ORGANOMETALLICS

Mechanistic Insight Into High-Spin Iron(I)-Catalyzed Butadiene Dimerization

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Supporting Information

ABSTRACT: Iron complexes are commonly used in catalysis, but the identity of the active catalyst is often unknown, which prevents a detailed understanding of structure-reactivity relationships for catalyst design. Here we report the isolation and electronic structure determination of a well-defined, low-valent iron complex that is an active catalyst in the synthesis of cis, cis-1,5-cyclooctadiene (COD) from 1,3-butadiene. Spectroscopic and magnetic characterization establishes a high-spin Fe(I) center, which is supported by DFT studies, where partial metalligand antibonding orbital population is proposed to allow for facile ligand exchange during catalysis.



INTRODUCTION

Iron salts are commonly used in catalysis,¹ yet the nature of the active catalyst is often unknown. The lack of understanding of structure-reactivity relationships complicates rational reaction development. Targeted synthesis of well-defined iron complexes has enabled the design of iron-catalyzed reactions.²⁻⁶ Understanding the relationship between electronic structure and reactivity, particularly for complexes featuring commonly used redox-active ligands, is crucial for the rational development of improved iron catalysts.⁷⁻¹² Herein we report a welldefined Fe(I) complex that catalyzes the dimerization of butadiene to produce cis, cis-1,5-cyclooctadiene (COD), a commodity chemical manufactured on a multikiloton scale every year, and we describe a detailed mechanistic study of the reaction.

While redox-active ligands have long been used in catalysis and enable novel chemistry with metals such as iron,^{7,10} even established iron-catalyzed reactions such as diene dimerizations are often still not well understood. Work by tom Dieck in the 1980s demonstrated that chemical reduction of diimineiron(II) halide complexes such as 1 results in the generation of highly active homogeneous catalysts for selective diene dimerization, including the formal [4 + 4] dimerization of butadiene to afford COD (Figure 1, top).^{13–18} However, the structure and oxidation state of the active iron catalyst in such reactions has remained unknown: all reported well-defined iron complexes that have been isolated from reduction of 1 require additional activating agents such as trialkylaluminum compounds to generate a catalytically active species for butadiene dimerization (Figure 1, complexes 3-5).¹³ In contrast, the formally 16-electron Fe(I) complex 2 is a chemically and kinetically competent catalyst in the synthesis of COD from

butadiene. Spectroscopic and magnetic characterization establishes that catalyst 2 has an electronic structure featuring a highspin Fe(I) center antiferromagnetically coupled to a ligandbased radical (Figure 1). We propose that facile ligand exchange during catalysis is a result of the high-spin $S = \frac{3}{2}$ nature of the Fe(I) center and the population of metal-COD ligand antibonding orbitals, which is corroborated by DFT (vide infra).

RESULTS AND DISCUSSION

Under conditions that mimic iron-catalyzed butadiene dimerization, iron complex 2 was synthesized by reduction of diimineiron(II) halide complex 1 with MeMgCl in a butadiene/COD mixture (Figure 2a). Recrystallization of 2 from a pentane solution at -35 °C afforded an air-sensitive dark brown crystalline solid, and single-crystal X-ray diffraction analysis confirmed the structure of 2. The bond metrics indicate a radical anion form of the diimine ligand, thus suggesting an oxidation state of +I for the Fe center in 2.18,19 A related (diimine)Fe(COD) complex was reported by the Chirik group, via reduction of a (diimine)FeCl₂ precursor with Na/Hg, but neither an electronic structure determination nor the reactivity in diene dimerization has previously been described.²

Catalyst 2 produces COD from butadiene, without any additional activating reagent, and 41 ppm catalyst loading is sufficient on a >100 g scale (Figure 2b). The reaction is performed without solvent, which enables COD isolation by distillation directly from the reaction vessel. Catalyst 2 provides high selectivity for COD, the major side product being the

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Figure 1. Well-defined iron complexes 2-5 isolated from reduction of 1 and their activities in the synthesis of COD from butadiene. X-ray structures are drawn with 50% probability ellipsoids, with H atoms omitted for clarity. Selected bond lengths are given in Å.



Figure 2. (a) Synthesis of Fe(I) complex 2 by reduction of 1. (b) Catalytic activity of 2 in selective butadiene dimerization to afford COD. (c) Kinetic profile of butadiene dimerization with 2, showing first-order kinetics with no induction period.

formal [4 + 2] addition product vinylcyclohexene (VCH), which is a common byproduct in COD synthesis. COD synthesized with isolated catalyst 2 shows COD:VCH ratios ranging from 97:3 up to 99:1, higher than values previously reported for iron-catalyzed COD synthesis with precatalyst 1. While dimerization of butadiene with Fe(II) precatalyst 1 and MeMgCl displays an induction period of 80 min at the same temperature and catalyst loading (Figure S4 in the Supporting Information), the reaction with 2 displays first-order kinetics, with no induction period (Figure 2c). Fe precatalyst 1 activated by MeMgCl (Figure S4) achieved a rate of more than 8 kg of butadiene/((g of Fe) h) at 60 $^{\circ}$ C, an order of magnitude higher than reported for the conventional nickel-phosphite catalysts that originated from Wilke's seminal work.^{21–24} In contrast, η^6 arene complexes 3 and 4 show a lack of reactivity toward diene dimerization, and complex 5 shows only a 21% yield of COD with an incomplete conversion of butadiene at 0.05 mol % catalyst loading.

The significant difference in reactivity between 2 and structurally similar low-valent Fe complexes such as 3 prompted us to probe the electronic structure of complex 2, using zero-field ⁵⁷Fe Mössbauer spectroscopy and SQUID magnetometry (Figure 3a).²⁵ To date, all reported iron complexes featuring diimine ligands that have been analyzed by Mössbauer spectroscopy display isomer shifts >0.50 mm/s and have been assigned as Fe(II).¹⁸ Complex 1 is consistent with previously reported (diimine)Fe(II) complexes and displays $\delta = 0.88$ mm/s and $|\Delta E_Q| = 2.60$ mm/s at 90 K (Figure S32 in the Supporting Information). Reduction of 1 to 2 produces one of two subtly distinct polymorphs upon crystallization, in which the conformation of the COD ligand binding to iron differs slightly (Figures S17–S19 in the Supporting Information).²⁶ One polymorph shows Mössbauer parameters of $\delta = 0.47$ mm/s and $|\Delta E_Q| = 1.37$ mm/s (Figure 3



Figure 3. Spectroscopic and magnetic characterization for 2: (top) zero-field ⁵⁷Fe Mössbauer spectrum obtained at 90 K; (bottom) $\chi_{\rm M}T$ data collected in an applied dc field of 0.5 T; (bottom inset) reduced magnetization at 1.8–10 K and at fields 1–7 T. The solid continuous lines in all plots correspond to the fit of the data according to the models discussed in the text.

top), while the other displays $\delta = 0.44$ mm/s and $|\Delta E_Q| = 0.88$ mm/s (Figure S33 in the Supporting Information), with the same magnetic behavior observed for both polymorphs (Figure S42). There are several examples in the literature where Fe polymorphs have different Mössbauer parameters.^{27–29}

The electronic ground state of 2 was investigated by collecting variable-field (1-7 T), variable-temperature (1.8-10 K) magnetization data.³⁰ The data was satisfactorily fit with the zero-field splitting spin Hamiltonian (equation S7 in the Supporting Information) as an S = 1 state with a positive axial zero-field splitting parameter of D = +3.5 cm⁻¹ and g = 2.02(Figure 3a, bottom inset).³¹ In agreement, the VT magnetic susceptibility $(\chi_M T)$ data for 2 correspond to an S = 1 ground state isolated up to room temperature that can be fit by equation S6 in the Supporting Information to give g = 2.06 and $|D| = 3.7 \text{ cm}^{-1}$. Two potential scenarios could afford the net S =1 spin ground state: (1) a high-spin $S = \frac{3}{2}$ Fe(I) center coupled antiferromagnetically to the diimine ligand radical S =1/2 or (2) a low-spin S = 1/2 Fe(I) coupled ferromagnetically to the ligand-based radical. The DFT calculation of complex 2 reproduced the experimental bond lengths and Mössbauer parameters (Table 1) and supports the assignment of complex 2 as a high-spin $S = \frac{3}{2}$ Fe(I) center coupled antiferromagnetically to the diimine ligand radical $(S = \frac{1}{2})$, as shown in Figure 4. A computed qualitative orbital diagram shows that one of the

Table 1. Experimental	and Calculated Parameters"	of
Complexes 2 and 3		

		Fe-N	diimine N–C	diimine C–C	δ^{b}	$ \Delta E_{\rm Q} ^{b,c}$
2						
	exptl	1.997(1)	1.348(2)	1.411(2)	0.47	1.37
		1.988(1)	1.346(2)			
	calcd	2.067	1.348	1.424	0.39	1.49
		2.066	1.348			
3						
	exptl	1.886(7)	1.358(1)	1.398(1)	0.44	0.27
		1.891(6)	1.369(9)			
	calcd	1.932	1.354	1.411	0.40	0.97
		1.928	1.353			

^{*a*}Selected bond lengths (Å) shown for diimine backbone. ^{*b*}In mm/s. ^{*c*}Sign of quadrupole splitting not determined experimentally.

 α -spins on the metal interacts magnetically with a β -spin on the diimine ligand with a large spatial overlap of S = 0.48, which represents antiferromagnetic coupling between the Fe center and the diimine ligand. The calculated spin density plot (Figure 4b) is consistent with three unpaired electrons on the Fe and one unpaired electron on the diimine ligand.

In complex 2, the molecular orbital on the iron that is magnetically coupled to the diimine ligand is singly occupied and shows an antibonding interaction along the Fe $-\pi$ bond of the COD ligand. We speculate that this antibonding interaction is what makes the COD ligand-metal bond weaker (Figure 4a) and enables fast dissociation of the COD ligand during catalysis.

The electronic structure of complex 2 was compared to those of the independently synthesized (diimine)Fe(η^6 -toluene) complex 3 and the related dimeric complex 4. In contrast to paramagnetic complex 2, formally 18-electron (diimine)Fe(η^6 arene) complexes such as 3 are diamagnetic and show no reactivity toward diene dimerization in the absence of activating reagents.^{20,25,32} In all cases, the η^6 -arene-bound Fe complexes have magnetic ground states of S = 0 and thus can be explained in two ways: either by a strong antiferromagnetic coupling between a low-spin S = 1/2 Fe(I) center and a S = 1/2 radical on the diimine ligand or alternatively by a hybrid structure of Fe(0) and Fe(II) that has been proposed for related compounds.^{33,34} DFT calculations suggest that a description of an open-shell ligand antiferromagnetically coupled to an Fe(I) center is lower in energy by about 4 kcal/mol than a closed-shell ligand and hybrid Fe(0)/Fe(II) structure for 3 (Figure S29 in the Supporting Information). The experimental bond lengths and isomer shift are reproduced from DFT calculations; the computed quadrupole splitting $|\Delta E_0|$ varies by 0.7 mm/s. While isomer shifts are often very well reproduced by DFT, it has been seen that quadrupole splittings are often complicated to compute and the error can vary up to 1.0 mm/s.³⁵⁻³⁷ Structural bond metrics of the α -diamine ligands measured by X-ray crystallography are also in agreement with an Fe(I) center and a radical anion on the diimine ligand (Figure 1).^{12,18,19} In either description of complexes 3 and 4, the electronic ground state of the (diimine)Fe(η^6 -arene) complexes is different from that of active catalyst 2 that features a high-spin Fe(I) center. The latter is reflected in certain bond lengths of the structures of 2-4; specifically, while the C-C and C-N bond distances of the diimine backbone are similar across these three complexes, the Fe–N bond lengths are significantly longer in 2 than in 3 or 4



Figure 4. (a) Qualitative MO diagram of Fe(I) complex 2 derived from BS (3,1) B3LYP/TZVP calculations. The singly and doubly occupied orbitals represent quasi-restricted orbitals, and the magnetically coupled orbitals are represented by corresponding orbitals (the overlap integral, *S*, is the calculated spatial overlap between the α - and β -spin components of the magnetic orbitals). (b) Spin-density plot of the Fe complex 2 derived from DFT calculations.

by ~ 0.11 Å, which is supported by the DFT calculations and is in support of the high-spin state of the Fe(I) center in complex 2.

Isolation of the kinetically competent catalyst 2 enabled us to conduct a detailed mechanistic study of diene dimerization. We determined that the catalyst resting state is the Fe(I) complex 2 by monitoring the reaction using ¹H NMR (Figure 5a). To further establish the relevance of complex 2 to catalysis, kinetic measurements were performed to determine the rate dependence on [Fe] for COD formation. A kinetic order of 1 was measured with respect to Fe catalyst 2 (Figure S9 in the Supporting Information). Furthermore, first-order kinetics were



Figure 5. (a) ¹H NMR spectra of the diene dimerization reaction at 14%, 75%, 95%, and full conversion and authentic samples of 1,3butadiene and COD in cyclohexane- d_{12} . (b) Proposed catalytic cycle for iron-catalyzed [4 + 4] butadiene dimerization.³⁸ COD dissociates from Fe after the turnover-limiting butadiene association step. (c) Eyring plot for dimerization of butadiene catalyzed by 2 (0.18 mol %) with data collected over a temperature range of -15 °C to +60 °C.

observed for butadiene and zero-order kinetics were observed for COD (Figures S6, S10, and S11 in the Supporting Information). Eyring analysis suggests an associative turnover-limiting step, such as butadiene coordination to Fe ($\Delta S^{\ddagger} = -16$

 \pm 6 eu, Figure 5c). Taken together, these data are consistent with the catalytic cycle proposed in Figure 5b: reversible dissociation of one of the olefins of COD (accelerated by the Fe d-COD π antibonding interaction) forms steady-state intermediate **A**, followed by turnover-limiting butadiene association. There are several closely related pathways that are also consistent with the kinetic data, such as a pathway that involves reversible butadiene association to complex **2** followed by slow dissociation of one of the olefins of COD (Figure S15b in the Supporting Information).

CONCLUSION

In summary, we report the synthesis, isolation, and characterization of a new Fe(I) complex (2) that exhibits high catalytic activity in selective butadiene dimerization to give COD and provide a detailed mechanistic study of the diene dimerization reaction. An electronic structure characterization of 2 establishes a high-spin ($S = \frac{3}{2}$) Fe center coupled antiferromagnetically to a ligand-based diimine radical. On the basis of DFT calculations, we propose that partial Fe–COD ligand antibonding orbital population allows for facile ligand exchange during catalysis. The identification of low-valent Fe complexes that are relevant to catalysis, and the determination of factors that are important for their reactivity, may be valuable in the development and understanding of low-valent iron catalysis in general.

EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out under an inert atmosphere using a nitrogen-filled glovebox or standard Schlenk techniques unless otherwise stated. All glassware was stored in an oven or was flame-dried prior to use. Anhydrous solvents were obtained either by filtration through drying columns (CH_2Cl_2 , pentane) on an MBraun system or by distillation over sodium/ benzophenone (benzene, Et_2O , hexane). Yields refer to isolated and spectroscopically pure compounds. Elemental analysis was performed by Robertson Microlit Laboratories (Madison, NJ).

All reagents were purchased from commercial suppliers (Aldrich, Strem, Alfa Aesar, or TCI) and used as received unless otherwise noted. 2,6-Dimethylaniline (Aldrich, 98%) was distilled prior to use. Iron(II) chloride (99.99% Aldrich) was used as received. Butadiene has a boiling point of -4.4 °C (at 1 atm) and was transferred into a closed vessel as a liquid below its boiling point for the reaction. Butadiene (99%, Aldrich) was distilled over $(n-Bu)_2Mg$ and degassed by the freeze–pump–thaw method prior to use. 1,5-Cyclooctadiene (COD) was purified by vacuum distillation and degassed by the freeze–pump–thaw method prior to use. (Bis(2,6-dimethylaniline)-butane-2,3-diimine)iron(II) chloride (1) was prepared according to the previously reported procedure.¹⁷ Elemental analyses of Fe complexes were returned low for carbon, presumably due to the instability of low-valent Fe complexes.

(Bis(2,6-dimethylaniline)butane-2,3-diimine)($\eta^2:\eta^2-1,5$ -COD)iron(I) (2). A 20 mL vial containing (bis(2,6-dimethylaniline)butane-2,3-diimine)iron(II) chloride (1; 155 mg, 0.370 mmol, 1.00 equiv) was cooled to -50 °C in the cold well of the glovebox. To the cooled vial were added COD (1 mL) and butadiene (3 mL) at -50 °C. The mixture was stirred for 10 min, and to the resulting suspension was added dropwise a solution of MeMgCl in THF (360 μ L, 2.90 M, 2.82 equiv) at -50 °C; a brown solution was observed. The vial was sealed with a Teflon-lined cap, and the reaction mixture was stirred for 30 min at -50 °C and slowly warmed to 23 °C over 30 min, and then the vial was opened and butadiene evaporation was observed. The volatiles were removed under reduced pressure. To the residue was then added pentane (6 mL), and the Teflon cap was used to close the vial. Centrifugation followed by decantation was performed to remove the magnesium salts, and then the supernatant was evaporated under

reduced pressure. The residue was dissolved in pentane (6 mL), placed in a vial closed with a Teflon cap, centrifugation of the vial was performed again to remove the remaining magnesium salts, and the supernatant was again decanted and evaporated under reduced pressure. The purification cycle of dissolving a residue with pentane followed by centrifugation of the vial and evaporation of the supernatant was repeated once more. The final residue was further dried under high vacuum to afford the title compound as a dark brown crystalline solid. The solids were dissolved in pentane (3 mL) and allowed to crystallize for 3 days at -35 °C, affording the title compound as a dark brown solid (169 mg, 64% yield). Mössbauer and magnetic data analysis of 2 are presented in the Spectroscopic Data section of the Supporting Information. X-ray analysis of 2 is presented in the X-ray Data section of the Supporting Information. NMR spectroscopy: ¹H NMR (500 MHz, C_6D_6 , 23 °C, δ) 6.08–4.53 (br m), 3.01–0.97 (m), 0.04 (s), -6.37 (s), -59.43 (br s, $\Delta \nu_{1/2}$ = 332 Hz); ¹³C NMR (125 MHz, C₆D₆, 23 °C, δ) 393.9, 351.6, 260.7, 159.6, 141.7, 18.1, -4.9.

(Bis(2,6-dimethylaniline)butane-2,3-diimine)(η^{6} -toluene) iron (3).²⁵ In a 20 mL vial containing mercury (6.70 g, 33.4 mmol, 90.0 equiv) in 10 mL of toluene was placed Na (34.1 mg, 1.48 mmol, 4.00 equiv), and the mixture was stirred for 1 h. The resulting amalgam in toluene was cooled to -50 °C in the cold well of the glovebox, and then (bis(2,6-dimethylaniline)butane-2,3-diimine)iron(II) chloride (1; 155 mg, 0.370 mmol, 1.00 equiv) was added. The mixture was stirred at -50 °C for 30 min and then was slowly warmed to 23 °C over 4 h. The reaction mixture was stirred for 2 days at 23 °C; then it was filtered through Celite and the filtrate was evaporated under reduced pressure. The resulting solid was dissolved in pentane (4 mL) and allowed to crystallize for 3 days at -35 °C, affording the title compound as a bright red solid (121 mg, 48% yield). Note that rapid warming of the reaction mixture yields a significant amount of byproduct 5. Mössbauer data of 3 are presented in the Spectroscopic Data section of the Supporting Information as 66:34 mixtures with byproduct 5. X-ray analysis of 3 is presented in the X-ray Data section of the Supporting Information. NMR spectroscopy: ¹H NMR (500 MHz, C_6D_{12} , 23 °C, δ) 7.12 (d, J = 7.6 Hz, 4H), 7.05 (t, J = 7.6 Hz, 4H), 5.22 (t, J = 5.4 Hz, 1H), 4.42–4.38 (m, 4H), 2.22 (s, 12H), 2.01 (s, 3H), 1.01 (s, 6H); ¹³C NMR (125 MHz, C₆D₆, 23 °C, δ) 157.2, 141.6, 131.0, 128.6, 124.6, 94.5, 82.0, 81.4, 80.8, 20.2, 18.3, 15.7.

Bis[(bis(2,6-dimethylaniline)butane-2,3-diimine)iron] (4). A 20 mL vial containing (bis(2,6-dimethylaniline)butane-2,3-diimine)iron(II) chloride (1; 155 mg, 0.370 mmol, 1.00 equiv) was cooled to -50 °C in the cold well of the glovebox. In the cooled vial were placed COD (1 mL) and isoprene (6 mL) at -50 °C. The mixture was stirred for 10 min, and to the resulting suspension was added a solution of MeMgCl in THF (255 μ L, 2.90 M, 2.00 equiv) at -50 °C. The vial was sealed with a Teflon-lined cap, and the reaction mixture was stirred for 30 min at -50 °C, warmed to 23 °C over 4 h, and stirred for 2 days. To the reaction mixture was then added hexanes (6 mL), and the vial was capped with a Teflon cap. Centrifugation of a vial followed by decantation of the supernatant removed magnesium salts. The supernatant was evaporated under reduced pressure. The residue was dissolved in hexanes (6 mL), centrifugation of a vial followed by decantation was performed again to remove the remaining magnesium salts, and the supernatant was evaporated under reduced pressure. The purification cycle of dissolving a residue with hexane followed by centrifugation of a vial and evaporation of the supernatant was repeated once more. The final residue was further dried under high vacuum to afford the title compound as a red/black crystalline solid. The solids were dissolved in hexanes (3 mL) and allowed to crystallize for 7 days at 23 °C, affording the title compound as dark red/black crystals (50.0 mg, 19% yield). Mössbauer data of 4 are presented in the Spectroscopic Data section of the Supporting Information. X-ray analysis of 4 is presented in the X-ray Data section of the Supporting Information. NMR spectroscopy: ¹H NMR (500 MHz, C₆D₆, 23 °C, δ) 7.29–7.22 (m), 5.48 (d, J = 6.5 Hz, 2H), 4.10 (t, J = 6.5 Hz), 2.41 (s, 12H), 2.37 (s, 12H), 1.04 (s, 6H), 0.70 (s, 6H); ¹³C NMR (125 MHz, C₆D₆, 23 °C, δ) 158.2, 142.8, 142.1, 130.9, 124.7, 118.5, 86.4,

82.9, 80.3, 18.6, 18.5, 15.8, 15.6; One peak was not observed due to the low solubility of complex 4.

Bis[bis(2,6-dimethylaniline)butane-2,3-diimine]iron (5). A dispersion of (bis(2,6-dimethylaniline)butane-2,3-diimine)iron(II) chloride (1; 77.5 mg, 0.185 mmol, 1.00 equiv) in COD (3 mL) was stirred overnight at 23 °C. To the resulting suspension was added a solution of MeMgCl in THF (128 µL, 2.89 M, 2.00 equiv) at 23 °C. The reaction mixture was stirred for 30 min at 23 °C, and the vial was closed with a Teflon cap. Centrifugation of the vial followed by decantation of the supernatant removed the magnesium salts, and then the supernatant was decanted and evaporated under reduced pressure. The residue was dissolved in pentane (6 mL), and placed in the vial closed with a Teflon cap. Centrifugation of the vial followed by decantation of the supernatant removed the remaining magnesium salts, and the supernatant was evaporated under reduced pressure. The purification cycle of dissolving a residue with pentane followed by centrifugation of the vial and evaporation of the supernatant was repeated once more. The final residue was dissolved in hexanes (3 mL) and allowed to crystallize for 3 days at -35 °C, affording the title compound as deep red crystals (38 mg, 32% yield). X-ray analysis of 5 is presented in the X-ray Data section of the Supporting Information. NMR spectroscopy: ¹H NMR (500 MHz, C_6D_6 , 23 °C, δ) 1.34 ($\Delta \nu_{1/2}$ = 160 Hz), -2.48 ($\Delta \nu_{1/2}$ = 50 Hz), -6.01 ($\Delta \nu_{1/2}$ = 120 Hz), -12.04 $(\Delta \nu_{1/2} = 60 \text{ Hz});$ ¹³C NMR (125 MHz, C₆D₆, 23 °C, δ) 394.8, 353.3, 168.4, 147.1, 32.9, 17.8, 15.9.

Representative Experimental Procedures for Large-Scale Butadiene Dimerization Reaction. All dimerization reactions were conducted under an inert nitrogen atmosphere using a glovebox or conventional Schlenk techniques (for the ≥ 100 g scale reactions). (Caution! Substantial pressure is generated upon heating butadiene (bp -4 °C at 1 atm) in a sealed vessel. The use of a thick-walled, defect-free pressure Schlenk vessel or other appropriate pressure equipment is essential, and the use of protective equipment such as a blast shield is strongly recommended.) In a 350 mL thick-walled pressure Schlenk tube was placed Fe(I) complex 2 (55.4 mg, 121 mmol, 0.00763 mol %), and the vessel was then cooled to -50 °C. In the cooled vessel was placed 86.0 g of butadiene (134 mL, 1.59 mol, 1.00 equiv), at -50 °C. The Schlenk tube was sealed and was warmed to ambient temperature, followed by heating in an oil bath at 60 °C. After 3 h (the contraction of the volume was then maximum), the reaction vessel was cooled to room temperature and then opened to air. No bubbling was observed, characteristic of a quantitative conversion of butadiene. An aliquot of the reaction mixture was removed and was analyzed by NMR spectroscopy, revealing >99% purity for COD without purification. NMR spectroscopy: ¹H NMR (500 MHz, CDCl₃, 23 °C, δ) olefinic H atoms 5.59 (s (br), 4H), aliphatic H atoms 2.03 (t, J = 2.4 Hz, 8H); ¹³C NMR (125 MHz, CDCl₃, 25 °C, δ) olefinic 128.8 (s), aliphatic 28.2 (s). Selectivity: cis,cis-1,5-cyclooctadiene/4-vinylcyclohexene > 99/1 (no trimer was observed for this reaction).

Note: to demonstrate the scalability of the reaction and to compare selectivities, we performed a butadiene dimerization reaction on an \sim 100 g scale, using both precatalyst 1 and Fe(I) complex 2 at two different catalyst loadings each. For yields and selectivities at different catalyst loadings, see Examples 1–4 in the Supporting Information.

General Procedure for Kinetics Measurements and Dilatometry. Reaction kinetics were monitored using dilatometry, by monitoring the volume of liquid in the reaction vessel. Dilatometry utilizes the volume change that occurs upon dimerization to follow conversion versus time. Reaction vessels with a large height/diameter ratio were used in order to most accurately observe changes in volume (for 100 g scale reactions, a 350 mL pressure Schlenk tube). Accurate determination of the corresponding volumes was performed postreaction by filling the empty marked vessel with water and measuring the corresponding masses. For fitting of the data to a first-order regression, linear natural log plots were obtained by using an infinite time point set to 100% conversion. For further information please see Reaction Kinetics section of the Supporting Information.

Determination of the Kinetic Order With Respect to [Fe]. In a 6 mL pressure tube was placed Fe(I) complex 2 (0.0074, 0.019, 0.078,

0.21, and 0.32 mol %) as a solid. The tube was cooled to -20 °C, followed by addition of 1,3-butadiene (1.9 g, 35 mmol) at -20 °C. The tube was then sealed and held at 28 °C, and the volume of the reaction mixture was monitored to maximum contraction. At this point the reaction vessel was opened to air, and no bubbling was observed, indicative of a quantitative conversion of butadiene. The volume change vs time was converted to percent conversion vs time using the general procedure for kinetics measurement described above. Extraction of pseudo-first-order rate constants (k_{obs}) by fitting of conversion up to 78% vs time curves is shown in Figure S8 in the Supporting Information, and the kinetic order of 1.07 was determined (Figure S9 in the Supporting Information).

Rate Dependence on 1,5-Cyclooctadiene. To monitor the rate dependence on 1,5-cyclooctadiene for the reaction, two samples with the same Fe catalyst and 1,3-butadiene concentrations was prepared, one with 1,5-cyclooctadiene (sample A) and one without 1,5-cyclooctadiene (sample B), and the reaction kinetics was monitored by dilatometry. Sample preparation is described below.

Sample A: in a 6 mL pressure tube was placed Fe(I) complex 2 (30 mg, 0.066 mol). 1,5-Cyclooctadiene (0.2 mL, 1.63 mmol) was then added and the tube was cooled to -20 °C in the cold well. 1,3-Butadiene (1.8 g, 2.8 mL, 33 mmol) was added, and the pressure tube was sealed and turned upside down for 2 s to allow mixing of 1,5-cyclooctadiene and 1,3-butadiene.

Sample B: in a 6 mL pressure tube was placed Fe(I) complex 2 (30 mg, 0.066 mol). A 0.2 mL portion of pentane was then added, and the tube was cooled to -20 °C in the cold well. 1,3-Butadiene (1.8 g, 2.8 mL, 33 mmol) was added, and the pressure tube was sealed and turned upside down for 2 s to allow mixing of pentane and 1,3-butadiene.

Two pressure tubes were then held at $28 \,^{\circ}$ C, and the volume of the reaction mixture was monitored to maximum contraction. At this point the reaction vessel was opened to air, and no bubbling was observed, indicative of a quantitative conversion of butadiene. The volume change vs time was converted to percent conversion vs time using the general procedure for kinetics measurement described above.

Eyring Analysis. In a 3 mL pressure tube was placed Fe(I) complex 2 (10 mg, 0.022 mmol, 0.18 mol %) as a solid. The tube was cooled to -50 °C, followed by addition of butadiene (0.64 g, 12 mmol, 1.0 equiv) at -50 °C. The tube was then sealed and held at the appropriate temperature (-15, 5, 27, 40, and 60 °C), and the volume contraction of the reaction mixture was monitored. The volume change vs time was converted to percent conversion vs time using the general procedure for kinetics measurements described above.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.6b00474.

Experimental procedures, characterization data, and details of DFT calculations (PDF) Crystallographic data (CIF) Cartesian coordinates of calculated structures (XYZ)

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Notes

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