Zwitterionic Iron(II) Compounds. Synthesis, Reactivity, and Catalytic Carbonylative Polymerization of Cyclic Ethers

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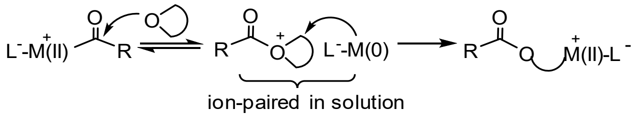
Keywords: Polymerization catalysis, carbonylation, zwitterionic Fe compounds.

Abstract: The generality of the zwitterionic strategy to design catalysts for carbonylative polymerization of cyclic ethers has been validated by applying it to Fe. The acyl group of the zwitterionic Fe catalyst is less electrophilic than that of the zwitterionic Ni catalyst, but the thermal stability of the octahedral Fe complex allows the copolymerization to be carried out at relatively high temperatures. The selectivity for carbonylative enchainment achieved at such temperatures with the Fe catalyst is marked better than that previously achieved with the Ni analogs at room temperature.

Iron is among the first transition metals investigated for stoichiometric and catalytic carbonylation reactions.[1-3] The earth abundance and relatively low toxicity of iron have stimulated renewed interests in Fe-based catalysis.[4-6] We recently demonstrated a zwitterionic design strategy that enabled Ni(II) complexes to catalyze the carbonylative polymerization of cyclic ethers.[7] The zwitterionic design is formulated on the basis of the following mechanistic hypothesis. The cationic charge at the Ni center of the zwitterion renders the Ni-acyl group to be electrophilic enough to react with a cyclic ether (Scheme 1), and ion-pairing between the resultant Ni(0) anion and cyclic ether-acylium promotes nucleophilic addition within the ion pair. This resulted in expansion of the catalysis of carbonylative polymerization of cyclic ethers from Co[8-13] to Ni. Since the zwitterionic Ni(II) catalysts are also active for CO-ethylene copolymerization,[14] the discovery of the Ni zwitterionic catalysts allowed the carbonylative copolymerization of two types of comonomers of vastly different reactivities, ethylene and cyclic ethers.[15] Here, we validate the generality of the zwitterionic design strategy by applying it to Fe.

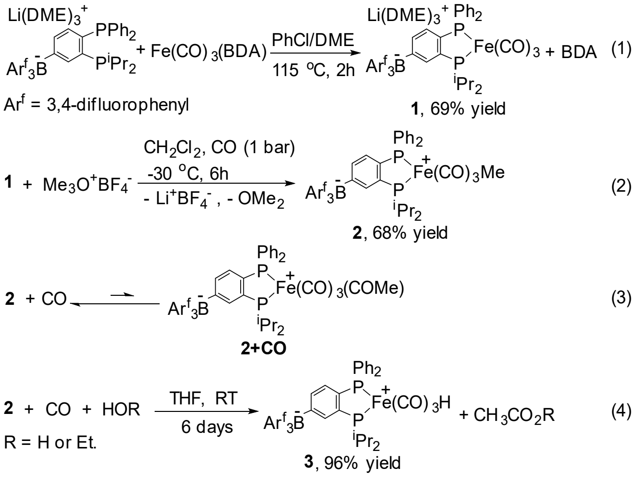
Scheme 1. Mechanistic hypothesis for designing zwitterionic catalysts for carbonylative polymerization of cyclic ethers.



M = Ni or Fe; L⁻ = phosphine ligand bearing an anionic charge; other ligands are omitted.

The anionic bidentate phosphine ligand[14] for synthesis of the zwitterionic Fe(II) compounds (Scheme 2) was previously used for Ni. Refluxing the ligand with (benzylideneacetone)iron tricarbonyl ($Fe(CO)_3(BDA)$)[16, 17] in chlorobenzene in the presence of DME gave **1** (eq 1). Methylation of **1** with trimethyloxonium tetrafluoroborate afforded **2** (eq 2) as a mixture of all three possible isomers in a 7.3 : 1.5 : 1.0 ratio according to ^1H nuclear magnetic

Scheme 2. Synthesis and stoichiometric reactions of zwitterionic iron(II) compounds.



resonance (NMR) integrations of the corresponding Fe-Me peaks (see Supporting Information). The isomers were not separated.

Two CO-stretching vibrations were observed at 2081 and 2017 cm^{-1} in the infrared (IR) spectrum of **2** in THF, suggesting that the major product likely is C_s-symmetric (*i.e.*, meridional) rather than C_1 (*i.e.*, facial). The IR bands of CO of **2** are at nearly identical wavenumbers as those of $Fe(CO)_3(PMe_3)_2(Me)^+BPh_4^-$ (2082 and 2018 cm^{-1}).[18] These CO vibration wavenumbers are higher as expected than those of the neutral octahedral complexes, for example, *cis*-$Fe(CO)_2(PMe_3)_2(Me)Cl$ at 2004 and 1943 cm^{-1}.[18]

Single crystals of **2** were studied by X-ray crystallography. The isomer that crystallized was indeed a *mer*-**2** (Figure 1). The ligand-Fe bond lengths as well as the carbonyl C-O bond lengths in the *mer*-**2** are within the proximity of those in the octahedral $Fe(CO)_2(PMe_3)_2(Me)I$ complex.[19] The differences in the electronic and steric characteristics of the ligands and the geometry of the P atoms of the neutral and zwitterionic complexes render detailed comparisons of the bond lengths moot. The cationic compound $Fe(CO)_3(PMe_3)_2(Me)^+BPh_4^-$ is more closely related to **2** but was not crystallgraphically characterized,[18] nor were other related cationic Fe(II) octahedral complexes.[20]

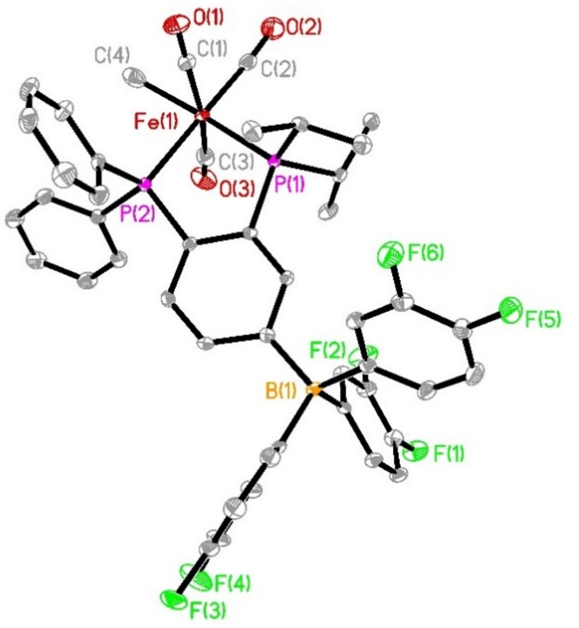
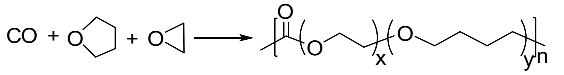


Figure 1 X-ray crystal structure of **2** with 35% thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths in **2**: Fe(1)-P(1) = 2.2740(7), Fe(1)-P(2) = 2.2725(7), Fe (1)-C(1) = 1.818(3), Fe(1)-C(2) = 1.826(3), Fe (1)-C(3) = 1.821(3), Fe (1)-C(4) = 2.117(4), C(1)-O(1) = 1.136(4), C(2)-O(2) = 1.112(4), and C(3)-O(3) = 1.139(4) Å.

When **2** was exposed to 1 atm of CO, no insertion product was observed by ^{1}H NMR (eq 3 in Scheme 2). High-pressure IR studies revealed that CO insertion was fast but had a small equilibrium constant, K = 0.072 bar^{-1} (see Supporting Information). This is in contrast to the neutral $Fe(CO)_2(PMe_3)_2(Me)X$ (X = Cl, Br, or I)[18, 21, 22] and $Fe(CO)_2(DIPPE)_2(R)X$ (DIPPE = 1,2-bis(diisopropylphosphino)ethane, R = neopentyl, and X = Cl or Br),[23] which react with CO under 1 atm to give the corresponding acyl complexes. The IR absorption of the acyl C=O stretching vibration of **2+CO** is at 1676 cm^{-1}, markedly higher than those of $Fe(CO)_2(DIPPE)_2(COR)Br$ at 1634 cm^{-1} and *cis*- and *trans*-$Fe(CO)_2(PMe_3)_2(COMe)Cl$ at 1600 and 1605 cm^{-1}, consistent with the expectation of a subdued back-donation to the π* orbital of the acyl C=O bond from the cationic Fe center of the zwitterionic complex.

The acetyl C=O band of **2+CO** is at a considerably lower wavenumber than that of acetyl-$Co(CO)_4$ at 1722 cm^{-1} and that of the 5-coordinate zwitterionic $L_2Ni(CO)_2(COMe)$ (L_2 is the same bidentate anionic phosphine ligand used here) at 1715 cm^{-1}. This suggests that the acetyl in **2+CO** is less electrophilic than those in the Ni and Co compounds. Nevertheless, it remains reactive enough to be cleaved by relatively weak nucleophiles under mild conditions. Under 1 atm of CO at room temperature in THF, water and ethanol quantitatively converted **2** to **3** in ~6 days and quantitatively gave the acetic acid and ethyl acetate byproduct, respectively (eq 4 in Scheme 2). Worth to note are that **2** does not react with water or ethanol in the absence of CO and that acetic acid and ethyl acetate are the expected byproducts of hydrolysis and alcoholysis of the Fe-acetyl bond of **2+CO**. Only a single set of ^{1}H NMR peaks of normal linewidths was observed for **3** with the Fe-H triplet ($J_{P\text{-}H}$ = 44.3 Hz) at -9.81 ppm, but the ^{31}P NMR spectrum of **3** suggested that all three possible isomers were again present in solution with two of comparable abundances and one being a minor component (see Supporting Information). The observed ^{1}H NMR peaks are therefore the dynamic average peaks of the isomers via relatively fast isomerization processes. Five bands of CO-stretching vibrations are resolved in the IR spectrum of **3** in nujol mull at 2083, 2040, 2030, 2003, and 1991 cm^{-1} (see Supporting Information), indicating co-existence of isomers in the solid state. For the purpose of comparison, the cationic hydrides, $Fe(CO)_3L_2H^+CF_3SO_3^-$ (L_2 is a bidentate diphosphine or a pair of monodentate phosphines) displayed a sharp CO band at

Table 1. Carbonylative copolymerization of EO and THF catalyzed by 2.[a]



(5)

Entry	reaction temp. (°C)	CO : EO : THF (1 : x : y) [b]	M_w [c] (g/mol)	Đ [c]	Yield (g)
1	80	1 : 9.0 : 8.0	10,000	1.88	0.33
2	100	1 : 3.0 : 1.0	6,700	1.77	0.27
3	130	1 : 3.4 : 1.1	5,600	2.43	0.37
4	150	1 : 3.6 : 1.2	3,900	2.27	0.09

[a] reaction conditions: **2** (15 mg) in a neat THF-EO mixture (1 mL each) under 300 psi of CO for 16 h. [b] Molar ratio of CO, EO, and THF incorporated in the product as shown in eq 5. [c] gel permeation chromatography against polystyrene standards.

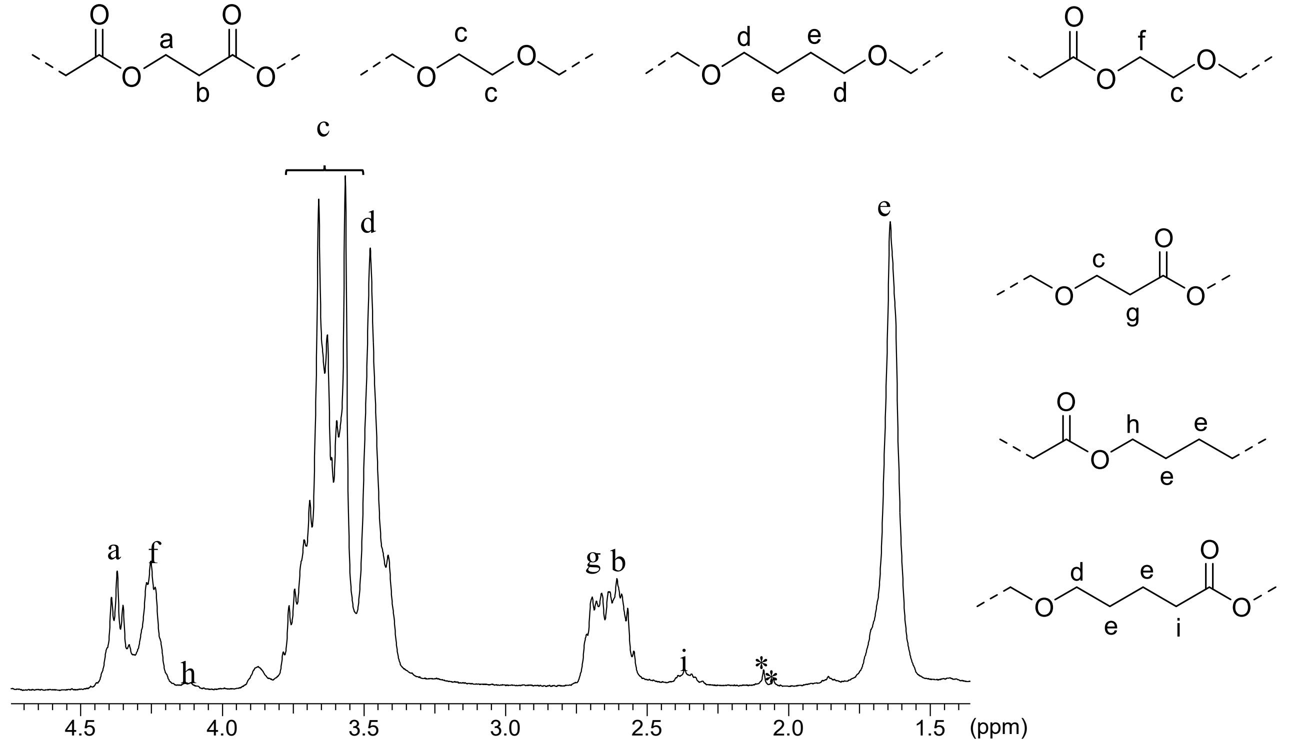
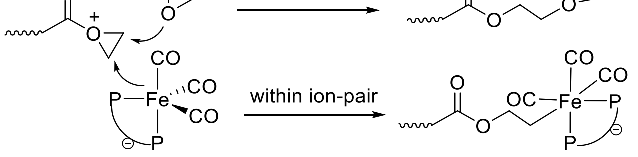


Figure 2. ^{1}H NMR spectrum of the product in entry 2, Table 1 with peak assignments. The peaks labelled with an asterisk are the acetyl end groups that originate from the catalyst.

2096 – 2079 cm^{-1} and a broad CO band at 2045 – 2023 cm^{-1}.[24] The isomer *fac*-**3** crystallized as single crystals and was crystallographically characterized (see Supporting Information).

Compound **2** was investigated as a catalyst for carbonylative polymerization of THF and ethylene oxide (EO) (Table 1). As in the cases with the Ni catalysts, the presence of both THF and EO is required for either of them to substantially polymerize. THF as a better nucleophile than EO promotes the nucleophilic attack of EO on the Fe-acyl group to afford EO-acylium, which ring-opens much more readily than THF-acylium and in turn gives rise to cationic THF enchainment.[7] Both carbonylative and simple ring-opening enchainments took place to afford the ester and ether units in the polymer chain, respectively (Figure 2). Most of the ester units arose from EO carbonylative enchainment (peaks a and f), and only a small fraction was due to THF carbonylative enchainment (peak h). The yield of the polymerization at 150 °C (entry 4) was significantly lower than those at lower temperatures (entries 1 - 3). Black precipitate was visible for the reaction at 150 °C after the reactor was opened, apparently suggesting catalyst decomposition. The selectivity for carbonylative enchainment is higher at 100 - 150 °C than at 80 °C. This is likely attributable to the enhanced entropic influences as the temperature increases, both in terms of the competition between the anionic Fe(0) species and cyclic ether as nucleophiles (Scheme 3) and the ceiling temperature of poly(THF). The selectivity for carbonylative enchainment observed here is markedly better than the best achievable with the zwitterionic Ni(II) catalysts so far.

Scheme 3. Competition between anionic Fe(0) species and cyclic ether as nucleophiles.



In conclusion, the viable transition metals that catalyze the carbonylative polymerization of cyclic ethers now include Fe. We estimate that the acyl group of the zwitterionic Fe catalyst is less electrophilic than the acyl groups of the previously reported zwitterionic Ni and neutral Co catalysts. However, the thermal stability of the octahedral Fe complex allows the copolymerization to be carried out at relatively high temperatures. The selectivity for carbonylative enchainment is entropically favored at such high temperatures. Although demonstrated in this work is a specific class of catalytic reaction, the zwitterionic design strategy may be applicable to other catalytic reactions involving heteroatom-containing substrates.

ASSOCIATED CONTENT

Supporting Information

Experimental details, NMR spectra, IR spectra, crystal structures of **1** and **3**, and details of X-ray crystallographic studies are included in the Supporting Information. The Supporting Information is available free of charge on the ACS Publications website.

AUTHOR INFORMATION

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Author Contributions

YD and JL contributed equally to the work. YD synthesized **1** and **3**. JL synthesized **2** and carried out the polymerizations. LZ carried out the high-pressure IR study of **3**. BRS performed the X-ray crystallographic studies. CJZ supervised the crystallographic studies. LJ conceived and supervised the work and wrote the manuscript.

Funding Sources

National Science Foundation (CHE-1900430).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

We thank the National Science Foundation (CHE-1900430) for supporting this work.

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