JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Subscriber access provided by UNIV OF DURHAM

Communication

Iron-Mediated Coupling of Carbon Dioxide and Ethylene: Macrocyclic Metallalactones Enable Access to Various Carboxylates

Stephan M. Rummelt, Hongyu Zhong, Ilia Korobkov, and Paul J. Chirik

J. Am. Chem. Soc., **Just Accepted Manuscript** • Publication Date (Web): 03 Sep 2018

Downloaded from http://pubs.acs.org on September 3, 2018

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

ACS Publications

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Iron-Mediated Coupling of Carbon Dioxide and Ethylene: Macrocyclic Metallalactones Enable Access to Various Carboxylates

Stephan M. Rummelt,[1] Hongyu Zhong,[1] Ilia Korobkov,[2] Paul J. Chirik*,[1]

[1]Department of Chemistry, Princeton University, Princeton, New Jersey 08544, United States

[2]SABIC Corporate Research & Development, Fundamental Catalysis, Thuwal 23955-6900, Saudi Arabia

Supporting Information Placeholder

ABSTRACT: Treatment of $(^{iPr}PDI)Fe(N_2)_2$ (^{iPr}PDI, 2,6-(2,6-$iPr_2C_6H_3N{=}CMe)_2C_5H_3N$) with CO_2 and ethylene resulted in the formation of a homologous series of saturated and unsaturated iron carboxylate products, $(^{iPr}PDI)Fe(O_2CR)$, the distribution of which depends on the ratio of the reagents. The solid-state and electronic structures of a saturated product, $(^{iPr}PDI)Fe(O_2CC_2H_5)$ was elucidated. Product distributions, deuterium labeling studies and stoichiometric experiments support initial formation of a five-membered metallalactone intermediate, which undergoes subsequent ethylene insertions to generate macrocyclic metallalactones. Competitive β-hydride elimination, CO_2 insertion or reaction with H_2 determine the fate of the metallalactone; the latter accounting for formation of iron complexes with saturated carboxylates. Similar reactivity was observed upon addition of propiolactone and ethylene to $(^{iPr}PDI)Fe(N_2)_2$, supporting C-O oxidative addition and C-C bond formation through metallacycle intermediates.

Carbon dioxide (CO_2) is an inexpensive and naturally abundant C_1-source and has received considerable attention for use in C–C bond forming reactions.[1] Because the supply of ethylene has increased due to the development of vast global natural gas deposits,[2] the discovery of new catalytic methods for the coupling of CO_2 and ethylene is an attractive route for the synthesis of commodity carboxylic acids such as succinic and acrylic acid.[3] While considerable effort has been devoted toward the synthesis of the latter, the unfavorable thermodynamics of the reaction (ΔG^o_{gas} = +14 kcal/mol; ΔG^o_{THF} = +5 kcal/mol) require the addition of stoichiometric additives, typically bases, to enable turnover under standard conditions.[4,5]

Oxidative coupling of CO_2 and ethylene with a reduced transition metal complex to form a five-membered metallalactone is the most well studied method for the synthesis of acrylic acid. Examples of this approach have been demonstrated with Ni,[4,6] Mo,[7] W,[7] Ti,[8] V,[9] Zr[10], Fe,[11] Pd,[5] and Rh.[12] However, the resulting metallacycles are typically resistant to β-hydrogen elimination or do not release free acrylic acid due to strong metal–oxygen bonds.[7,13] Lewis acids have been shown to promote β-hydride elimination often leading to ring contraction through reinsertion to the corresponding four-membered metallalactones.[14]

One attractive strategy for overcoming the thermodynamics of CO_2-ethylene coupling is to incorporate additional equivalents of alkene – each successive C–C bond forming event adds approximately 12 kcal/mol of driving force to the reaction (Figure 1a).[15] The corresponding products, both saturated and unsaturated, long-chain carboxylic acids and diacids are useful building blocks in chemical synthesis and for materials.[16] While an attractive approach, few metal complexes promote the coupling of CO_2 with multiple ethylene units. At 65 °C, DBU-supported (DBU= 1,8-diazabicyclo[5.4.0]undec-7-ene) five-membered nickel-metallalactones have been shown to insert an additional ethylene unit to generate the corresponding seven-membered ring products.[17] These intermediates undergo rapid β-hydride elimination, supporting the notion that five-membered metallalactones are rigid and exhibit a high barrier for β-H transfer.[6] Here we describe CO_2-ethylene coupling reactions with a pyridine(diimine) iron dinitrogen complex that promotes multiple insertions of ethylene depending on the ratio of the reagents (Figure 1c). The degree of saturated versus unsaturated carboxylate product varies with the chain length and highlights important reactivity differences between metallalactones depending on ring size.

Reports of iron-meditated CO_2-ethylene coupling are rare due to competitive decarbonylation and formation of iron carbonate complexes.[18] Hoberg and coworkers reported that addition of CO_2 to phosphine-supported iron bis(ethylene) complexes followed by acid-mediated methanolysis yielded mixtures of succinic and methylmalonic methyl esters depending on the identity of the added phosphine ligand.[11] No carboxylates arising from single CO_2 incorporation or any organometallic intermediates were observed.[11] In complementary work, our laboratory has reported that reduced, aryl-substituted pyridine(diimine) iron compounds exhibit a rich catalytic [2+2] cycloaddition[19] and hydrovinylation[20] chemistry upon treatment with alkenes or alkenes and dienes. Mechanistic studies and product distributions are consistent with oxidative coupling of the olefins to form iron metallacycles,[19b,21] and in the case of cyclobutane formation, C(sp^3)- C(sp^3) reductive elimination from an intermediate-spin Fe(III) complex where the redox-active pyridine diimine adopts its radical, monoreduced form (Figure 1b).[21] Metal complexes bearing redox-active ligands are attractive for CO_2-ethylene coupling as they can pacify the oxophilicity of transition metals, ultimately assisting product release from metallalactones or metal carboxylates. Prime examples include iron complexes with reduced azophilicity that promote azide hydrogenation[22] as well as zirconium compounds that reversibly coordinate dioxygen.[23]

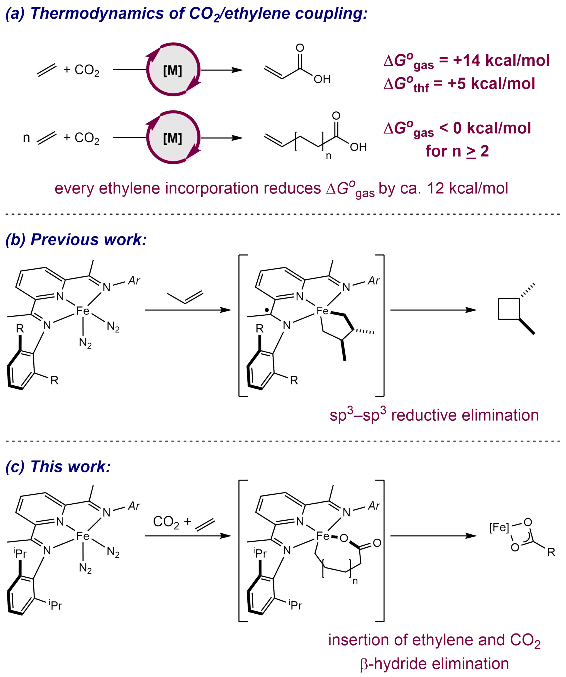


Figure 1. (a) Thermodynamics of CO_2/ethylene coupling. (b) Metallacycles as intermediates in iron-catalyzed [2+2] cycloaddition of olefins and (c) iron-mediated coupling of CO_2 and ethylene.

Our studies commenced with the addition of excess ethylene (50 equiv) and CO_2 (5 equiv) to a toluene solution of (^{iPr}PDI)Fe(N_2)$_2$ (**1-N_2**, Figure 2a). Excess ethylene was used in initial experiments to minimize possible formation of iron carbonates. This procedure yielded a mixture of paramagnetic pyridine(diimine) iron compounds, the major being identified as the propionate derivative, (**1-$O_2CC_2H_5$**) as judged by ^{1}H NMR spectroscopy and comparison to an independently prepared sample (see SI for details).[24] The zero-field ^{57}Fe Mößbauer spectrum of the product mixture following addition of ethylene and CO_2 exhibits a single doublet with an isomer shift of δ = 0.98 mm/s and quadrupole splitting of $|\Delta E_Q|$ = 1.53 mm/s, signaling formation of iron products with an electronic structure and coordination environment identical to **1-$O_2CC_2H_5$**. Treatment of the iron products with ethanol and HCl and analysis by GC-MS established formation of a range of ethyl esters with carbon numbers ranging from C_3-C_{21}, with the latter being the heaviest detectable homologue by GC (Figure 2b). With the C_3- and C_5-derived esters, only saturated products were observed; for products C_7 or higher, unsaturated derivatives were detected the ratio of which increased with increasing chain length. Additionally, linear bis-carboxylates were detected as minor products, with the C_{16}-derivative as the heaviest GC-detectable homologue.

The solid-state structure of **1-$O_2CC_2H_5$** was determined by X-ray diffraction and established an distorted trigonal bipyramidal coordination environment around the iron center with a κ^2*O,O'*-carboxylate (Fe–O1 = 2.095(13) Å; Fe–O2 = 2.109(13) Å). Bond distances of the bis(imino)pyridine chelate (C_{imine}–N_{imine} = 1.305(2), 1.307(2) Å; C_{ipso}–C_{imine} = 1.454(2) and 1.447(2) Å) are consistent with the one-electron-reduced form of the chelate (Figure 2c).[25] A solid-state magnetic moment of 3.6 μB (23 °C) supports an overall $S = 3/2$ ground state arising from a high spin iron(II) center ($S = 2$) engaged in antiferromagnetic coupling with the ligand radical anion. The zero-field ^{57}Fe Mößbauer spectrum of **1-$O_2CC_2H_5$** at 80 K exhibited nearly identical features to that of the mixture obtained after CO_2-ethylene coupling (δ = 1.01 mm/s; $|\Delta E_Q|$ = 1.56 mm/s), also consistent with a high spin iron(II) center.[26]

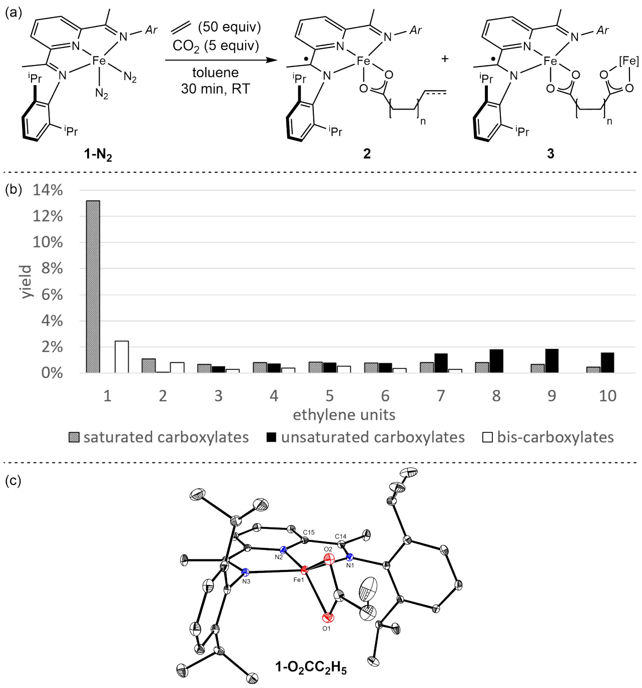


Figure 2. (a) Iron-mediated coupling of CO_2 and ethylene. (b) Yields and distribution of ethyl carboxylates after acid-mediated ethanolysis as determined by GC. (c) Solid-state structure of **1-$O_2CC_2H_5$** at 30% probability ellipsoids. Hydrogen atoms were omitted for clarity. [Fe] = (^{iPr}PDI)Fe.

With an iron-mediated CO_2-ethylene coupling method in hand, the effect of different CO_2-ethylene ratios on the product distribution was studied. Inversion of the reagent ratio (50 equiv of CO_2 and 5 equiv of ethylene) followed by ethanolysis yielded a mixture of diethyl adipate (0.6%), ethyl propionate (5.6%) and diethyl succinate (4.6%) as judged by GC-MS. The low yield is likely a result of iron carbonate formation from reaction of reduced (PDI)Fe complexes with CO_2 alone.[18] Accordingly, if CO_2 is added to **1-N_2** prior to the addition of olefins, no iron carboxylates were detected by ^{1}H NMR spectroscopy. Analysis of the iron product, **3** prior to ethanolysis by Mößbauer spectroscopy revealed a single signal (δ = 0.96 mm/s; ΔE_Q = 1.53 mm/s) similar to the data obtained for **1-$O_2CC_2H_5$**, supporting an identical electronic structure. The benzene-d_6 ^{1}H NMR spectrum of **3** exhibits paramagnetically shifted resonances distinct from **1-$O_2CC_2H_5$** suggesting a different structure. DOSY NMR experiments established a significantly lower diffusion coefficient (4.12×10^{-6} m^2/s in C_6D_6 at 25 °C) for **3** (n = 1) than **1-$O_2CC_2H_5$** (6.01×10^{-6} m^2/s in C_6D_6 at 25 °C), suggesting a dimeric structure with bridging carboxylate ligands. Degradation experiments also support biscarboxylate formation.

The observed products likely arise from a pathway involving oxidative coupling between CO_2 and several equivalents of ethylene to form multiple metallalactones. To probe metallacycle formation, a pentane solution of **1-N_2** was treated with 1 equiv of β-propiolactone and the saturated iron carboxylate, **1-$O_2CC_2H_5$** was obtained, consistent with the known ability of the iron complex to promote the oxidative cleavage of C–O bonds (Figure 3).[27,28] Repeating the reaction in the presence of 10 equiv of ethylene resulted in higher homologues of the iron carboxylates. Likewise, when CO_2 was added in excess, **3** was formed as the major product. Taken together, these results are consistent with the intermediacy of the five-membered metallalactone, **4** as a common intermediate in iron-promoted CO_2-ethylene coupling and chain elongation.

Deuterium labeling experiments were conducted to determine the origin of the saturated iron carboxylates (Figure 4). Because pyridine(diimine) iron alkyl,[29] metallacycles,[30] and products from addition of olefins to **1-N_2** are known to undergo cyclometallation of the 2,6-isopropyl aryl substituents,[29] CO_2-ethylene coupling was explored with these positions deuterated.[31] Analysis of the resulting iron propionate by ^2H NMR spectroscopy and degradation experiments revealed no deuterium incorporation into the propionate ligand nor PDI-dehydrogenation products.[29,30,32] A similar lack of isotopic incorporation was observed when the imine methyl groups were labeled or the reaction was conducted in benzene-d_6 or toluene-d_8, arguing against a radical process. In contrast, using ethylene-d_4 resulted in principally perdeuerated esters following acid-mediated ethanolysis as determined by GC-MS. All saturated ethyl carboxylates with a carbon count greater than three were mainly perdeuterated (70%), whereas ethyl propionate was mainly formed as the d_4-isotopolog (97%). The observed saturated carboxylates are likely a result of D_2 gas formation following the β-deuteride elimination when ethylene-d_4 is used. To further test this hypothesis, the CO_2-ethylene coupling was conducted in the presence of ~1 atm of D_2, which resulted in formation of **1-$O_2CCH_2CH_2D$**, where the deuterium is exclusively located on the methyl group of the propionate ligand.

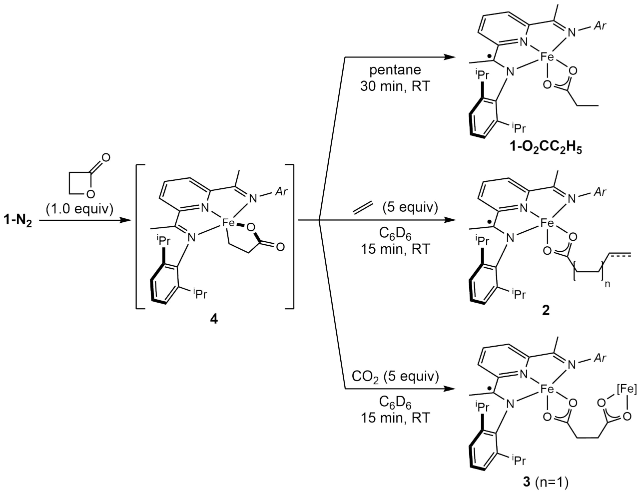


Figure 3. Generation of **4** through oxidative addition of propiolactone and its reactivity with CO_2 and ethylene. [Fe]= (^{iPr}PDI)Fe.

Performing iron-mediated CO_2-ethylene coupling in the presence of 1 equiv of D_2O also yielded **1-$O_2CCH_2CH_2D$** as the sole organometallic product detected by ^1H and ^2H NMR spectroscopies. The protonated ethyl propionate-d_4 observed following CO_2-ethylene-d_4 coupling as well as **1-$O_2CC_2H_5$** from the reaction of **1-N_2** and propiolactone likely derives from trace protic impurities. Despite significant efforts devoted to exclude all potential proton sources, the reaction outcome was not altered. Although other pathways cannot be fully excluded, this highlights the extremely high reactivity of the metallalactone intermediates, that likely originates in the high thermodynamic driving force to form iron κ^2*O,O'*-carboxylates. Thus far, all efforts to observe such compounds have been unsuccessful, a distinguishing feature from the pure hydrocarbon analogs.[19b,21]

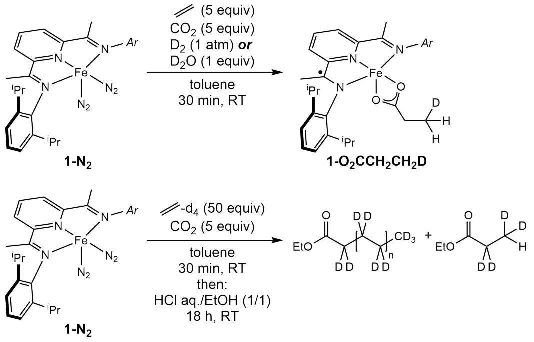


Figure 4. Deuterium labeling with D_2, D_2O and ethylene-d_4.

The observed product distribution and deuterium labeling studies are rationalized by the mechanism proposed in Figure 5. The generation of both unsaturated- and bis-carboxylates provides evidence for the formation of metallalactones during the reaction that undergo either β-hydride elimination or insertion of a second CO_2 molecule. The formation of **1-$O_2CCH_2CH_2D$** as the sole organometallic product after CO_2-ethylene coupling in the presence of D_2 or D_2O suggests that the five-membered metallalactone, **4** is the first common intermediate, which reacts with these molecules preferentially over ethylene and CO_2. The macrocyclic metallalactones, **5** are likely generated through consecutive insertion of ethylene following initial formation of **4**.[33] Iron complexes bearing saturated carboxylates are likely derived from reaction of H_2 or iron hydride species generated from β-hydride elimination with the various metallalactones **5**. Consistent with this hypothesis, perdeuterated saturated carboxylates were detected by GC-MS when the procedure was conducted with ethylene-d_4. The acrylate was not observed in the reaction mixture, likely because of the inherent rigidity of the five-membered metallalactone **4**,[6] which has a high barrier for β-H elimination and is therefore susceptible to interception by H_2 gas. The prominence of this effect diminishes with increasing ring size of the metallalactones **5**, allowing gradually more facile β-hydride elimination and hence more *unsaturated* iron carboxylates (Figure 2b). The iron bis-carboxylates **3** are generated through insertion of a second molecule of CO_2 into metallalactones **5** followed by comproportionation with a reduced (PDI)Fe complex. Although an inverted sequence of events cannot be ruled out, a dimeric structure generated directly from a metallalactone and a reduced (PDI)Fe compound is likely more prone to β-hydride elimination and therefore generation of (PDI)Fe-acrylate, which has not been detected.

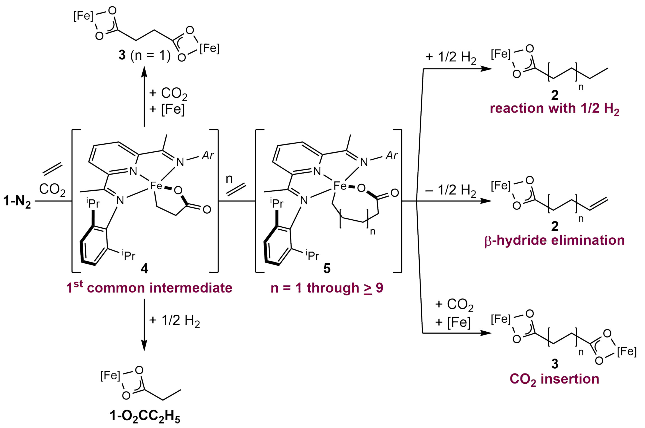


Figure 5. Proposed mechanism for the formation of **1-$O_2CC_2H_5$**, **2** and **3** from **1-N_2**, CO_2 and ethylene. [Fe]= (^{iPr}PDI)Fe.

To explore removal of the carboxylate from the coordination sphere of the iron, several conditions were evaluated with the goal of completing a synthetic cycle. While treatment of **1-$O_2CC_2H_5$** with metallic zinc produced no reaction, addition of magnesium butadiene generated a mixture of **1-N_2** and $(^{iPr}PDI)Fe(C_4H_6)$ along with magnesium propionate, which was identified by ^1H and ^{13}C NMR spectroscopies and by comparison to an authentic sample.

In summary, an iron-mediated coupling of CO_2 and ethylene to produce a homologous series of iron carboxylates has been developed. The composition of the carboxylate can be tuned using an appropriate CO_2 to ethylene ratio and eviden ce was provided for chain lengths of ≤21. These studies provide a new outlook for the synthesis of carboxylic acids from abundant carbon sources and demonstrate the ability of metallacyclic intermediates to control reaction outcome.

ASSOCIATED CONTENT

Supporting Information

Complete experimental procedures including general considerations and characterization data and NMR spectra as PDF. Crystallographic data are included as CIF. The Supporting Information is available free of charge at pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*pchirik@princeton.edu

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

We thank SABIC for financial support.

REFERENCES

(1) (a) Aresta, M.; Dibenedetto, A.; Angelini, A. "Catalysis for the Valorization of Exhaust Carbon: from CO_2 to Chemicals, Materials, and Fuels. Technological Use of CO_2." *Chem. Rev.* **2014**, *114*, 1709–1742. (b) Huang, K.; Sunwa, C.-L.; Shi, Z.-J. "Transition-metal-catalyzed C–C bond formation through the fixation of carbon dioxide." *Chem. Soc. Rev.* **2011**, *40*, 2435–2452. (c) Cokoja, M.; Bruckmeier, C.; Rieger, B.; Herrmann, W. A.; Kühn, F. E. "Transformation of Carbon Dioxide with Homogeneous Transition-Metal Catalysts: A Molecular Solution to a Global Challenge?" *Angew. Chem. Int. Ed.* **2011**, *50*, 8510–8537. (d) Mikkelsen, M.; Jørgensen, M.; Krebs, F. C. "The teraton challenge. A review of fixation and transformation of carbon dioxide". *Energy Environ. Sci.* **2010**, *3*, 43–81. (e) Aresta, M. "Carbon Dioxide as Chemical Feedstock." WILEY-VCH Gmbh & Co. KGaA: Weinheim, **2010**.

(2) (a) *Short-Term Outlook for Hydrocarbon Gas Liquids*; U.S. Energy Information Administration, U.S. Department of Energy: Washington, D.C., March 2016; https://www.eia.gov/outlooks/steo/special/supplements/2016/hgl/pdf/2016_sp_01.pdf. (b) *Short Term Energy Outlook*; U.S. Energy Information Administration, U.S. Department of Energy: Washington, D.C., April 2017; https://www.eia.gov/outlooks/steo/pdf/steo_full.pdf. (c) U. S. E. I. Administration U.S. Crude Oil and Natural Gas Proved Reserves **2011**; pp 1–49 (2013). (d) George, D. L.; Bowles, E. B., Jr. *Pipeline Gas J.* **2011**, *238*, 38–41.

(3) (a) Wang, X.; Wang, H.; Sun, Y. "Synthesis of Acrylic Acid Derivatives from CO_2 and Ethylene." *Chem* **2017**, *3*, 211–228. (b) Kraus, S.; Rieger, B. "Ni-Catalyzed Synthesis of Acrylic Acid Derivatives from CO_2 and Ethylene." *Top. Organomet. Chem.* **2016**, *53*, 199–223.

(4) (a) Huguet, N.; Jevtovikj, I.; Gordillo, A.; Lejkowski, M. L.; Lindner, R.; Bru, M.; Khalimon, A. Y.; Rominger, F.; Schunk, S. A.; Hofmann, P.; Limbach, M. "Nickel-Catalyzed Direct Carboxylation of Olefins with CO_2: One-Pot Synthesis of α,β-Unsaturated Carboxylic Acid Salts." *Chem. Eur. J.* **2014**, *20*, 16858–16862. (b) Hendriksen, C.; Pidko, E. A.; Yang, G.; Schäffner, B.; Vogt, D. "Catalytic Formation of Acrylate from Carbon Dioxide and Ethene." *Chem. Eur. J.* **2014**, *20*, 12037–12040. (c) Plessow, P. N.; Schäfer, A.; Limbach, M.; Hofmann P. "Acrylate Formation from CO_2 and Ethylene Mediated by Nickel Complexes: A Theoretical Study." *Organometallics*, **2014**, *33*, 3657–3668; (d) Lejkowski, M. L.; Lindner, R.; Kageyama, T.; Bódizs, G. É.; Plessow, P. N.; Müller, I. B.; Schäfer, A.; Rominger, F.; Hofmann, P.; Futter, C.; Schunk, S. A.; Limbach, M. "The First Catalytic Synthesis of an Acrylate from CO_2 and an Alkene—A Rational Approach." *Chem. Eur. J.* **2012**, *18*, 14017–14025.

(5) Stieber, S. C. E.; Huguet, N.; Kageyama, T.; Jevtovikj, I.; Ariyananda, P.; Gordillo, A.; Schunk, S. A.; Rominger, F.; Hofmann, P.; Limbach, M. "Acrylate formation from CO_2 and ethylene: catalysis with palladium and mechanistic insight." *Chem. Commun.* **2015**, *51*, 10907–10909.

(6) Hoberg, H.; Peres, Y.; Krüger, C.; Tsay, Y.-H. "A 1-Oxa-2-nickela-5-cyclopentanone from Ethene and Carbon Dioxide: Preparation, Structure, and Reactivity." *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 771–773.

(7) (a) Alvarez, R.; Carmona, E.; Galindo, A.; Gutierrez, E.; Marin, J. M.; Monge, A.; Poveda, M. L.; Ruiz, C.; Savariault, J. M. "Formation of carboxylate complexes from the reactions of carbon dioxide with ethylene complexes of molybdenum and tungsten. X-ray and neutron diffraction studies." *Organometallics* **1989**, *8*, 2430–2439. (b) Alvarez, R.; Carmona, E.; Cole-Hamilton, D. J.; Galindo, A.; Gutierrez-Puebla, E.; Monge, A.; Poveda, M. L.; Ruiz, C. "Formation of acrylic acid derivatives from the reaction of carbon dioxide with ethylene complexes of molybdenum and tungsten." *J. Am. Chem. Soc.* **1985**, *107*, 5529–5531.

(8) Cohen, S. A.; Bercaw, J. E. "Titanacycles Derived from Reductive Coupling of Nitriles, Alkynes, Acetaldehyde, and Carbon Dioxide with Bis(pentamethylcyclopentadienyl)(ethylene)titanium(II)" *Organometallics* **1985**, *4*, 1006–1014.

(9) Hessen, B.; Meetsma, A.; van Bolhuis, F.; Teuben, J. H.; Helgesson, G.; Jagner, S. "Chemistry of Carbon Monoxide Free Cyclopentadienylvanadium(I) Alkene and Alkyne Complexes." *Organometallics* **1990**, *9*, 1925–1936.

(10) Alt, H. G.; Denner, C. E. "Metallacyclen des Zirkonocens." *J. Organomet. Chem.* **1990**, *390,* 53–60.

(11) Hoberg, H.; Jenni, K.; Angermund, K.; Krüger, C.; "CC-Linkages of Ethene with CO_2 on an Iron(0) Complex—Synthesis and Crystal Structure Analysis of $[(PEt_3)_2Fe(C_2H_4)_2]$." *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 153–155.

(12) Aresta, M.; Quaranta, E. "Synthesis, characterization and reactivity of $[Rh(bpy)(C_2H_4)Cl]$. A study on the reaction with C_1 molecules (CH_2O, CO_2) and $NaBPh_4$." *J. Organomet. Chem.* **1993**, *463*, 215–221.

(13) Fischer, R.; Langer, J.; Malassa, A.; Walther, D.; Görls, H.; Vaughan; G. "A key step in the formation of acrylic acid from CO_2 and ethylene: the transformation of a nickelalactone into a nickel-acrylate complex." *Chem. Commun.* **2006**, 2510–2512.

(14) (a) Jin, D.; Williard, P. G.; Hazari, N.; Bernskoetter, W. H. "Effect of Sodium Cation on Metallacycle β-Hydride Elimination in CO_2–Ethylene Coupling to Acrylates." *Chem. Eur. J.* **2014**, *20*, 3205–3211. (b) Jin, D.; Schmeier, T. J.; Williard, P. G.; Hazari, N.; Bernskoetter, W. H. "Lewis Acid Induced β-Elimination from a Nickelalactone: Efforts toward Acrylate Production from CO_2 and Ethylene." *Organometallics*, **2013**, *32*, 2152–2159.

(15) Price, C. J.; Reich, B. J. E.; Miller, S. A. "Thermodynamic and kinetic considerations in the copolymerization of ethylene and carbon dioxide." *Macromolecules* **2006**, *39*, 2751-2756.

(16) Tortajada, A,; Juliá-Hernández, F.; Börjesson, M.; Moragas, T.; Martin, R. "Transition metal-catalyzed carboxylation reactions with carbon dioxide." *Angew. Chem. Int. Ed.* 10.1002/anie.201803186.

(17) Hoberg, H.; Peres, Y.; Milchereit, A. "C–C-Verknüpfung von Alkenen mit CO_2 an Nickel(0); n-Pentensäuren aus Ethen." *J. Organomet. Chem.* **1986**, *307,* C41–C43.

(18) Karsh, H. H. "Funktionelle Trimethylphosphinderivate, III. Ambivalentes Verhalten von Tetrakis(trimethylphosphin)eisen: Reaktion mit CO_2" *Chem. Ber.* **1977**, *110*, 2213.

(19) (a) Hoyt, J. M.; Schmidt, V. A.; Tondreau, A. M.; Chirik, P. J. "Iron-catalyzed intermolecular [2+2] cycloadditions of unactivated alkenes." *Science* **2015**, *349*, 960–963 (b) Russell, S. K.; Lobkovsky, E.; Chirik, P. J. "Iron-Catalyzed Intermolecular [2π + 2π] Cycloaddition." *J. Am. Chem. Soc.* **2011**, *133*, 8858–8861.

(20) Schmidt, V. A.; Kennedy, C. R.; Bezdek, M. J.; Chirik, P. J. "Selective [1,4]-Hydrovinylation of 1,3-Dienes with Unactivated Olefins Enabled by Iron Diimine Catalysts" *J. Am. Chem. Soc.* **2018***, 140,* 3443–3453.

(21) Hoyt, J. M.; Sylvester, K. T.; Semproni, S. P.; Chirik, P. J. "Synthesis and Electronic Structure of Bis(imino)pyridine Iron Metallacyclic Intermediates in Iron-Catalyzed Cyclization Reactions." *J. Am. Chem. Soc.* **2013**, *135*, 4862–4877.

(22) Bart, S. C., Lobkovsky, E.; Bill, E.; Chirik, P. J. "Synthesis and hydrogenation of bis(imino)pyridine iron imides" *J. Am. Chem. Soc.* **2006**, *128*, 5302-5303.

(23) Stanciu, C.; Jones, M. E.; Fanwick, P. E.; Abu-Omar, M. M. "Multi-electron Activation of Dioxygen on Zirconium(IV) to Give an Unprecedented Bisperoxo Complex." *J. Am. Chem. Soc.* **2007**, *129*, 12400–12401.

(24) A homologous series of linear α-olefins was also generated under these conditions.

(25) (a) Bart, S. C.; Chłopek, K.; Bill, E.; Bouwkamp, M. W.; Lobkovsky, E.; Neese, F.; Wieghardt, K.; Chirik, P. J. "Electronic Structure of Bis(imino)pyridine Iron Dichloride, Monochloride, and Neutral Ligand Complexes: A Combined Structural, Spectroscopic, and Computational Study." *J. Am. Chem. Soc.* **2006**, *128*, 13901–13912. (b) de Bruin, B.; Bill, E.; Bothe, E.; Weyhermüller, T.; Wieghardt, K. "Molecular and Electronic Structures of Bis(pyridine-2,6-diimine)metal Complexes $[ML_2](PF_6)_n$ (n = 0, 1, 2, 3; M = Mn, Fe, Co, Ni, Cu, Zn)." *Inorg. Chem.* **2000**, *39*, 2936–2947.

(26) Gütlich, P.; Bill, E.; Trautwein, A. X., *Mössbauer Spectroscopy and Transition Metal Chemistry: Fundamentals and Applications*; Springer-Verlag: Berlin Heidelberg, **2011**, p 85.

(27) Trovitch, R. J.; Lobkovsky, E.; Bouwkamp, M. W.; Chirik, P. J. "Carbon−Oxygen Bond Cleavage by Bis(imino)pyridine Iron Compounds: Catalyst Deactivation Pathways and Observation of Acyl C−O Bond Cleavage in Esters." *Organometallics* **2008**, *27*, 6264–6278.

(28) Aye, K.-T.; Colpitts, D.; Ferguson, G.; Puddephatt, R. J. "Activation of a β-Lactone by Oxidative Addition and the Structure of a Platina(IV)lactone." *Organometallics* **1988**, *7*, 1454–1456.

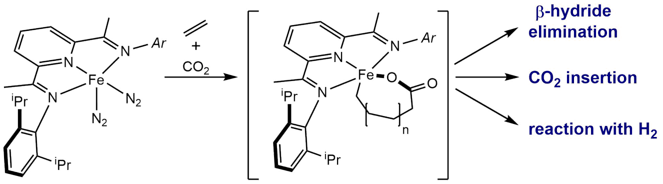
(29) Trovitch, R. J.; Lobkovsky, E.; Chirik, P. J. "Bis(imino)pyridine Iron Alkyls Containing β-Hydrogens: Synthesis, Evaluation of Kinetic Stability, and Decomposition Pathways Involving Chelate Participation." *J. Am. Chem. Soc.* **2008**, *130*, 11631–11640.

(30) Sylvester, K. T.; Chirik, P. J. "Iron-Catalyzed, Hydrogen-Mediated Reductive Cyclization of 1,6-Enynes and Diynes: Evidence for Bis(imino)pyridine Ligand Participation." *J. Am. Chem. Soc.*, **2009**, *131*, 8772–8774.

(31) Bart, S. C.; Lobkovsky, E.; Chirik, P. J. "Preparation and Molecular and Electronic Structures of Iron(0) Dinitrogen and Silane Complexes and Their Application to Catalytic Hydrogenation and Hydrosilation." *J. Am. Chem. Soc.* **2004**, *126*, 13794–13807.

(32) Bart, S. C.; Bowman, A. C.; Lobkovsky, E.; Chirik, P. J. "Iron Diazoalkane Chemistry: N−N Bond Hydrogenation and Intramolecular C−H Activation." *J. Am. Chem. Soc.* **2007**, *129*, 7212–2713.

(33) (a) Tomov, A. K.; Chirinos, J. J.; Jones, D. J.; Long, R. J.; Gibson, V. C. "Experimental Evidence for Large Ring Metallacycle Intermediates in Polyethylene Chain Growth Using Homogeneous Chromium Catalysts." *J. Am. Chem. Soc.* **2005**, *127*, 10166–10167; (b) Tomov, A. K.; Chirinos, J. J.; Long, R. J.; Gibson, V. C.; Elsegood, M. R. J. "An Unprecedented α-Olefin Distribution Arising from a Homogeneous Ethylene Oligomerization Catalyst." *J. Am. Chem. Soc.* **2006**, *128*, 7704–7705; (c) McGuinness, D. S.; Suttil, J. A.; Gardiner, M. G.; Davies, N. W. "Ethylene Oligomerization with Cr−NHC Catalysts: Further Insights into the Extended Metallacycle Mechanism of Chain Growth." *Organometallics,* **2008**, *27*, 4238–4247.



macrocyclic metallalactone intermediates in CO_2-ethylene coupling