CF$_3$ **24** can be activated by Mn(CO)$_5^-$ generated *in situ* from Mn$_2$(CO)$_{10}$, giving complex **25** in the gas phase (detected by mass spectrometry), carbon monoxide and carbonyl fluoride COF$_2$ (Scheme 4b).[69]



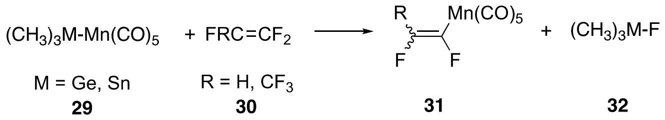
Scheme 4. C(sp^3)-F activation of fluoroalkanes with (a) Fe and (b) Mn carbonyl anions.

As an alternative approach, bimetallic cooperativity may be used to help neutral, non-nucleophilic metal carbonyls react with organofluorides. Bruce et al. reported reactions of Mn$_2$(CO)$_{10}$ with pentafluoroazobenzene **26**, giving products **27** and **28** in a combined yield of 18% (Scheme 5).[70] The authors propose that product **28** forms first, along with HMn(CO)$_5$, in a step that involves bimetallic C-H activation. Then HMn(CO)$_5$ attacks another molecule of pentafluoroazobenzene **26** in a reaction involving C-F activation and subsequent removal of fluoride as hydrogen fluoride, giving product **27**.

It is also known that heterobimetallic Mn-Sn[71] and Mn-Ge[72] bonds of complexes **29** help with C-F activation of fluoroolefins **30** with formation of trialkylgermanium or -tin fluoride **32** and corresponding vinyl manganese carbonyl complexes **31** (Scheme 6). In a way, Me_3Ge and Me_3Sn groups increase nucleophilicity of Mn, making it a "masked" analog of $Mn(CO)_5$. Similar reactions involving C-F activation are also reported for Fe-Sn bimetallic carbonyls.[73]



Scheme 5. Reaction of pentafluoroazobenzene **26** with $Mn_2(CO)_{10}$.



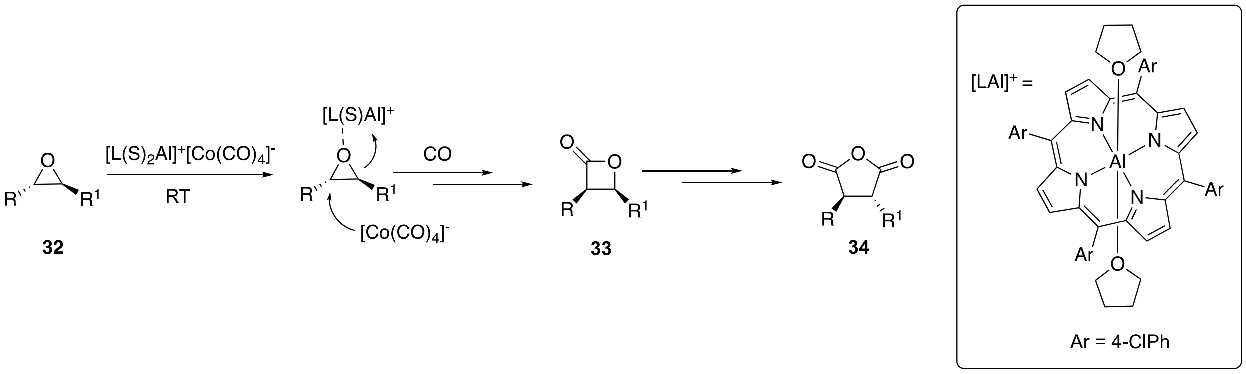
Scheme 6. Bimetallic C-F activation of fluoroolefins with Mn-Sn and Mn-Ge complexes.

Therefore, it can be concluded that Mn, Fe and Co carbonyls can be quite useful for C-F activation; further investigation of their reactivity may reveal unexpected, "hidden" reaction pathways which may lead to the development of new, better synthetic protocols for C-F activation.

Metal carbonyls (Mn, Fe, Co) in C-O activation

Activation of inert C-O bonds in various reaction intermediates and reactants is a crucial step in many useful synthetic transformations, such as cross-coupling with C-O electrophiles,[74,75] conversion of epoxides to alcohols[76] or reactions involving capturing of CO_2.[77] The development of efficient and selective C-O activation reactions has significant implications in pharmaceutical synthesis, fine chemical production, and materials science.[76,78–80] It enables the construction of complex organic molecules and provides access to novel chemical transformations.[81,82] C-O activation can be achieved through different catalytic methods, including transition metal-catalyzed processes and non-metal catalysis.[83,84] Common transition metal catalysts contain late transition metals, such as palladium, platinum, rhodium, iridium; however, copper, iron and cobalt are also widely used.[74,77] In this chapter, we will spotlight selected C-O activation agents based on Mn, Fe and Co carbonyls.

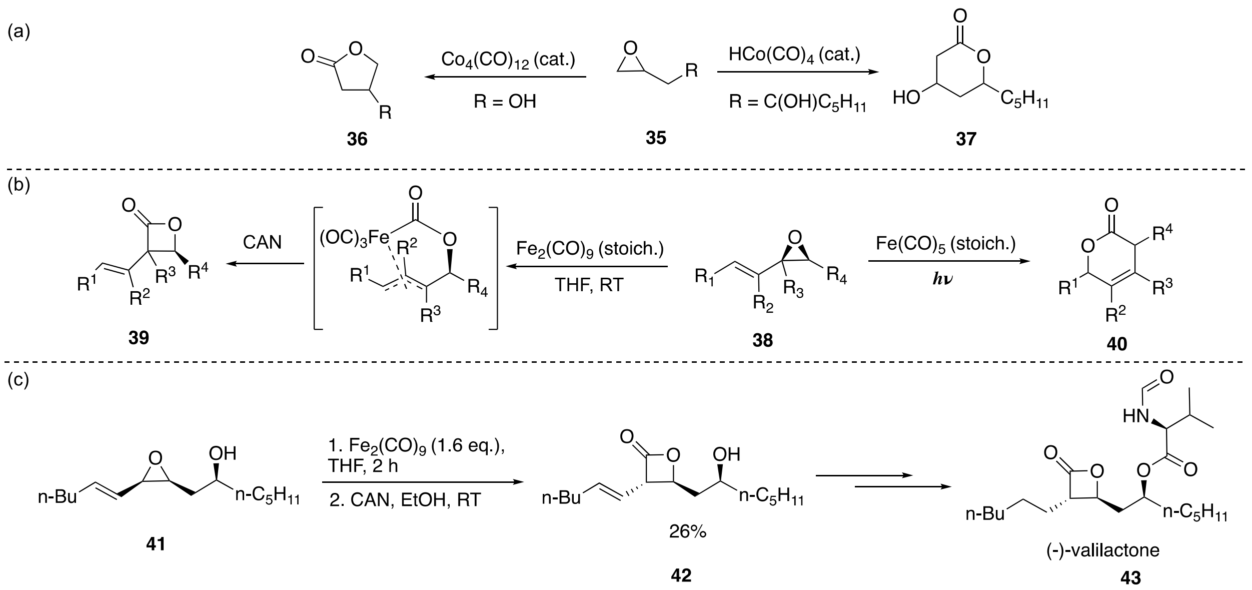
Just like with C-F activation, metal carbonyls can activate C-O bonds as nucleophiles or as reducing agents, either alone or with a co-catalyst. For the former, it is hard to think of a more seminal work than a 2007 study by Coates and coworkers, who developed the first catalytic method for conversion of epoxides to succinic anhydrides. (Scheme 7).[85]



Scheme 7. Double carbonylation of epoxides to succinic anhydrides (S = solvent).

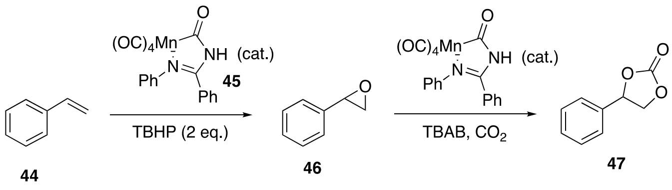
The whole process consists of two steps: at first, the epoxide **32** is carbonylated to form a β-lactone **33**, and then this lactone gets carbonylated again to afford the final product, a succinic anhydride **34**. Each of these steps involves pre-activation of the starting epoxide or β-lactone by the aluminum co-catalyst and subsequent nucleophilic ring-opening S_N2-like attack by $[Co(CO)_4]^-$. After CO insertion into Co-alkyl bond and subsequent elimination, both co-catalysts are regenerated to repeat the cycle again in this tandem reaction. This study became a cornerstone for the development of many similar systems operating as a frustrated Lewis acid/base pair.[86]

Cobalt carbonyl anion, indeed, is not the only metal carbonyl capable of epoxide ring opening. Neutral Co carbonyl complex $Co_4(CO)_{12}$, for instance, can be utilized for the synthesis of γ-lactones **36** from glycidols **35** (Scheme 8a).[87] More acidic $HCo(CO)_4$ can selectively carbonylate epoxides to form δ-lactones **37** via protonation of the epoxide **35** and subsequent ring opening by the Co complex.[88] Neutral Fe carbonyls are also capable to successfully promote synthesis of β-lactones **39** and δ-lactones **40** (Scheme 8b);[89,90] in this manner, stoichiometric amounts of $Fe_2(CO)_9$ were used to promote the synthesis of the β-lactone core **42** of (–)-valilactone **43** (Scheme 8c).[89] Such transformations show that a third way of C-O activation via oxidative addition is impossible, unlike for C-F activation.



Scheme 8. Carbonylation of epoxides with neutral (a) Co and (b, c) Fe carbonyls.

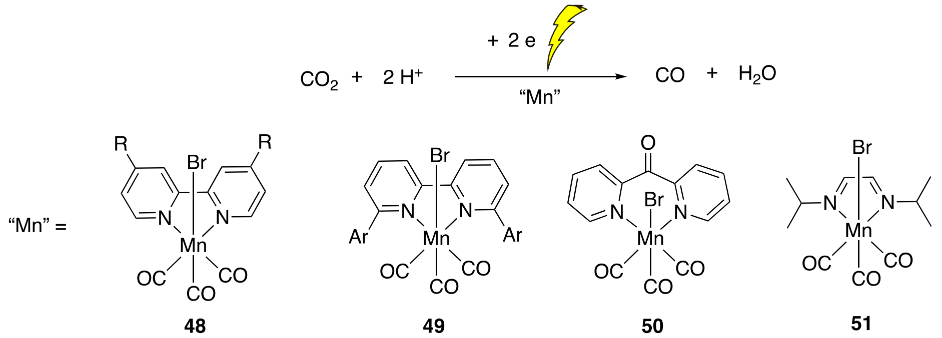
Echoing Coates' 2007 study, Mn carbonyl can also be used to produce succinic anhydrides, with the difference that for such reaction CO_2 should be used in rather than CO. In 2023, Li, Sun and coworkers reported one-pot epoxidation of alkenes and subsequent cycloaddition of CO_2, catalyzed by a manganese carbamoyl carbonyl complex **45** (Scheme 9).[91] Here Mn(I) complex was proposed to transfer oxygen atom from TBHP to styrene **44**, forming an epoxide **46** via oxidation of olefin by putative Mn(II)-O and Mn(III)-O oxo species. Then, with help of bromide from TBAB (NH_4Br) Mn complex **45** activates the epoxide **46** and facilitates insertion of CO_2 and conversion of the epoxide to a cyclic carbonate ester **47**.



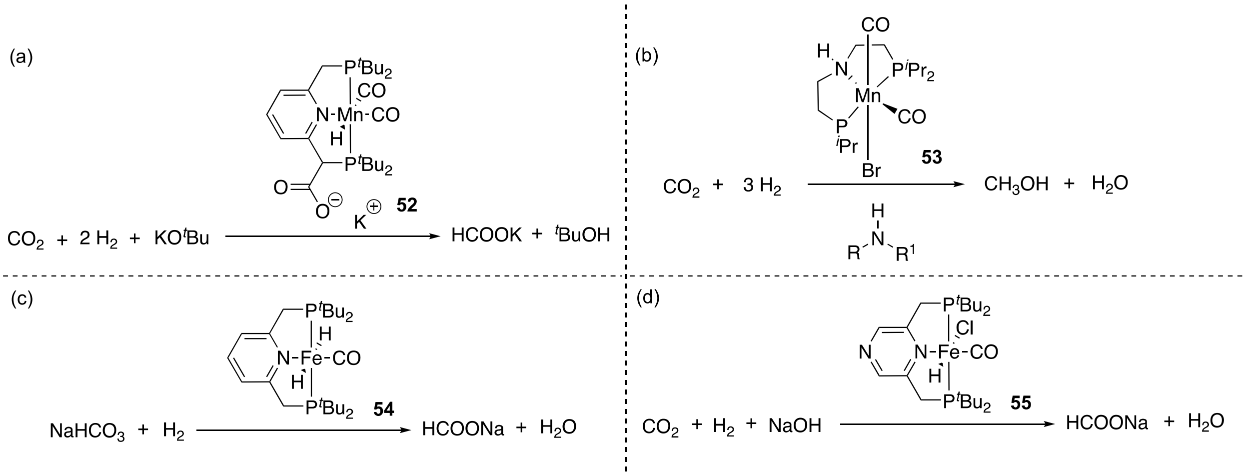
Scheme 9. Synthesis of epoxides and cyclic carbonates using Mn carbamoyl complex.

In general, Mn and Fe carbonyls are widely used to capture and reduce inert CO_2 molecules either chemically or electrochemically. For the electrochemical reduction, a whole series of diimine (particularly bipyridine)-based Mn complexes **48-51** was developed by multiple research groups to facilitate CO_2 reduction to CO, owing to easily tunable HOMO and LUMO energies of Mn(I), very well summarized in a 2018 review by Wasielewski, Sohail and coworkers (Scheme 10, selected examples).[92] In a typical catalytic cycle, a $Mn^{I}(bpy)(CO)_3Br$ complex undergoes a 2-electron reduction and after losing halide becomes $[Mn^{0}(bpy)(CO)_3]^{-}$, which then can add to CO_2. The resulting $[Mn(bpy)(CO)_3(CO_2)]^{-}$ complex undergoes protonation, forming a $[Mn(bpy)(CO)_3(CO_2H)]$ intermediate. Via subsequent protonation / 1e-reduction or 1e-reduction / protonation, CO_2 reduction products, H_2O and CO molecules, are released.[92]

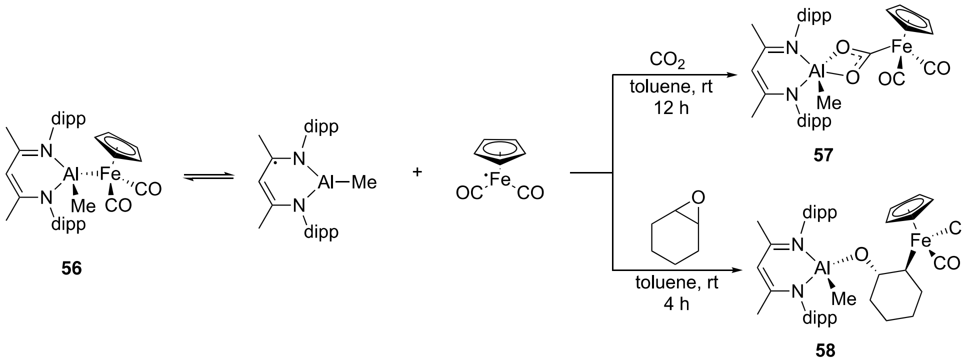
Both Mn and Fe carbonyl complexes are able of chemical reduction of CO_2 to formates. Good examples of such reduction are studies in 2021 by Saouma[93] (Scheme 11a) and 2017 by Prakash[94] studies (Scheme 11b). In both cases, a Mn(I)-PNP carbonyl complex **52** or **53** catalyzes one-pot CO_2 hydrogenation to an alcohol, using a base either as a promoter or as a co-catalyst. Iron carbonyl complexes **54** and **55** of similar architecture unsurprisingly show similar performance, giving a formate and water as products, as shown in studies by Milstein et al. (Scheme 11c and 11d, selected examples).[95,96] For all shown reactions it is believed that reduction of CO_2 occurs via interaction with a M_{CO}-H species formed in situ with subsequent release of a formate with concurrent regeneration of the catalysts' active forms.



Scheme 10. Electrocatalytic CO_2 reduction with bipyridyl manganese carbonyl complexes.



Scheme 11. Chemical reduction of CO2 with Mn and Fe carbonyl complexes.

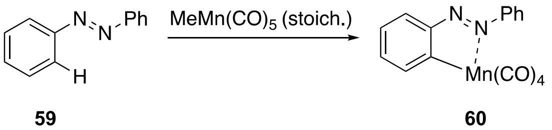


Scheme 12. Biradical activation of CO_2 and epoxide with a heterobimetallic Al-Fe_{CO} complex.

Very recently, in 2022, our group published a study on a heterobimetallic Al-Fe carbonyl system **56** capable of C-O activation in both CO_2 and epoxide, giving both CO_2 insertion **57** and epoxide ring opening **58** products (Scheme 12).[97] This bimetallic complex **56** features unique reactivity via unusual radical-pair mechanism, in which Al-Fe homolytic dissociation precedes pairwise metalloradical addition to substrate. Radical origin of reactivity was confirmed by detailed kinetic and theoretical studies. The "radical pair" mechanism described in our study represents a fundamentally novel approach to cooperative CO_2 activation, and its potential application in epoxide ring opening could open new avenues for C-O activation.

Metal carbonyls (Mn, Fe, Co) in C-H activation

Breaking a carbon-hydrogen (C-H) bond in an organic molecule and replacing the hydrogen atom with another functional group or bond is a very challenging but important undertaking, since C-H bonds are so abundant in any organic compound.[98] Historically, C-H bonds have been considered inert, as they are hard to manipulate due to their high bond strength.[20,99] Fortunately, with the advancement of C-H activation protocols, it has become possible to selectively activate specific C-H bonds and incorporate new functionalities into organic molecules without the need for prefunctionalized starting materials.[100]



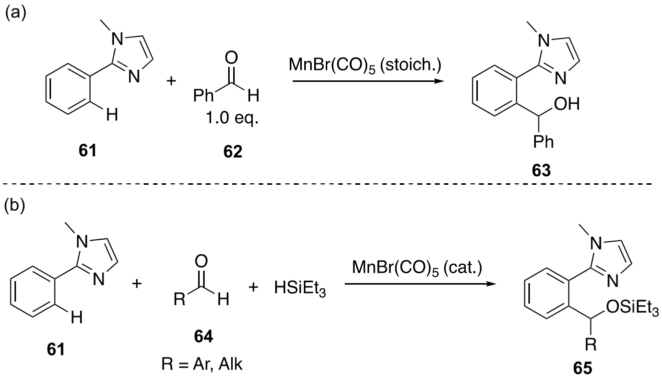
Scheme 13. First stoichiometric C-H activation by a manganese carbonyl complex.

C-H activation has many advantages over other functionalization strategies. In particular, these reactions are efficient (direct transformation of C-H bonds without prefunctionalization), quite often selective (activation of only specific C-H bonds within molecules is achieved by use of appropriate catalysts and reaction conditions) and atom efficient (i.e. most of the atoms present in the starting materials are retained in the final product).[20,101] This contributes to more sustainable and environmentally friendly synthetic processes.[100] In addition, many C-H activation methods are compatible with a broad range of functional groups.[20,101]

Typical strategies for C-H activation include transition metal-catalyzed reactions (mostly with noble metals, such as Pd, Rh and Ru),[20,102] photoredox catalysis (using light to facilitate cleavage of C-H bonds)[103] and organocatalysis.[104] Overall, C-H activation has revolutionized organic synthesis by providing new synthetic tools and strategies. It has found applications in the synthesis of complex natural products, pharmaceuticals, agrochemicals, and functional materials.[20,100] The ongoing development of C-H activation methodologies continues to expand the synthetic possibilities and push the boundaries of organic chemistry.[20,98,101] This article examines C-H activation from the standpoint of using Mn, Fe and Co carbonyl complexes as catalysts to achieve such transformations.

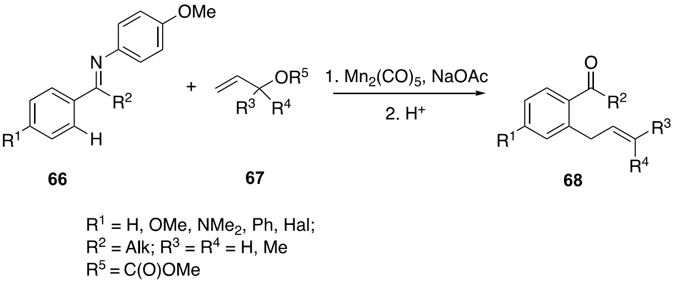
Among those three metals, manganese truly shines due to abundance of reports on selective Mn(I) catalysts used in C-H activation chemistry, becoming a quickly emerging area of organic synthesis on its own.[105–107] Two Mn carbonyl catalysts in particular, $MnBr(CO)_5$ and $Mn_2(CO)_{10}$, are responsible for most reports in the field as in some cases they reveal selectivity not present for catalysts based on noble metals (such as Ru and Pd).[20]

One of the first examples of Mn-mediated C-H activation was reported in 1970 by Bruce et al., where azobenzene **59** reacts with stoichiometric amounts of methyl manganese carbonyl to form manganacycle **60** (Scheme 13).[108] Selectivity in this case was determined by the presence of directing azo group.



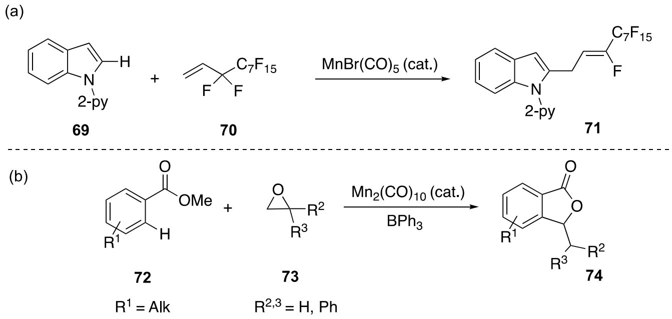
Scheme 14. Insertion of aldehydes into aromatic C-H bond catalyzed by Mn carbonyl complexes.

As the chemistry of Mn carbonyl evolved, new reports demonstrated that catalytic C-H activation reactions are feasible. In 2007, Kuninobu, Takai and coworkers closed the gap between Mn-based stoichiometric and catalytic C-H activation (Scheme 14).[109] They showed that Mn(I) complex $MnBr(CO)_5$ was able to insert a polar C=O bond of aldehydes **62** and **64** into an aromatic C-H bond of **61** not only when used in stoichiometric amounts (Scheme 14a), but catalytically as well (if sacrificial $HSiEt_3$ was used to additional provide driving force; Scheme 14b). It is very interesting to note that while another Mn catalyst, $Mn_2(CO)_{10}$, worked in this case, catalysts based on noble/rare metals, such as Re, Ru, Rh and Ir did not show any activity.



Scheme 15. Mn carbonyl catalyzed C-H allylation.

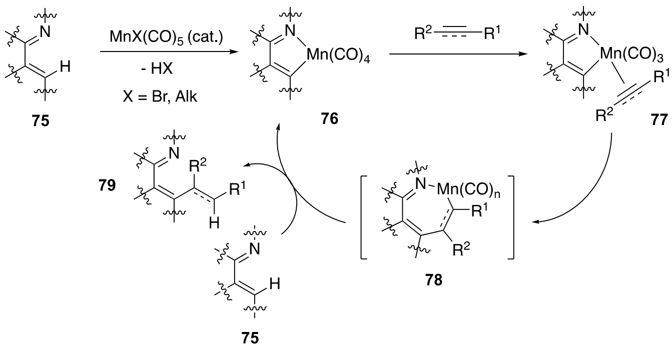
Another classic example of such a reaction would be Mn-catalyzed C–H allylation of aryl- and hetaryl-imines, reported by Ackermann and coworkers in 2016, where imines **66** were coupled with various electrophiles **67** (Scheme 15).[110] Presence of imine functional group was crucial for this reaction, which acted as a directing group. It is worth mentioning that, again, both $MnBr(CO)_5$ and $Mn_2(CO)_{10}$ showed great activity and selectivity. Also, similar methods were developed for alkynes,[111–113] α,β-unsaturated esters,[114] isocyanates[115] and many other substrates.[102]



Scheme 16. Mn carbonyl catallyzed (a) C-F/C-H functionalization of indoles and (b) C-O/C-H functionalization of aromatic esters.

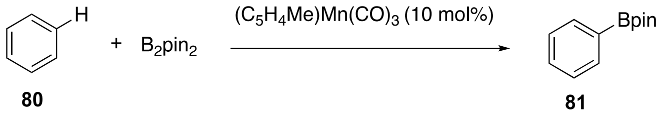
In addition, Mn-catalyzed C-H activation can be coupled with functionalization of other robust bonds, such as C-F and C-O bonds. Ackermann et al. in 2017 reported a Mn carbonyl-catalyzed allylative C-F/C-H functionalization of indoles **69** with perfluoroalkenes **70** under mild conditions, with Mn doing both C-H activation with subsequent migratory insertion of the olefin and β-F elimination (Scheme 16a).[116] As for one-pot C-O/C-H activation, Kuninobu et al. reported in 2016 cooperative $Mn_2(CO)_{10}$/borane system that catalyzed the synthesis of isobenzofuranones **74** from various esters **72** and epoxides **73** (Scheme 16b).[117] This protocol is also the first example of a Mn-catalyzed C-H activation directed by an oxygen-directing group.

A generalized mechanism of Mn-catalyzed C-H activation consists of the following steps:[118,119] 1. initial cyclomanganation / C-H activation at Mn(I) **76**; 2. loss of CO and coordination of the unsaturated substrate on Mn(I) **77**; 3. migratory insertion and formation of the 7-membered manganocycle **78**; 4. protonation, release of the product **79** and formation of the initial 5-membered manganocycle **76**, which starts the catalytic cycle anew. The mechanisms were extensively investigated and confirmed experimentally with isolation of 7-membered manganocycles. (Scheme 17).[119]



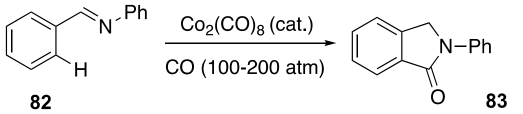
Scheme 17. Manganese carbonyl catalyzed C-H activation: formation of a 7-membered manganacycle.

Another useful transformation was reported in 1999 by Hartwig and coworkers, who accessed C-H borylation product **81** from benzene **80** under photochemical conditions and CO atmosphere using a Mn(I) carbonyl catalyst (Scheme 18).[11] The authors proposed that this reaction proceeds via either oxidative addition or σ-bond metathesis.



Scheme 18. Mn carbonyl-catalyzed photochemical borylation of benzene.

Of course, C-H activation is not limited to carbonyls of manganese. Cobalt carbonyls are also capable of C-H activation, with one of the first reports published by Murahashi in 1955 featuring synthesis of phthalimidines **83** from Schiff bases **82** (Scheme 19).[120]



Scheme 19. Cobalt carbonyl catalyzed synthesis of phthalimidines.

Most of the other examples of cobalt carbonyl-catalyzed C-H activation reactions are based on a Co(III) complex, $Cp^*CoI_2(CO)$. As selected examples, Ackermann and coworkers reported reactions of indoles **84** with unactivated alkenes and carbonyl compounds, using 1-$AdCO_2H$ to control *anti*-Markovnikov **85** vs Markovnikov **86** regioselectivity of these reactions (Scheme 20a).[121] In 2017 Li et al. reported coupling of indoles **84** with alkynes via C-H activation, using only catalytic amounts of $Cp^*CoI_2(CO)$ to get vinylindoles **87** (Scheme 20a).[122] The same catalyst can also be used for annulations (Scheme 20b, Zhang's 2016 study on annulation of esters **88** with alkynes **89** to indenones **90** as an example),[123] C-H nitrogenation[124], halogenation[125,126] and C-F/C-H functionalization.[127] It is interesting to note that for many of the reactions catalyzed by $Cp^*CoI_2(CO)$, the mechanism is similar to the reactions catalyzed by Mn(I) complexes and involves formation of 7-membered cobaltocycles.

C-H activation reactions catalyzed by Fe carbonyls are noticeably less abundant; however, precedents are reported in the literature. Iron carbonyls are capable of $C(sp^2)$-H and $C(sp^3)$-H activation. For instance, diiron nonacarbonyl can react with Schiff bases (ketimines) **91** via oxidative addition of the $C(sp^2)$-H bond to the one of the Fe(0) centers, as shown by groups of Reed and Mills in 1960s (Scheme 21a), forming complex **92**.[128,129] On the other hand, Captain et al. reported that a bimetallic cluster complex **93**, being refluxed in toluene, gives complex $Fe_2[\mu\text{-}Sn^tBu(CH_2Ph)]_2(CO)_8$ **94**, a product of replacement of tert-butyl groups with benzyl groups via selective benzylic $C(sp^3)$-H activation of toluene (Scheme 21b).[130] The authors proposed that the mechanism of this reaction is radical in nature.

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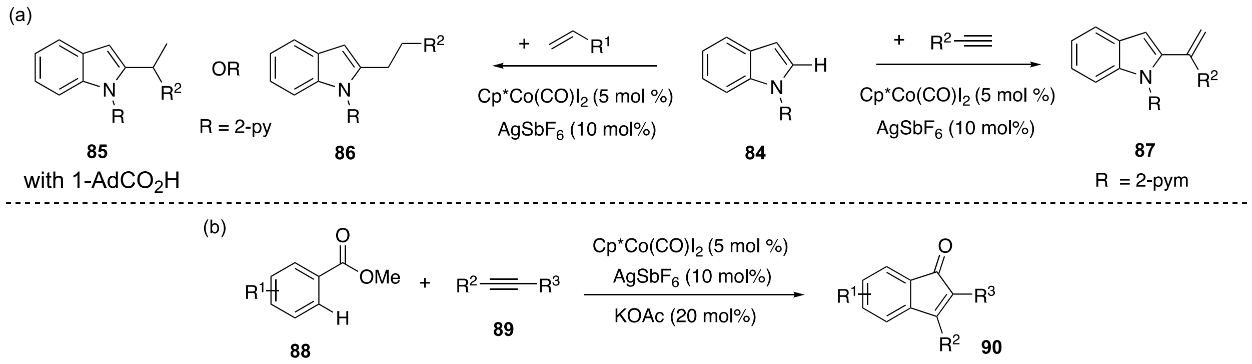
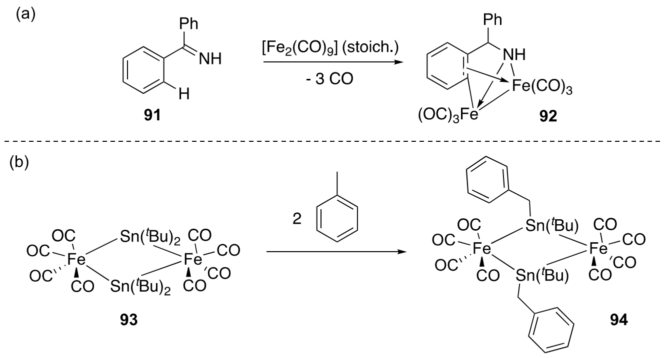
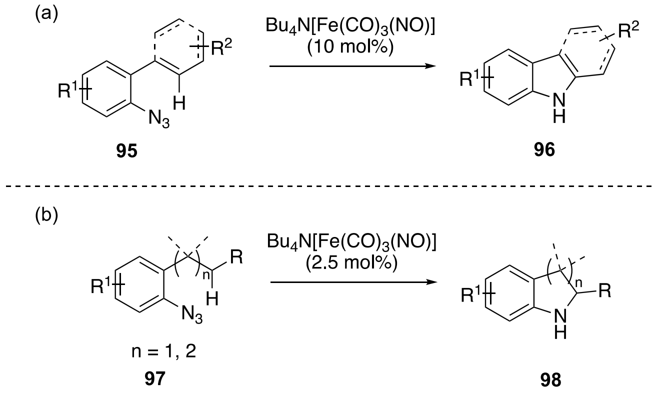


Scheme 20. Co carbonyl catalyzed reactions of (a) indoles with alkynes and alkenes and (b) of aromatic esters with alkynes.

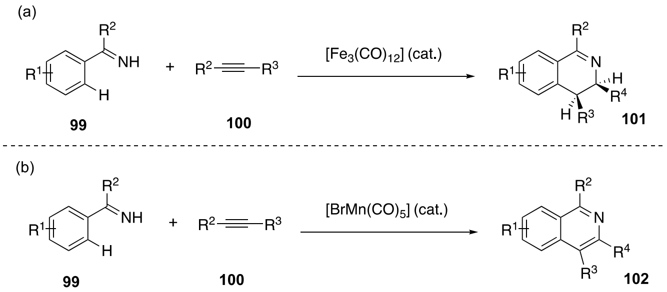


Scheme 21. Fe carbonyl promoted (a) C(sp^2)-H and (b) C(sp^3)-H activations.



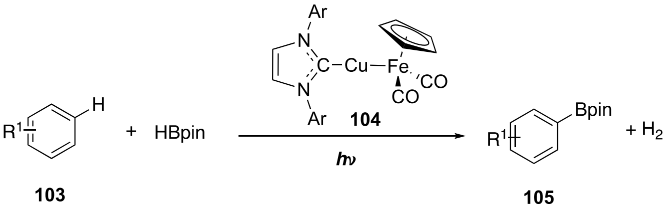
Scheme 22. Fe carbonyl catalyzed denitrogenative (a) C(sp^2)-H and (b) C(sp^3)-H aminations.

Fe carbonyl complex can also be used in catalytic amounts to promote denitrogenative C(sp^2)-H **96** and C(sp^3)-H **98** aminations of azides **95** and **97** (Scheme 22a&b), as shown by the group of Plietker in a series of work on a nucleophilic Fe(0) complex, Bu$_4$N[Fe(CO)$_3$(NO)].[131,132] Likely the step-wise mechanism involves formation of an iron nitrene intermediate, which facilitates formation of the C-N bond.



Scheme 23. (a) Fe carbonyl-catalyzed and (b) dehydrogenative Mn carbonyl catalyzed annulation of N-H imines with alkynes.

Annulation is also possible with iron carbonyl complex as a catalyst, a good example of which is a 2016 study by Wang, Chen and coworkers. They reported redox-neutral annulation of N-H imines and internal alkynes using Fe$_3$(CO)$_9$ as a catalyst, which yielded *cis*-3,4-dihydroisoquinolines as major products (Scheme 23a).[133] It is interesting that a Mn-based system (with BrMn(CO)$_5$) enabled a dehydrogenating version of this reaction, giving isoquinolines as major products instead (Scheme 23b).[112]

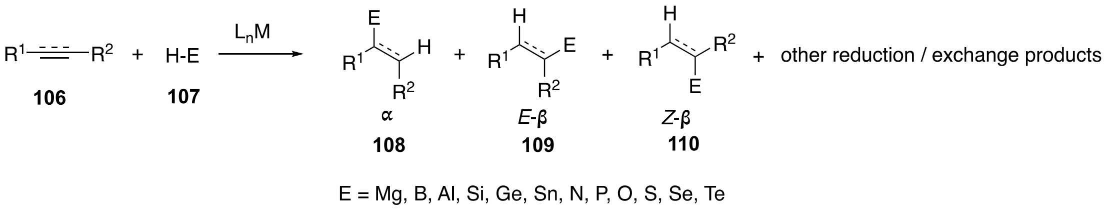


Scheme 24. Bimetallic Cu-Fe$_{CO}$ C-H borylation of arenes under photochemical conditions.

Finally, in 2013 our group reported a photochemical C-H borylation of arenes **103**, using a bimetallic NHC-Cu-Fe$_{CO}$ catalyst **104**. This transformation previously required the use of noble metals (Scheme 24) [134] except for the single example with Mn reported by Hartwig (see Scheme 18). The proposed mechanism involves cooperative bimetallic versions of oxidative addition and reductive elimination as reaction steps, making it potentially possible to generalize the bimetallic cooperativity mechanistic paradigm to other reactions.

Regioselectivity control with Mn, Fe, Co carbonyls in hydroelementation reactions of unsaturated hydrocarbons

Hydroelementation reactions represent a prominent class of transformations in organic and organometallic chemistry. In essence, hydroelementation is the addition of E–H compounds (where E = e.g. Mg, B, Al, Si, Ge, Sn, N, P, O, S, Se, Te) to unsaturated C–C double and triple bonds in olefins and alkynes, C–N double and triple bonds in imines and nitriles, and C-O double bonds in carbonyl compounds.[135] These reactions are extensively studied and are considered pivotal for obtaining functionalized compounds.[136,137] They can occur through catalytic or uncatalyzed processes, and the stereo- and regioselectivity of the reactions depend on various factors including the catalyst, reagent, and reaction conditions.[138]

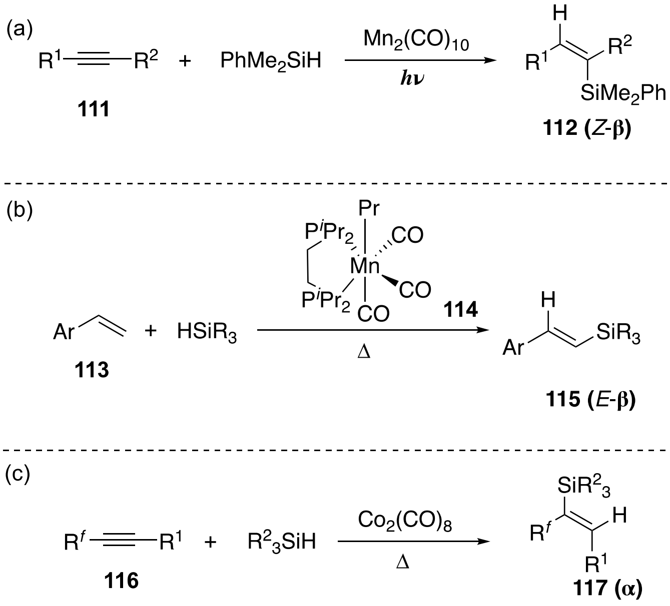


Scheme 25. Possible products of alkyne/alkene hydroelementation.

In particular, hydroelementation of alkynes **106** and dehydrogenative hydroelementation alkenes is a straightforward and efficient method for synthesizing unsaturated vinyl organometallic compounds (Scheme 25).[139] It offers atom economy by directly incorporating elements into the target molecules. Various hydroelementation processes, such as hydroborylation, hydrosilylation, hydroamination, hydrostannylation, and, recently, hydrogermylation are particularly valuable, as they provide essential building blocks.[140] The literature extensively covers the hydroelementation of both terminal and internal alkynes, highlighting their versatile reactivity and synthetic utility.

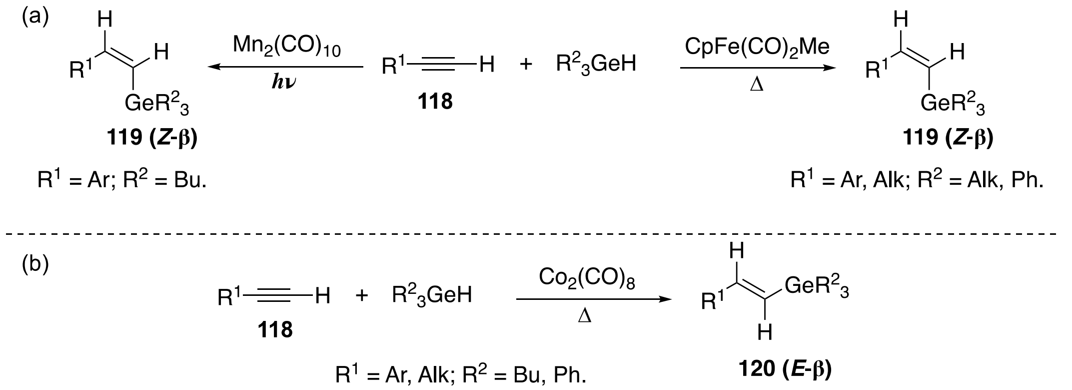
However, achieving control over regio- and stereoselectivity in such reactions continues to pose a significant challenge (e.g. Markovnikov **108** vs anti-Markovnikov, **109** *cis*- vs **110** *trans*-regioselectivity, Scheme 25). In numerous instances, the selectivity is heavily reliant on tailored reaction conditions or the presence of specific functional groups.[141] Fortunately, significant advances have been made towards optimizing product selectivity via thorough design of the metal core and ligand environment of a number of catalysts, which also includes Mn, Fe and Co carbonyls.[139]

Carbonyl complexes of all three earth-abundant metals can be effectively used to selectively access major regioisomers (i.e. α- and *cis*-, *trans*-β-isomers) in a variety of hydroelementation reactions. Manganese and cobalt carbonyls have been successfully used to cover three major isomers in hydrosilylation reactions of alkynes, which are one of the most important and straightforward methods for the synthesis of vinylsilanes. For instance, Zhi-Hao Zhang, Bo Zhang and coworkers reported in 2019 reported *trans*-selective hydrosilylation of alkynes **111**, catalyzed by dimanganese decacarbonyl complex $Mn_2(CO)_{10}$ under photochemical conditions, giving the *Z*-β product **112** (Scheme 26a).[142] On the other hand, Kirchner et al. showed in a 2021 study that a biphosphine tricarbonyl Mn(I) complex *fac*-$[Mn(dippe)(CO)_3(CH_2CH_2CH_3)]$ **114** can be used to make *E*-β vinylsilanes **115** from styrenes **113** under thermal conditions (Scheme 26b).[143] Furthermore, cobalt carbonyl $Co_2(CO)_8$ was successfully utilized as a catalyst by the Konno group to obtain α-trifluoroalkylvinylsilanes **117** from fluoroalkylated alkynes **116** with high yields and selectivity (Scheme 26c).[144]

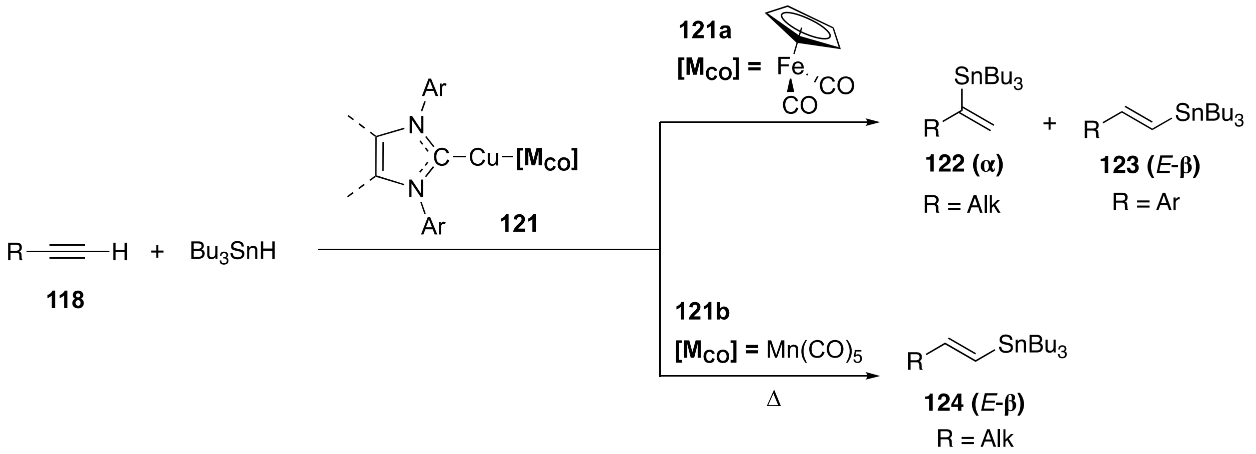


Scheme 26. Mn carbonyl catalyzed (a) *Z*-β and (b) *E*-β selective hydrosilylations of alkenes and alkynes; and (c) Co carbonyl catalyzed Markovnikov hydrosilylation of fluoroalkylated alkynes.

Regioselectivity can also be controlled with Mn, Fe and Co carbonyls in hydrogermylation reactions, as vinylgermanes have recently emerged as alternative, more stable, less toxic Pd cross-coupling partners, compared to organosilanes, organostannanes and organoboronic acids.[145] Using either manganese carbonyl $Mn_2(CO)_{10}$ (Z.-H. Zhang, B. Zhang, 2019)[142] under photochemical conditions (Scheme 27a) or methyliron carbonyl $CpFe(CO)_2Me$ under thermal conditions (Scheme 27a, Nakazawa, 2011)[146] affords the *Z*-β vinylgermanes **119** and **120** as the major product via hydrogermylation of terminal alkynes **118** with trialkyl and triarylgermanes. Recently, in 2021, our group reported Co carbonyl complexes for the first time as viable catalysts for *E*-β **120** selective hydrogermylation of terminal alkynes **118** (Scheme 27b).[147] Our method demonstrated broad functional group tolerance and practical utility for the late-stage hydrogermylation of natural products.



Scheme 27. (a) Mn and Fe carbonyl catalyzed *Z*-β selective hydrogermylation of terminal alkynes; and (b) Co carbonyl catalyzed *E*-β selective hydrogermylation of terminal alkynes.



Scheme 28. Heterobimetallic hydrostannylation of terminal alkynes.

Regioselectivity of hydrostannylation reactions can also be controlled using different metal carbonyls. Vinylstannanes hold great significance in synthetic chemistry due to their ability to undergo versatile transformations in various reactions;[148] however, controlling regio- and stereoselectivity of hydrostannylation reactions may pose a significant challenge.[149] Sometimes, when typical mononuclear metal catalysts are ineffective, alternative paradigms for catalyst design may achieve the desired outcomes. One of such alternative strategies can be bimetallic catalysis, which has emerged as a crucial strategy in synthetic chemistry, offering distinct reactivity modes and/or selectivity patterns that go beyond what is achievable with conventional monometallic catalysts.[150,151]

In this manner, our group reported in 2019 a synthetic protocol that provides access to (E)-β-vinylstannanes and challenging α-vinylstannanes from terminal alkynes **118**, relying on tunable heterobimetallic catalysts.[152] Using NHC-Cu-$[M_{CO}]$ complexes **121**, both regioisomers were obtained. If metal carbonyl part has iron core $FeCp(CO)_2$ **121a**, then the major product would be an α-vinylstannane **122** if alkylacetylene was used, and the product would be an (E)-β-vinylstannane **123** if arylacetylene was reacted instead (Scheme 28). Upon switching the metal carbonyl part from $Mn(CO)_5$ **121b**, (E)-β-vinylstannanes **124** were observed as the major product. Mechanistic studies confirmed the bimetallic mode of operation for both Cu-Fe and Cu-Mn complexes. The mechanisms were also modeled computationally in a recent study by Li and coworkers.[153]

Conclusions

Overall, metal carbonyls play a vital role in industrial processes and academic research. Their unique properties and reactivity make them valuable tools in various areas of chemistry and contribute to advancing our understanding of organometallic chemistry and catalysis. Metal carbonyl catalysts based on Mn, Fe and Co are of particular interest because of these metals' abundance, low cost and low toxicity.

As we showed in our review, Mn, Fe and Co carbonyls are capable of activating strong C-F, C-O and C-H bonds, as well as controlling regioselectivity of hydrofunctionalization reactions. Of course, even more amazing transformations are possible with other Mn, Fe and Co catalysts, but our aim was to highlight capability for activating robust covalent bonds by carbonyl complexes of the aforementioned metals.

Metal carbonyls are likely to continue playing a vital role in catalytic processes, especially in the realm of homogeneous catalysis. Further exploration of their reactivity and coordination modes could lead to the development of new catalytic reactions with enhanced efficiency and selectivity. Metal carbonyls also offer opportunities for sustainable chemistry practices, including the utilization of CO_2 as a feedstock for the synthesis of value-added chemicals. The development of efficient and selective metal carbonyl-based catalysts for CO_2 conversion could contribute to the remediation of greenhouse gas emissions and the transition to a more sustainable chemical industry.

Despite these significant advances in the field, there is always room for improvement. Since many of the aforementioned metal carbonyls are air sensitive, we expect to see development of new, air and benchtop stable metal carbonyl catalysts in the future. Applying new mechanistic paradigms to metal carbonyls, like bimetallic catalysis, may expand their chemistry even further. Anticipated future research includes a growing focus on the applications of metal carbonyls in the fields of electrochemistry and photochemistry. More broadly, in the future we will likely see more research on metal carbonyls that involves collaborations between different areas of chemistry, combining concepts from traditional coordination chemistry with emerging fields, such as nanotechnology[154] and materials science.[155]

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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