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Pyridine(diimine) Iron Diene Complexes Relevant to Catalytic [2+2]-Cycloaddition Reactions

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Abstract

The synthesis, characterization, and catalytic activity of pyridine(diimine) iron piperylene and isoprene complexes are described. These diene complexes are competent precatalysts for (i) the selective cross-[2+2]-cycloaddition of butadiene or (*E*)-piperylene with ethylene and α -olefins and (ii) the 1,4-hydrovinylation of isoprene with ethylene. In the former case, kinetic analysis implicates the diamagnetic η^4 -piperylene complex as the resting state prior to rate-determining oxidative cyclization. Variable temperature ¹H NMR and EXSY experiments established that diene exchange from the diamagnetic, 18e⁻ complexes occurs rapidly in solution at ambient temperature through a dissociative mechanism. The solid-state structure of (^{Me}(Et)PDI)Fe(η^4 -piperylene) (^{Me}(Et)PDI = 2,6-(2,6-Me₂-C₆H₃N=CEt)₂C₅H₃N), was determined by single-crystal X-ray diffraction and confirmed the *s-trans* coordination of the monosubstituted 1,3-diene. Possible relationships between ligand-controlled diene coordination geometry, metallacycle denticity, and chemoselectivity of iron-mediated cycloaddition reactions are discussed.

Graphical Abstract

Keywords

cycloaddition; diene ligands; iron; metallacycles

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Dedicated to Professor Eric N. Jacobsen on the occasion of his 60th birthday.

Introduction

Olefins are among the most versatile and widely used building blocks for the syntheses of both small molecules and polymers.^[1–3] Conjugated dienes are particularly valuable as they offer multiple sites for elaboration through either 1,2- or 1,4-functionalizations and cycloadditions.^[4] Furthermore, many conjugated dienes are readily available as petrochemical or biomass-derived feedstocks.^[1,4–6] Transition metal catalysis has proven to be enabling for selective transformations of 1,3-dienes,^[7–12] and metal complexes of 1,3-diene substrates are frequently implicated as catalytic intermediates.^[8–13] While significant structural work has enabled the detailed characterization of diene complexes of both early transition metals and noble metals,^[13–16] less is known about diene complexes with the late 3d elements (e.g. Fe, Co, Ni, Cu) that are increasingly applied for catalysis.^[17]

Functionalized cyclobutanes are valuable, conformationally constrained molecules and important building blocks in the synthesis of natural products and industrially relevant small molecules including pharmaceutical candidates.^[18] In 2011, our research group reported that reduced iron complexes supported by pyridine-2,6-diimine (PDI) ligands catalyze the cross-selective [2+2]-cycloaddition of butadiene and ethylene (Scheme 1A).^[17g] Diene and metallacyclopentane complexes ($[(^{\text{Me}}\text{PDI})\text{Fe}(\eta^4\text{-butadiene})]$ and $[(^{\text{Me}}\text{PDI})\text{Fe}(\eta^1, \eta^3\text{-C}_6\text{H}_{10})]$ where $^{\text{Me}}\text{PDI} = 2,6\text{-(2,6-Me}_2\text{-C}_6\text{H}_3\text{N=CMe)}_2\text{C}_5\text{H}_3\text{N}$) were isolated, characterized, and implicated as catalytically relevant species.^[17g,h] Notably, the butadiene complex exhibited an *s-trans* coordination geometry, in contrast to the more commonly observed *s-cis* configuration.^[13–17,19] Exposure of isoprene and ethylene to the conditions identified for butadiene–ethylene [2+2]-cycloaddition instead resulted in diene hydrovinylolation (Scheme 1B); however, subsequent modification of the iron precatalyst enabled cross-selective [2+2]-cycloaddition of numerous 2-substituted-1,3-dienes and α -olefins to generate value-added 1,3-disubstituted cyclobutanes.^[20] Nonetheless, the effects of substrate modifications on catalyst speciation and diene coordination, along with their relationship to reaction chemoselectivity, remained unknown.

Here we describe the synthesis, dynamics, and reactivity of a family of $[(\text{PDI})\text{Fe}]$ complexes of isoprene and (*E*)-piperylene (Scheme 1C). The piperylene complex $(^{\text{Me}}\text{PDI})\text{Fe}(\eta^4\text{-piperylene})$ was identified as the catalyst resting state in cross-[2+2]-cycloadditions between (*E*)-piperylene and various α -olefins. The combination of X-ray crystallographic data, NMR experiments, and kinetic measurements suggest that both $(^{\text{Me}}\text{PDI})\text{Fe}(\eta^4\text{-piperylene})$ and the coordinatively saturated complexes isolated previously^[17g] are off-cycle species. These findings highlight the interplay of ligand and substrate substituent effects in accessing the metallacyclopentane intermediate required for productive [2+2]-cycloaddition.

Results and Discussion

Our studies commenced with re-examination of the effects of diene substitution on the selectivity of non-canonical cycloaddition reactions catalyzed by $[(^{\text{Me}}\text{PDI})\text{Fe}(\text{N}_2)]_2(\mu_2\text{-N}_2)$. As reported previously,^[17g] exposure of a benzene-*d*₆ solution containing an equimolar mixture of ethylene and isoprene to the iron precatalyst afforded exclusively hydrovinylolation product **5** (Scheme 1B, top). By contrast, exposure of an equimolar ratio of ethylene and (*E*)-

backbone was evaluated. In previous studies, introduction of ethyl substituents improved the crystallinity of resulting iron, cobalt, and vanadium complexes.^[20,24] Treatment of a pentane solution of $[(^{\text{Me}}(\text{Et})\text{PDI})\text{Fe}(\text{N}_2)]_2(\mu_2\text{-N}_2)$ with (*E*)- or (*E/Z*)-piperylene produced the same rapid color change. Following recrystallization from diethyl ether/pentane at $-35\text{ }^\circ\text{C}$, $(^{\text{Me}}(\text{Et})\text{PDI})\text{Fe}(\eta^4\text{-piperylene})$ was obtained in 63% yield (Scheme 4). The zero-field ^{57}Fe Mössbauer spectrum (solid-state, 80 K, Figure 1) of the bulk material exhibited a quadrupole doublet, consistent with a single iron-containing product, with parameters ($\delta = 0.38\text{ mm/s}$, $|E_Q| = 0.78\text{ mm/s}$) in good agreement with those measured for $(^{\text{Me}}\text{PDI})\text{Fe}(\eta^4\text{-butadiene})$ ($\delta = 0.38\text{ mm/s}$, $|E_Q| = 0.50\text{ mm/s}$).

A second recrystallization of bulk $(^{\text{Me}}(\text{Et})\text{PDI})\text{Fe}(\eta^4\text{-piperylene})$ afforded single crystals suitable for X-ray diffraction. The overall molecular geometry is best described as square pyramidal with the 4-substituted diene carbon occupying the apical position. The bond lengths of the pyridine(diimine) are consistent with significant contributions from a closed-shell, two-electron reduced description of the redox-non-innocent ligand.^[17f,25] Although the piperylene fragment exhibited positional disorder in the unit cell (half-occupancy in either of two orientations), the structure provided unambiguous support for an *s-trans* coordination geometry. As such, $(^{\text{Me}}(\text{Et})\text{PDI})\text{Fe}(\eta^4\text{-piperylene})$, like the parent butadiene complex, is one of few known *s-trans* diene complexes, especially with 3d metals.^[13,15j,15k,17e-g,19] Full-molecule density functional theory using the M06-L functional^[26,27] reproduced the experimentally observed preference for *s-trans* butadiene and piperylene coordination. Comparison of the lowest energy *s-cis* and *s-trans* structures (Figure 2) suggested that the *s-trans* isomers were lower in energy by $>7\text{ kcal/mol}$ ($G = 8.9\text{ kcal/mol}$ for butadiene, $G = 7.1\text{ kcal/mol}$ for piperylene, at 298 K). Evaluation of the lowest-energy *s-cis* and *s-trans* isomers predicted for $(^{\text{Me}}\text{PDI})\text{Fe}(\eta^4\text{-isoprene})$ suggested a similar preference favoring the *s-trans* coordination geometry; however, significant distortion induced by projection of the 2-substituent toward the flanking aryl groups resulted in a smaller energy difference between the isomers ($G = 4.3\text{ kcal/mol}$ at 298 K).

As observed for $(^{\text{Me}}\text{PDI})\text{Fe}(\eta^4\text{-piperylene})$, the ^1H NMR spectra of $(^{\text{Me}}(\text{Et})\text{PDI})\text{Fe}(\eta^4\text{-piperylene})$ in benzene- d_6 or toluene- d_8 at $23\text{ }^\circ\text{C}$ were consistent with diene exchange resulting in an observed C_{2v} symmetric molecule in solution.^[29] The origin of this behavior was evaluated by variable temperature (VT) ^1H NMR spectroscopy in toluene- d_8 over a $130\text{ }^\circ\text{C}$ range (-93 to $38\text{ }^\circ\text{C}$; Figure 3A). At temperatures at or below $-20\text{ }^\circ\text{C}$, the resonances sharpened, and clear separation of two (C3 and C5) pyridine CH , two imine backbone CH_3 , and four benzylic CH_3 signals was observed, consistent with the idealized C_s symmetry observed in the solid state. At $40\text{ }^\circ\text{C}$ the resonances also sharpened due to rapid exchange on the NMR timescale. The rates of diene exchange leading to this coalescence were extracted from total lineshape analysis at each temperature evaluated over this range,^[30] and Eyring analysis afforded activation parameters of $H^\ddagger = +27.7\text{ kcal mol}^{-1}$ and $S^\ddagger = +48.3\text{ cal mol}^{-1}\text{ K}^{-1}$ (Figure 3B).^[31] These results, particularly the large positive entropy of activation, suggest that diene exchange occurs through a dissociative mechanism. However, these data cannot distinguish between mechanisms involving rate-determining partial or full diene dissociation, to form $[(^{\text{Me}}(\text{Et})\text{PDI})\text{Fe}(\eta^2\text{-piperylene})]$ or $[(^{\text{Me}}(\text{Et})\text{PDI})\text{Fe} + \text{piperylene}]$, respectively, prior to coordination of another molecule of piperylene.

In order to gain deeper understanding of the mechanism of diene exchange, a series of ^1H - ^1H EXSY (EXchange SpectroscopY) experiments was conducted on $(^{\text{Me}}(\text{Et})\text{PDI})\text{Fe}(\eta^4\text{-piperylene})$ at 23 °C.^[32] A solution of $(^{\text{Me}}(\text{Et})\text{PDI})\text{Fe}(\eta^4\text{-piperylene})$ in benzene- d_6 was treated with an equimolar quantity of free (*E*)-piperylene. The resonances corresponding to free and coordinated piperylene (6 each) were resolved by $\delta = 1.3\text{--}1.8$ ppm in the 1D ^1H NMR spectrum, and in-phase cross-peaks indicative of exchange between them were readily apparent in the 2D EXSY spectrum (Figure 4A).^[33] The rate of exchange was extracted from the normalized area under the EXSY cross-peaks observed as a function of added piperylene concentration (1–5 equiv, 0.04–0.15 M). An inverse relationship was observed between the first-order rate constant for exchange (k_{obs}) and the concentration of free (*E*)-piperylene ([4b]; Figure 4B). A plausible mechanism for diene exchange, accounting for both the calculated activation parameters and the inhibitory effect of excess diene, is presented in Figure 4C. The reversible formation of $(^{\text{Me}}(\text{Et})\text{PDI})\text{Fe}(\eta^2\text{-piperylene})_2$ competitive with rate-determining diene dissociation accounts for the observed inhibition; however, alternative possibilities were not ruled out.

Given the observed lability of both isoprene and piperylene ligands in pyridine(diimine) iron complexes, this feature was exploited to quantitate the relative coordination affinities of the dienes. The equilibrium ratios of free and coordinated diene were measured by ^1H NMR spectroscopy of pairwise combinations of either $(^{\text{Me}}\text{PDI})\text{Fe}(\text{diene})$ or $(^{\text{Me}}(\text{Et})\text{PDI})\text{Fe}(\text{diene})$ and a second, distinct diene in benzene- d_6 at 23 °C (Scheme 5). The relative diene coordination affinities were determined as: butadiene > piperylene > isoprene. The relative binding affinities measured experimentally were in reasonable agreement with those calculated for the isodesmic reactions using DFT ($G_{\text{butadiene-piperylene}} = 2.1$ kcal/mol, $G_{\text{butadiene-isoprene}} = 4.9$ kcal/mol, $G_{\text{piperylene-isoprene}} = 2.8$ kcal/mol at 298 K). The poor coordination ability of isoprene relative to butadiene and piperylene is consistent with the vacuum instability that precluded isolation of the compound (*vide supra*).

To better understand the role that the diene complexes played in the mechanism of catalytic [2+2]-cycloaddition, a series of stoichiometric experiments was performed. Exposure of $(^{\text{Me}}(\text{Et})\text{PDI})\text{Fe}(\eta^4\text{-piperylene})$ in benzene- d_6 to excess ethylene (5 equiv) at ambient temperature caused the characteristic resonances in the ^1H NMR spectrum to broaden, suggestive of the formation of a new unidentified species. The volatile reaction components were collected after 40 hours, and ^1H NMR analysis supported the assignment of cyclobutane and 1,5-heptadiene in $\leq 5\%$ yield; propenylcyclobutane (**6**) was not detected (Scheme 6A). The residue remaining after the reaction was reconstituted in benzene- d_6 , and the resulting ^1H NMR spectrum supported that $(^{\text{Me}}(\text{Et})\text{PDI})\text{Fe}(\eta^4\text{-piperylene})$ remained the single, major identifiable iron compound. By contrast, exposure of the diene complex to a mixture of both piperylene and ethylene resulted in clean formation of propenylcyclobutane (Scheme 6B). The requirement for additional equivalents of diene to induce C–C bond-forming reductive elimination is consistent with the observed reactivity in the butadiene–ethylene [2+2]-cycloaddition.^[17g] However, in this parent case, the metallacycle formed through stoichiometric reactions (Scheme 1A) persisted until a strong-field ligand such as butadiene or carbon monoxide was added. Such a diamagnetic metallacycle was not detected in the experiments with $(^{\text{Me}}(\text{Et})\text{PDI})\text{Fe}(\eta^4\text{-piperylene})$.

To elucidate the origins of these similarities and differences, stoichiometric experiments were supplemented by reaction progress kinetic analysis under catalytically relevant conditions^[34] using $[(^{\text{Me}}\text{PDI})\text{Fe}(\text{N}_2)]_2(\mu_2\text{-N}_2)$ or $(^{\text{Me}}\text{PDI})\text{Fe}(\eta^4\text{-butadiene})$ as the precatalyst. The disappearance of diene (either butadiene^[35] or piperylene) and the formation of the corresponding [2+2]-cycloadduct (either vinylcyclobutane (**3**) or propenylcyclobutane (**6**)) could be monitored readily over the entire course of the reaction through ^1H NMR spectroscopy. In both cases, runs initiated at different concentrations of diene but with the same excess concentration of ethylene^[36] afforded concentration vs. time data that overlaid graphically, indicating that no catalyst decomposition or product inhibition occurred over the course of the reactions (Figure 5).

Despite the catalyst fidelity in both case studies examined, the catalyst resting states differed. Metallocycle $(^{\text{Me}}\text{PDI})\text{Fe}(\eta^1, \eta^3\text{-C}_6\text{H}_{10})$ was clearly resolved by ^1H NMR as the major (PDI)Fe-containing species at intermediate conversion during catalysis of the cross-[2+2]-cycloaddition of butadiene and ethylene. By contrast, diene complex $(^{\text{Me}}\text{PDI})\text{Fe}(\eta^4\text{-piperylene})$ was detected as the major (PDI)Fe-containing species at intermediate conversion during catalysis of the cross-[2+2]-cycloaddition of piperylene and ethylene. The differences in catalyst resting state were further reflected in kinetic profiles of the reactions. The linearity of the [butadiene] versus time plot (Figure 5A) indicated that the reaction obeys a zero-order rate dependence up to >80% conversion. Conversely, the [piperylene] versus time plot exhibited a clear exponential decay consistent with a first-order rate dependence overall (Figure 5B). Trials conducted with a different excess in the initial concentration of ethylene relative to piperylene also resulted in kinetic profiles that overlaid, indicating a first-order rate dependence on the concentration of ethylene and no rate dependence on the concentration of piperylene (Figure 6). Trials conducted with either pure (*E*)-piperylene or (*E*)-piperylene in a mixture with (*Z*)-piperylene and cyclopentene afforded comparable results, establishing that (*Z*)-piperylene and cyclopentene are kinetically innocent and unchanged over the course of the reaction with (*E*)-piperylene. Taken together, these findings are consistent with competing kinetic manifolds in a common mechanism involving oxidative cyclization, C–C reductive elimination, and intramolecular isomerization steps (Scheme 7). In particular, the zero-order dependence in the cross-cycloaddition of ethylene and butadiene suggests that an intramolecular event is rate determining. Given that the resting-state metallocycle $(^{\text{Me}}\text{PDI})\text{Fe}(\eta^1, \eta^3\text{-C}_6\text{H}_{10})$ is coordinatively saturated, isomerization to an on-cycle coordinatively unsaturated metallacyclopentane $(^{\text{Me}}\text{PDI})\text{Fe}(\eta^1, \eta^1\text{-C}_5\text{H}_8)$ is hypothesized to be rate-determining prior to a ligand-induced C–C bond-forming reductive elimination.^[37] Conversely, the first-order dependence on ethylene in its cross-[2+2]-cycloaddition with piperylene is most consistent with a mechanism in which ethylene coordination or oxidative cyclization is rate-determining. Given the steric penalty that would be associated with accessing η^3 -coordination of the substituted metallocycle, on-cycle $(^{\text{Me}}\text{PDI})\text{Fe}(\eta^1, \eta^1\text{-s-}trans\text{-C}_7\text{H}_{12})$ metallacyclopentane is posited to be the major intermediate sampled *en route* to C–C reductive elimination.

Given these insights into the reactivity differences between butadiene and piperylene, the placement of diene substituents in an incipient metallocycle is likely the origin of the chemoselectivity differences observed in the cross-reaction of ethylene and isoprene

(Scheme 8). Because the substitution pattern of isoprene would also disfavor η^3 -coordination analogous to that observed in $(^{\text{Me}}\text{PDI})\text{Fe}(\eta^1, \eta^3\text{-C}_6\text{H}_{10})$, reaction through the *s-cis* diene conformation to access the $(^{\text{Me}}\text{PDI})\text{Fe}(\eta^1, \eta^1\text{-s-cis-C}_7\text{H}_{12})$ metallacycloheptene would become kinetically accessible. As such, the flexibility of the larger metallacycle would enable facile β -H elimination,^[38] thereby providing a kinetically accessible pathway to C–H reductive elimination and the formation of the observed hydrovinylation product **5**.

Conclusion

The structures and reactivity of pyridine(diimine) iron diene complexes implicated in non-canonical cycloaddition reactions were studied. These complexes exhibited an unusual *s-trans* coordination geometry, and the ligand dynamics and lability were examined by VT ^1H NMR and EXSY experiments. These iron complexes supported by the readily prepared $(^{\text{Me}}\text{PDI})$ ligand were found to be competent for the selective cross-[2+2] cycloaddition of (*E*)-piperylene and α -olefins. Stoichiometric experiments and kinetic analyses suggested that isolable, coordinatively saturated diene and metallacyclic complexes are off-cycle, but that rapid dissociation and/or isomerization enable productive C–C bond-forming oxidative cyclization and reductive elimination, respectively. This study underscores that nuanced consideration of the interplay of ligand and substrate substituent effects is necessary in understanding the relationships between ligand-controlled diene coordination geometry, metallacycle denticity, and the chemoselectivity of iron-mediated cycloaddition reactions. Further work in our laboratory is directed toward exploiting this understanding to design new transformations that upgrade abundant hydrocarbon building blocks using iron catalysis.

Experimental Section

General Considerations:

All air- and moisture-sensitive manipulations were carried out using standard Schlenk techniques on a high vacuum line or in an M. Braun glovebox containing an atmosphere of purified N_2 . Reagents were purchased in reagent grade from commercial suppliers and used without further purification unless described otherwise. Pure (*E*)-piperylene and (*E/Z*)-piperylene were purchased from TCI, but crude (*E/Z*)-piperylene (also containing cyclopentene) was provided by Firmenich. Ethylene (**2**) and propylene (**7a**) were stored over activated 4 Å molecular sieves in a thick-walled glass pressure vessel for >24 hours prior to use. Butadiene (**1**) and 3-methyl-1-butene (**7g**) were stored over calcium hydride in a thick-walled glass pressure vessel for >24 hours then degassed prior to use. Isoprene (**4a**), piperylene (**4b**), allyl benzene (**7f**), and tributyl(vinyl)stannane (**7h**) were stirred over calcium hydride for >48 hours, degassed, and distilled under high vacuum. 1-Nonene (**7b**), 1-decene (**7c**), 4,4-dimethyl-1-pentene (**7d**), and 4-methyl-1-pentene (**7e**) were stirred over lithium aluminum hydride for >48 hours, degassed, and distilled under high vacuum. The liquid reagents were then either passed through a plug of activated alumina and/or stored over activated 4 Å molecular sieves in the glovebox. Solvents (diethyl ether, dichloromethane, n-hexane, n-pentane, tetrahydrofuran, and toluene) used for air- and moisture-sensitive manipulations were dried and deoxygenated by passage through an

activated alumina column.^[39] Deuterated solvents for NMR spectroscopy of air- and moisture-sensitive species (benzene-*d*6, cyclohexane-*d*12, or toluene-*d*8) were distilled from sodium metal under an atmosphere of argon and stored over 4 Å molecular sieves. Deuterated chloroform (CDCl₃) was stored over anhydrous potassium carbonate. The iron complexes Me [(^{Me}PDI)Fe(N₂)₂](μ₂-N₂), [(Et)PDI)Fe(N₂)₂](μ₂-N₂), and [(^{Me}PDI)Fe(η⁴-butadiene)] were prepared as reported previously.^[17g,40] NMR spectroscopy experiments were performed at the Princeton University Nuclear Magnetic Resonance Facility. Mass spectrometric data were obtained at the Princeton University Mass Spectrometry Facility. All DFT calculations were performed using ORCA^[27a,b] on the Princeton Della Research Computing Cluster. Computed structures were rendered using CYLview.^[28] CCDC-1956377 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Additional considerations are described in the Supporting Information.

Representative Procedure for Cross-[2+2]-Cycloaddition with Gaseous Alkenes:

In a glovebox filled with an inert atmosphere of purified N₂, a J. Young NMR tube was charged with [(^{Me}(Et)PDI)Fe(N₂)₂](μ₂-N₂) (0.012 g, 0.0125 mmol dimer, 0.025 mmol [Fe], 2.5 mol%) as a solution in C₆D₆ (0.5 mL). Piperylene (52 wt% (*E*)-piperylene, 27 wt% (*Z*)-piperylene in a mixture with cyclopentene and cyclopentane; 193 μL, 1.0 mmol (*E*)-piperylene, 1.0 equiv) was added via microliter syringe. The tube was sealed, removed from the glovebox and frozen in liquid N₂. The headspace was evacuated, and then propylene (**7a**, 1.2 mmol, 1.2 equiv) was added by vacuum transfer via a calibrated gas bulb. The tube was sealed under static vacuum, and gradually warmed to ambient temperature (23 °C). Reaction progress was monitored by ¹H NMR analysis. Upon consumption of the substrates, the volatiles were transferred by way of a vacuum transfer tube to another J. Young NMR tube for analysis. Product **8a** was obtained in 86% yield (95% [2+2], 77:23 d.r.) after 63 hours. Analogous procedures were followed for reactions with ethylene (**2**) and 3-methyl-1-butene (**7g**). Organic product characterization data are provided in the Supporting Information.

Representative Procedure for Cross-[2+2]-Cycloaddition with Liquid Alkenes:

In a glovebox filled with an inert atmosphere of purified N₂, a 1.5 mL vial was charged with allylbenzene (**7f**, 0.355 g, 3.0 mmol, 1.2 equiv) and piperylene (52 wt% (*E*)-piperylene, 27 wt% (*Z*)-piperylene in a mixture with cyclopentene and cyclopentane; 482 μL, 2.5 mmol (*E*)-piperylene, 1.0 equiv). Precatalyst [(^{Me}(Et)PDI)Fe(N₂)₂](μ₂-N₂) (0.012 g, 0.0125 mmol dimer, 0.025 mmol [Fe], 1.0 mol%) was added as a solid to initiate the reaction. A PTFE-coated magnetic stir bar was added, and the vial was sealed. The vial was maintained with stirring at ambient temperature (~23 °C). Reaction progress was monitored by GC analysis of aliquots removed from the reaction mixture. Upon consumption of the substrates, the vial was removed from the glovebox. The contents were exposed to air, and the product mixture was filtered through a plug of silica, eluting with pentane (5 × 2 mL). The filtrate was concentrated under reduced pressure to afford **8f** as a colorless oil in 92% yield (98% [2+2], 62:38 d.r.) after 26 hours. Analogous procedures were followed for reactions with 1-nonene (**7b**), 1-decene (**7c**), 4,4-dimethyl-1-pentene (**7d**), 4-methyl-1-pentene (**7e**), and

tributyl(vinyl)stannane (**7h**). Organic product characterization data are provided in the Supporting Information.

Synthesis of (^{Me}PDI)Fe(η⁴-isoprene):

In a glovebox filled with an atmosphere of purified N₂, a J. Young NMR tube was charged with [(^{Me}PDI)Fe(N₂)]₂(μ₂-N₂) (20.0 mg, 0.0214 mmol dimer, 0.043 mmol [Fe], 1.0 equiv) and 600 μL of benzene-*d*₆. Isoprene (5 μL 0.05 mmol, 1 equiv per [Fe]) was added via microliter syringe, and the tube was sealed and removed from the glovebox. After mixing by repeated inversion at ambient temperature for 2 hours, the reaction mixture was analyzed by ¹H NMR spectroscopy to reveal (^{Me}PDI)Fe(η⁴-isoprene) as the single major species. No remaining [(^{Me}PDI)Fe(N₂)]₂(μ₂-N₂) was observed. The complex persisted in solution at ambient temperature with a half-life of ~ 3 hours. NMR parameters for (^{Me}PDI)Fe(η⁴-isoprene) have been reported previously.^[17g] ¹H NMR (300 MHz, C₆D₆) δ 8.00 (d, *J* = 7.6 Hz, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.10 – 6.70 (m, 5H), 6.55 (d, *J* = 7.3 Hz, 1H), 4.65 (s, 1H), 4.15 (s, 1H), 3.52 (d, *J* = 8.8 Hz, 1H), 2.59 (q, *J* = 7.3 Hz, 1H), 2.35 (d, *J* = 8.9 Hz, 2H), 1.98 (s, 3H), 1.79 (s, 3H), 1.72 (s, 3H), 1.64 (s, 3H), 1.26 (s, 3H), 0.90 (s, 3H), –0.05 (d, *J* = 6.1 Hz, 3H)

Synthesis of (^{Me}PDI)Fe(η⁴-piperylene):

In a glovebox filled with an atmosphere of purified N₂, a 20-mL scintillation vial was charged with [(^{Me}PDI)Fe(N₂)]₂(μ₂-N₂) (0.100 g, 0.12 mmol dimer, 0.24 mmol [Fe], 1.0 equiv), pentane (4.8 mL, 0.05 M), and a PTFE-coated magnetic stir bar. Piperylene (52 wt% (*E*)-piperylene, 27 wt% (*Z*)-piperylene in a mixture with cyclopentene and cyclopentane; 230 μL, 1.2 mmol (*E*)-piperylene, 5.0 equiv) was added via microliter syringe. The vial was sealed, and the reaction was maintained at ambient temperature with gentle stirring. After 1 hour, the volatiles were removed in vacuo to afford a deep raspberry red solid. The solid was resuspended in pentane, stored at –35 °C overnight, then dried in vacuo. A sample of the crude solid was analyzed by ¹H NMR spectroscopy to reveal (^{Me}PDI)Fe(η⁴-piperylene) as the single major species with minor organic impurities. No remaining [(^{Me}PDI)Fe(N₂)]₂(μ₂-N₂) was observed. The crude solid was recrystallized from diethyl ether (~1 mL) at –35 °C over two weeks to afford a pure sample of (^{Me}PDI)Fe(η⁴-piperylene) (0.040 g, 0.09 mmol, 39% yield) for further analysis. Additional crude material was collected from the supernatant. ¹H NMR (400 MHz, C₆D₆) δ 8.10 (br. s, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 6.90 (t, *J* = 7.4 Hz, 2H), 6.86 – 6.79 (m, 4H), 4.75 (dd, *J* = 12.3, 9.0 Hz, 1H), 4.47 (dt, *J* = 13.2, 8.2 Hz, 1H), 3.85 (dq, *J* = 12.9, 6.5 Hz, 1H), 3.38 (d, *J* = 13.1 Hz, 1H), 3.13 (d, *J* = 7.2 Hz, 1H), 1.65 (s, 6H), 1.61 (br. s, 12H), 0.34 (d, *J* = 6.5 Hz, 3H). ¹³C NMR (101 MHz, C₆D₆) δ 150.97, 150.25, 125.04, 117.12, 100.43, 98.38, 75.64, 65.96, 19.37, 17.01, 13.98, four resonances not detected. Elemental analysis calculated for C₃₀H₃₅FeN₃: 73.02 %C, 7.15 %H, 8.52 %N; found: 72.79 %C, 6.76 %H, 8.07 %N.

Synthesis of (^{Me}(Et)PDI)Fe(η⁴-piperylene):

In a glovebox filled with an atmosphere of purified N₂, a 20-mL scintillation vial was charged with [(^{Me}(Et)PDI)Fe(N₂)]₂(μ₂-N₂) (0.200 g, 0.23 mmol dimer, 0.46 mmol [Fe], 1.0 equiv), pentane (10 mL, 0.05 M), and a PTFE-coated magnetic stir bar. Piperylene (52 wt%

(*E*)-piperylene, 27 wt% (*Z*)-piperylene in a mixture with cyclopentene and cyclopentane; 450 μ L, 2.3 mmol (*E*)-piperylene, 5.0 equiv) was added via microliter syringe. The vial was sealed, and the reaction was maintained at ambient temperature with gentle stirring. After 1 hour, the volatiles were removed in vacuo to afford a deep raspberry red solid. The crude solid was recrystallized from ~1:1 diethyl ether/pentane at -35°C overnight to afford a pure sample of (^{Me}(Et)PDI)Fe(η^4 -piperylene) (0.150 g, 0.29 mmol, 63% yield). Additional crude material was collected from the supernatant. ¹H NMR (400 MHz, C₆D₆) δ 8.04 (br. s, 2H), 7.47 (t, *J* = 7.7 Hz, 1H), 6.90 (t, *J* = 7.3 Hz, 2H), 7.02–6.66 (m, 4H), 4.73 (dd, *J* = 12.2, 9.1 Hz, 1H), 4.48 (td, *J* = 13.1, 9.1, 7.2 Hz, 1H), 3.67 (dq, *J* = 12.2, 6.5 Hz, 1H), 3.31 (d, *J* = 13.1 Hz, 1H), 3.15 (d, *J* = 7.2 Hz, 1H), 2.35 (br. s, 4H), 1.67 (br. s, 12H), 0.86 (t, *J* = 7.5 Hz, 6H), 0.23 (d, *J* = 6.5 Hz, 3H). ¹³C NMR (126 MHz, C₆D₆) δ 149.55, 128.35, 125.04, 118.01, 101.09, 97.31, 75.55, 68.12, 24.28, 22.74, 19.69, 14.29, 13.31, 12.18, four resonances not detected. Elemental analysis calculated for C₃₂H₃₉FeN₃: 73.70 %C, 7.54 %H, 8.06 %N; found: 73.28 %C, 7.38 %H, 7.95 %N

Supplementary Material

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References

- [1]. Schmidt R, Griesbaum K, Behr A, Biedenkapp D, Voges H-W, Garbe D, Paetz C, Collin G, Mayer D, Höke H, Hydrocarbons In Ullmann's Encyclopedia of Industrial Chemistry; Wiley: Chichester, U.K., 2014.
- [2]. Corey EJ, Cheng X-M. In The Logic of Chemical Synthesis, Wiley, New York, 1989.
- [3]. Chain Polymerization of Vinyl Monomers, In Polymer Science: A Comprehensive Reference, Vol. 3 (Eds: Matyjaszewski K, Möller M), Elsevier, 2012, 1–954;b)Claverie JP, Schaper F, MRS Bull. 2013, 38, 213–218;c)Domski GJ, Rose JM, Coates GW, Bolig AD, Brookhart M, Prog. Polym. Sci 2007, 32, 30–92.
- [4]. a)Grub J, Löser E. Butadiene, In Ullmann's Encyclopedia of Industrial Chemistry; Wiley: Chichester, U.K., 2012, 381–396;b)Weitz HM, Löser E. Isoprene, In Ullmann's Encyclopedia of Industrial Chemistry; Wiley: Chichester, U.K., 2012, 83–101.
- [5]. Matar S, Hatch LF, Chemistry of Petrochemical Processes, 2nd ed; Gulf Professional: Boston, 1991.
- [6]. a)Behr A, Johnen L, Chem. Sus. Chem 2009, 2, 1072–1095;b)Morais ARC, Dworakowska S, Reis A, Gouveia L, Matos CT, Bogdał D, Bogel-Lukasik R, Catal. Today, 2015, 239, 38–43;c)Sun R, Zheng M, Li X, Pang J, Wang A, Wang X, Zhang T, Green Chem. 2017, 19, 638–642.
- [7]. For select reviews:a)RajanBabu TV, In Comprehensive Asymmetric Catalysis (Eds. Jacobsen EN, Pfaltz A, Yamamoto H), Springer, Berlin, 1999, 417–427;b)RajanBabu TV, Synlett, 2009, 853–885; [PubMed: 19606231] c)Hilt G, Eur. J. Org. Chem 2012, 4441–4451;d)McNeill E, Ritter T. Acc. Chem. Res 2015, 48, 2330–2343; [PubMed: 26214092] e)Röse P, Hilt G, Synthesis, 2016; 48, 463–492;f)Holmes M, Schwartz LA, Krische MJ, Chem. Rev 2018, 118, 6026–6052; [PubMed: 29897740] g)Hirano M, ACS Catal. 2019, 9, 1408–1430;h)Doerksen RS, Meyer CC, Krische MJ, Angew. Chem. Int. Ed 2019, 58, 2–12.

- [8]. For select recent examples of [Fe] catalysis: a) Moreau B, Wu JY, Ritter T, *Org. Lett* 2009, 11, 337–339; [PubMed: 19093845] b) Wu JY; Moreau B, Ritter T, *J. Am. Chem. Soc* 2009, 131, 12915–12917; [PubMed: 19702262] c) Wu JY, Stanzl BN, Ritter T, *J. Am. Chem. Soc* 2010, 132, 13214–13216; [PubMed: 20809631] d) Raynaud J, Wu JY, Ritter T, *Angew. Chem. Int. Ed* 2012, 51, 11805–11808; e) Lee H, Campbell MG, Hernández Sánchez R, Börgel J, Raynaud J, Parker SE, Ritter T, *Organometallics*, 2016, 35, 2923–2929; f) Schmidt VA, Kennedy CR, Bezdek MJ, Chirik PJ, *J. Am. Chem. Soc* 2018, 140, 3443–3453; [PubMed: 29414238] g) Kennedy CR, Zhong H, Macaulay RL, Chirik JP, *J. Am. Chem. Soc* 2019, 141, 8557–8573.
- [9]. For select recent examples of [Co] catalysis: a) Hilt G, Treutwein J, *Chem. Commun* 2009, 1395–1397; b) Hilt G, Janikowski J, *Org. Lett* 2009, 11, 773–776; [PubMed: 19125626] c) Hilt G, Danz M, Treutwein J, *Org. Lett* 2009, 11, 3322–3325; [PubMed: 19583205] d) Hilt G, Arndt M, Weske DF, *Synthesis*, 2010, 1321–1324; e) Arndt M, Reinhold A, Hilt G, *J. Org. Chem* 2010, 75, 5203–5210; [PubMed: 20597480] f) Sharma RK, RajanBabu TV, *J. Am. Chem. Soc* 2010, 132, 3295–3297; [PubMed: 20163120] g) Hilt G, Roesner S, *Synthesis*, 2011, 662–668; h) Bohn MA, Schmidt A, Hilt G, Dindaro lu M, Schmalz H, *Angew. Chem. Int. Ed* 2011, 50, 9689–9693; i) Erver F, G. Hilt. *Org. Lett* 2011, 13, 5700–5703; j) Arndt M, Dindaro lu M, Schmalz H-G, Hilt G, *Org. Lett* 2011, 13, 6236–6239; [PubMed: 22040103] k) Kersten L, Hilt G, *Adv. Synth. Catal* 2012, 354, 863–869; l) Arndt M, Dindaro lu M, Schmalz H-G, Hilt G, *Synthesis*, 2012; 44, 3534–3542; m) Pünner F, Hilt G, *Chem. Commun* 2012, 48, 3617–3619; n) Erver F, Kuttner JR, Hilt G, *J. Org. Chem* 2012, 77, 8375–8385; [PubMed: 22694267] o) Schmidt A, Hilt G, *Org. Lett* 2013, 15, 2708–2711; [PubMed: 23662814] p) Schmidt A, Maiterth E, Hilt G, *Synthesis*, 2014, 46, 2040–2044; q) Kuttner JR, Hilt G, *Macromolecules*, 2014, 47, 5532–5541; r) Chen Q-A, Kim DK, Dong VM, *J. Am. Chem. Soc* 2014, 136, 3772–3775; [PubMed: 24588202] s) Möckel R, Hilt G, *Org. Lett* 2015, 17, 1644–1647; [PubMed: 25794242] t) Timsina YN, Sharma RK, RajanBabu TV, *Chem. Sci* 2015, 6, 3994–4008; [PubMed: 26430505] u) Raya B, Jing S, Balasanthiran V, RajanBabu TV, *ACS Catal.* 2017, 7, 2275–2283; [PubMed: 28593082] v) Jing SM, Balasanthiran V, Pagar V, Gallucci JC, RajanBabu TV, *J. Am. Chem. Soc* 2017, 139, 18034–18043; [PubMed: 29120629] w) Thullen SM, Rovis T, *J. Am. Chem. Soc* 2017, 139, 15504–15508; [PubMed: 29048886] x) Pagar VV, RajanBabu TV, *Science*, 2018, 361, 68–72; [PubMed: 29976822] y) Parsutkar MM, Pagar VV, RajanBabu TV, *J. Am. Chem. Soc* 2019, 141, 15367–15377. [PubMed: 31476274]
- [10]. For select recent examples of [Ni] catalysis: a) Saito N, Kobayashi A, Sato Y, *Angew. Chem. Int. Ed* 2012, 51, 1228–1231; b) Biswas S, Zhang A, Raya B, RajanBabu TV, *Adv. Synth. Catal* 2014, 356, 2281–2292; [PubMed: 25395919] c) Lian X, Chen W, Dang L, Li Y, Ho C-Y, *Angew. Chem. Int. Ed* 2017, 56, 9048–9052; d) Tortajada A, Ninokata R, Martin R, *J. Am. Chem. Soc* 2018, 140, 2050–2053; [PubMed: 29376353] e) Tran G, Shao W, Mazet C, *J. Am. Chem. Soc* 2019, 141, 14814–14822. [PubMed: 31436415]
- [11]. For select recent examples of [Cu] catalysis: a) Smith KB, Brown MK, *J. Am. Chem. Soc* 2017, 139, 7721–7724; [PubMed: 28581713] b) Sardini SR; Brown MK, *J. Am. Chem. Soc* 2017, 139, 9823–9826; [PubMed: 28699339] c) Gui Y-Y, Hu N, Chen X-W, Liao L-L, Ju T, Ye J-H, Zhang Z, Li J, Yu D-G, *J. Am. Chem. Soc* 2017, 139, 17011–17014; [PubMed: 29125759] d) Smith KB, Huang Y, Brown MK, *Angew. Chem. Int. Ed* 2018, 57, 6146–6149; e) Jia T, He Q, Ruscoe RE, Pulis AP, Procter DJ, *Angew. Chem. Int. Ed* 2018, 57, 11305–11309; f) Liu Y, Fiorito D, Mazet C, *Chem. Sci* 2018, 9, 5284–5288; [PubMed: 29997884] g) Jia T, Smith MJ, Pulis AP, Perry GJP, Procter DJ, *ACS Catal.* 2019, 9, 6744–6750; h) Bergmann AM, Sardini SR, Smith KB, Brown MK, *Isr. J. Chem* 2019, DOI:10.1002/ijch.201900060; i) Li C, Shin K, Liu R, Buchwald S, *Angew. Chem. Int. Ed* 2019, 58, 17074–17080.
- [12]. For select recent examples of [Ru], [Rh], [Pd], and [Ir] catalysis: a) Zbieg JR, Yamaguchi E, McInturff EL, Krische MJ, *Science*, 2012, 336, 324–327; [PubMed: 22442385] b) Goldfogel MJ, Roberts CC, Meek SJ, *J. Am. Chem. Soc* 2014, 136, 6227–6230; [PubMed: 24742315] c) Roberts CC, Matías DM, Goldfogel MJ, Meek SJ, *J. Am. Chem. Soc* 2015, 137, 6488–6491; [PubMed: 25961506] d) Chen T-Y, Tsutsumi R, Montgomery TP, Volchkov I, Krische MJ, *J. Am. Chem. Soc* 2015, 137, 1798–1801; [PubMed: 25642996] e) McCammant MS, Sigman MS, *Chem. Sci* 2015, 6, 1355–1361; [PubMed: 25705367] f) Goldfogel MJ, Meek SJ, *Chem. Sci* 2016, 7, 4079–4084; [PubMed: 30155052] g) Oda S, Franke J, Krische MJ, *Chem. Sci* 2016, 7, 136–141; [PubMed: 29861974] h) Nguyen KD, Herkommer D, Krische MJ, *J. Am. Chem. Soc* 2016, 138, 14210–14213; [PubMed: 27762549] i) Goldfogel MJ, Roberts CC, Manan RS, Meek SJ, *Org.*

Lett 2017, 19, 90–93; [PubMed: 27996276] j) Marcum JS, Roberts CC, Manan RS, Cervarich TN, Meek SJ, J. Am. Chem. Soc 2017, 139, 15580–15583; [PubMed: 29058881] k) Yang X-H; Dong VM, J. Am. Chem. Soc 2017, 139, 1774–1777; [PubMed: 28128936] l) Yang X-H, Lu A, Dong VM, J. Am. Chem. Soc 2017, 139, 14049–14052; [PubMed: 28953374] m) Sato H, Fukaya K, Poudel BS, Krische MJ, Angew. Chem. Int. Ed 2017, 56, 14667–14671; n) Yang X-H, Davison RT, Dong VM, J. Am. Chem. Soc 2018, 140, 10443–10446; [PubMed: 30091909] o) Nie S-Z, Davison RT, Dong VM, J. Am. Chem. Soc 2018, 140, 16450–16454; [PubMed: 30451496] p) Trost BM, Huang Z, Murhade GM, Science, 2018, 362, 564–568. [PubMed: 30385573] q) Yang X-H, Davison RT, Nie S-Z, Cruz FA, McGinnis TM, Dong VM, J. Am. Chem. Soc 2019, 141, 3006–3013; [PubMed: 30735362] r) Marcum JS, Cervarich TN, Manan RS, Roberts CC, Meek SJ, ACS Catal. 2019, 9, 5881–5889; s) Fiorito D, Mazet C, ACS Catal. 2018, 8, 9382–9387; t) Zhang Q, Yu H, Shen L, Tang T, Dong D, Chai W, Zi W, J. Am. Chem. Soc 2019, 141, 14554–14559. [PubMed: 31478648]

- [13]. a) Solan GA, Reactions of Transition Metal π -Complexes of Alkenes, Alkynes and Dienes, In Organometallic Chemistry, Vol. 32 (Ed. Green M), RSC, 2005, pp. 342–347; b) Crabtree RH, In The Organometallic Chemistry of the Transition Metals, 5th ed, Wiley, Hoboken, 2009, pp. 132–134; c) Hartwig JF, In Organotransition Metal Chemistry, University Science Books, United States, 2010, pp 439–442.
- [14]. Select diene complexes of early transition metals: a) Erker G, Wicher J, Engel K, Rosenfeldt F, Dietrich W, Krüger C, J. Am. Chem. Soc 1980, 102, 6344–6346; b) Erker G, Wicher J, Engel K, Krüger C, Chem. Ber 1982, 115, 3300–3309; c) Yasuda H, Kajihara Y, Mashima K, Nagasuna K, Lee K, Nakamura A, Organometallics, 1982, 1, 388–396; d) Hunter AD, Legzdins P, Nurse CR, Einstein FWB, Willis AC, J. Am. Chem. Soc 1985, 107, 1791–1792; e) Hunter AD, Legzdins P, Nurse CR, Einstein FWB, Willis AC, Bursten BE, Gatter MG, J. Am. Chem. Soc 1986, 108, 3843–3844; f) Christensen NJ, Hunter AD, Legzdins P, Organometallics, 1989, 8, 930–940; g) Benyunes SA, Green M, Grimshire MJ, Organometallics, 1989, 8, 2268–2270; h) Vong W-J, Peng S-M, Liu R-S, Organometallics, 1990, 9, 2187–2189; i) Christensen NJ, Legzdins P, Einstein FWB, Jones RH, Organometallics, 1991, 10, 3070–3080; j) Debad JD, Legzdins P, Young MA, Batchelor RJ, Einstein FWB, J. Am. Chem. Soc 1993, 115, 2051–2052; k) Wang L-S, Fettingner JC, Poli R, J. Am. Chem. Soc 1997, 119, 4453–4464; l) Poli R, Wang L-S, J. Am. Chem. Soc 1998, 120, 2831–2842; m) Beddows CJ, Box MR, Butters C, Carr N, Green M, Kursawe M, Mahon MF, J. Organomet. Chem 1998, 550, 267–282; n) Wang L-S, Fettingner JC, Poli R, Meunier-Prest R, Organometallics, 1998, 17, 2692–2701; o) Ng SHK, Adams CS, Hayton TW, Legzdins P, Patrick BO, J. Am. Chem. Soc 2003, 125, 15210–15223; [PubMed: 14653756] p) Erker G, Kehr G, Frölich R, J. Organomet. Chem 2004, 689, 4305–4318; q) Nakamura A, Mashima K, J. Organomet. Chem 2004, 689, 4552–4563; r) Erker G, Kehr G, Frölich R, Adv. Organomet. Chem 2004, 51, 109–162; s) Joannou MV, Bezdek MJ, Al-Bahily K, Korobkov I, Chirik PJ, Organometallics, 2017, 36, 4215–4223.
- [15]. Select diene complexes of [Cr]: a) Koerner von Gustorf EA, Jaenicke O, Polansky OE, Angew. Chem. Int. Ed 1972, 11, 532–533; b) Koerner von Gustorf EA, Jaenicke O, Wolfbeis O, Eady CR, Angew. Chem. Int. Ed 1975, 14, 278–286; c) Fischler I, Budzwait M, Koerner von Gustorf EA, J. Organomet. Chem 1976, 105, 325–330; d) Kreiter CG, Özkaz S, J. Organomet. Chem 1978, 152, C13–C18; e) Kotzian M, Kreiter CG, Özkaz S, J. Organomet. Chem 1982, 229, 29–42; f) Kreiter CG, Kotzian M, J. Organomet. Chem 1985, 289, 295–308; g) Wang NF, Wink DJ, Dewan JC, Organometallics, 1990, 9, 335–340; h) Betz P, Döhring A, Emrich R, Goddard R, Jolly PW, Krüger C, Romão C, Schönfelder KU, Tsay Y-H, Polyhedron, 1993, 12, 2651–2662; i) Döhring A, Göhre J, Jolly PW, Kryger B, Rust J, Verhovnik GPJ, Organometallics, 2000, 19, 388–402; j) Norman DW, Ferguson MJ, McDonald R, Stryker JM, Organometallics, 2006, 25, 2705–2708; k) Monillas WH, Young JF, Yap GPA, Theopold KH, Dalton Trans. 2013, 42, 9198–9210. [PubMed: 23493916]
- [16]. Select diene complexes of late 4d and 5d metals: a) Melendez E, Ilarraza R, Yap GPA, Rheingold AL, J. Organomet. Chem 1996, 522, 1–7; b) Gemel C, Mereiter K, Schmid R, Kirchner K, Organometallics, 1997, 16, 2623–2626; c) Fukumoto H, Mashima K, Organometallics, 2005, 24, 3932–3938; d) Fukumoto H, Mashima K, Eur. J. Inorg. Chem 2006, 5006–5011; e) Hirano M, Sakate Y, Inoue H, Arai Y, Komine N, Komiya S, Wang X.-q., Bennett MA, J. Organomet. Chem 2012, 708–709, 46–57.

- [17]. Select diene complexes of [Fe]:a)Knölker H-J, Chem. Rev 2000, 100, 2941–2962; [PubMed: 11749311] b)Reihlen H, Gruhl A, Hessling G. v., Pfrengle O, Liebigs Ann. Chem 1930, 482, 161–182;c)Hallam BF, Pauson PL, J. Chem. Soc 1958, 642–645;d)Bachler V, Grevels F-W, Kerpen K, Olbrich G, Schaffner K, Organometallics, 2003, 22, 1696–1711;e)Bouwkamp MW, Bowman AC, Lobkovsky E, Chirik PJ, J. Am. Chem. Soc 2006, 128, 13340–13341; [PubMed: 17031930] f)Russell SK, Milsman C, Lobkovsky E, Weyhermüller T, Chirik PJ, Inorg. Chem 2011, 50, 3159–3169; [PubMed: 21395246] g)Russell SK, Lobkovsky E, Chirik PJ. J. Am. Chem. Soc 2011, 133, 8858–8861; [PubMed: 21598972] h)Hu L, Chen H, J. Am. Chem. Soc 2017, 139, 15564–15567. [PubMed: 29063756]
- [18]. a)Rappoport Z, Liebman JF, In The Chemistry of Cyclobutanes, Wiley, Chichester, UK, 2005, pp. 281–355;b)Xu Y, Conner ML, Brown MK, Angew. Chem. Int. Ed 2015, 54, 11918–11928;c)Secci F, Frongia A, Piras PP, Molecules, 2013, 18, 15541–15572; [PubMed: 24352013] d)Winkler JD, Bowen CM, Liotta F, Chem. Rev 1995, 95, 2003–2020;e)Lee-Ruff E, Mladenova G, Chem. Rev 2003, 103, 1449–1484; [PubMed: 12683788] f)Dembitsky VM Phytomedicine, 2014, 21, 1559–1581; [PubMed: 25442265] g)Carreira EM, Fessard TC, Chem. Rev 2014, 114, 8257–8322; [PubMed: 25003801] h)Wager TT, Pettersen BA, Schmidt AW, Spracklin DK, Mente S, Butler TW, Howard H, Lettiere DJ, Rubitski DM, Wong DF, Nedza FM, Nelson FR, Rollemma H, Raggon JW, Aubrecht J, Freeman JK, Marcek JM, Cianfrogna J, Cook KW, James LC, Chatman LA, Iredale PA, Banker MJ, Homiski ML, Munzner JB, Chandrasekaran RY, J. Med. Chem 2011, 54, 7602–7620; [PubMed: 21928839] i)Blakemore DC, Bryans JS, Carnell P, Carr CL, Chessum NEA, Field MJ, Kinsella N, Osborne SA, Warren AN, Williams SC, Bioorg. Med. Chem. Lett 2010, 20, 461–464; [PubMed: 20005103] j)Slade J, Bajwa J, Liu H, Parker D, Vivello J, Chen G-P, Calienni J, Villhauer E, Prasad K, Repi O, Blacklock TJ, Org. Process Res. Dev 2007, 11, 825–835;k)Singh J, Bisacchi GS, Ahmad S, Godfrey JD, Kissick TP, Mitt T, Kocy O, Vu T, Papaioannou CG, Wong MK, Heikes JE, Zahler R, Mueller RH, Org. Process Res. Dev 1998, 2, 393–399.
- [19]. Mashima K, Nakamura A, J. Organomet. Chem 2002, 663, 5–12.
- [20]. Hoyt JM, Schmidt VA, Tondreau AM, Chirik PJ, Science, 2015, 349, 960–963. [PubMed: 26315433]
- [21]. Trace amounts of cyclobutane, (*Z*)-propenylcyclobutane, and a linear product tentatively assigned as 1,5-heptadiene were also observed.
- [22]. Formation of mixed [2+2]-cycloadducts from the combination of (*E*)-piperylene and ethylene using a titanium catalyst has been observed previously:Cannell LG, J. Am. Chem. Soc 1972, 94, 6867–6869.
- [23]. a)Appukuttan VK, Liu Y, Son BC, Ha C-S, Suh H, Kim I, Organometallics, 2011, 30, 2285–2294;b)Hoyt JM, Sylvester KT, Semproni SP, Chirik PJ, J. Am. Chem. Soc 2013, 135, 4862–4877. [PubMed: 23448301]
- [24]. a)McTavish S, Britovsek GJP, Smit TM, Gibson VC, White AJP, Williams DJ, J. Mol. Cat. A, 2007, 261, 293–300;b)Perry MR, Allan LEN, Decken A, Shaver MP, Dalton Trans. 2013, 42, 9157–9165; [PubMed: 23340495] c)Schmidt VA, Hoyt JM, Margulieux GW, Chirik PJ, J. Am. Chem. Soc 2015, 137, 7903–7914. [PubMed: 26030841]
- [25]. a)Römelts C, Weyhermüller T, Wieghardt K, Coord. Chem. Rev 2019, 380, 287–317;b)Bart SC, Chlopek K, Bill E, Bouwkamp MW, Lobkovsky E, Neese F, Wieghardt K, Chirik PJ, J. Am. Chem. Soc 2006, 128, 13901–13912; [PubMed: 17044718] c)Bart SC, Lobkovsky E, Bill E, Wieghardt K, Chirik PJ, Inorg. Chem 2007, 46, 7055–7063. [PubMed: 17655227]
- [26]. a)Zhao Y, Truhlar DG, Theor. Chem. Account, 2008, 120, 215–241;b)Wang Y, Jin X, Yu HS, Truhlar DG, He X, Proc. Nat. Acad. Sci. U.S.A 2017, 114, 8487–8492.
- [27]. Calculations were performed with the ZORA-def2-TZVP(-f) basis set augmented by SARC/J terms for Fe, N, and C atoms in the primary coordination sphere, and the ZORA-def2-SVP basis set augmented with SARC/J terms for all other atoms:a)Neese F, WIREs Comput. Mol. Sci 2012, 2, 73–78;b)Neese F, WIREs Comput. Mol. Sci 2018, 8, e1327;c)Pople JA, Gill PMW, Handy NC, Int. J. Quantum Chem 1995, 56, 303–305;d)Weigend F, Ahlrichs R, Phys. Chem. Chem. Phys 2005, 7, 3297–3305; [PubMed: 16240044] e)Weigend F, Phys. Chem. Chem. Phys 2006, 8, 1057–1065; [PubMed: 16633586] f)Ekstrom U, Visscher L, Bast R, Thorvaldsen AJ, Ruud K, Chem J. Theory Comput. 2010, 6, 1971–1980;g)van Wüllen C, J. Chem. Phys 1998, 109, 392–399;h)Pantazis DA, Chen X-Y, Landis CR, Neese F, Chem J. Theory Comput. 2008, 4, 908–919.

- [28]. CYLview, 1.0b; Legault CY, Université de Sherbrooke, 2009 (<http://www.cylview.org>)
- [29]. The dynamic behavior was recapitulated both under an atmosphere of N₂ and following three freeze-pump-thaw cycles. This observation suggests that the mechanism for exchange does not involve N₂.
- [30]. The spectrum recorded at -93 °C exhibited globally broadened resonances due to the increased viscosity of the toluene solvent at this temperature. As such, data at this temperature were not included in the Eyring analysis.
- [31]. a)Anet FAL, Bourn AJR, J. Am. Chem. Soc 1967, 89, 760–768;b)Brookhart M, Hauptman E, Lincoln D, J. Am. Chem. Soc 1992, 114, 10394–10401;c)Gasparro FP; Kolodny NH, J. Chem. Ed 1977, 54, 258–261;d)Diaz A, Radzewich C, Wicholas M, J. Chem. Ed 1995, 72, 937–938.
- [32]. Perrin CL, Dwyer TJ, Chem. Rev 1990, 90, 935–967.
- [33]. A second 2D EXSY spectrum was recorded for a sample of (^{Me}(Et)PDI)Fe(η⁴-piperylene) with no added piperylene; nonetheless, the same cross-peaks were observed.
- [34]. a)Blackmond DG, Angew. Chem. Int. Ed 2005, 44, 4302–4320;b)Blackmond DG, J. Am. Chem. Soc 2015, 137, 10852–10866; [PubMed: 26285166] c)Nielsen CD-T, Burés J, Chem. Sci 2019, 10, 348–353. [PubMed: 30746083]
- [35]. While butadiene is a gas at ambient temperature and pressure, its high solubility coefficient in hydrocarbon solvents renders its vapor pressure negligible under the conditions examined. See:Hayduk W, Minhas BS. J. Chem. Eng. Data, 1987, 32, 285–290.
- [36]. The presence of ethylene in solution was also readily detected under these reaction conditions. Due to the extremely long relaxation time of the C₂H₄ resonance, as well as its spectral overlap with propenylcyclobutane CH resonances, reliable quantitation under the reaction conditions proved challenging. However, approximate ethylene concentrations estimated from peak fitting deconvolution were in reasonable agreement with values expected from the absolute amount of ethylene added in the reaction head space (see Supporting Information). Taken together, these observations suggest that reaction rates are not limited by diffusion of ethylene into solution. See also:a)Zhuze TP, Zhurba AS. Russ. Chem. Bull 1960, 9, 335–337;b)Sahgal A, Hayduk W. J. Chem. Eng. Data, 1979, 24, 222–227.
- [37]. However, an alternative mechanism, wherein reductive coupling is rate-determining and is followed by diene coordination prior to or concomitant with product dissociation, cannot be excluded on the basis of the data available.
- [38]. a)Briggs JR. J. Chem. Soc. Chem. Commun 1989, 674–675;b)Dixon JT, Green MJ, Hess FM, Morgan DH, J. Organomet. Chem 2004, 689, 3641–3668;c)McGuinness DS. Chem. Rev 2011, 111, 2321–2341; [PubMed: 20873753] d)Rummelt SM, Zhong H, Korobkov I, Chirik PJ, J. Am. Chem. Soc 2018, 140, 11589–11593. [PubMed: 30173506]
- [39]. Pangborn AB, Giardello MA, Grubbs RH, Rosen RK, Timmers FJ, Organometallics, 1996, 15, 1518–1520.
- [40]. a)Russell SK, Darmon JM, Lobkovsky E, Chirik PJ, Inorg. Chem 2010, 49, 2782–2792; [PubMed: 20143847] b)Russell SK, Hoyt JM, Bart SC, Milsmann C, Stieber SCE, Semproni SP, DeBeer S, Chirik PJ. Chem. Sci 2014, 5, 1168–1174. ...

A. **B.**

Figure 1. Zero-field ^{57}Fe Mößbauer spectra of (A.) $(\text{MePDI})\text{Fe}(\eta^4\text{-butadiene})$ and (B.) $(\text{Me(Et)PDI})\text{Fe}(\eta^4\text{-piperylene})$ recorded at 80 K in the solid state. Simulated spectra with the listed parameters are plotted in red.

Figure 2.

Lowest-energy optimized structures for the *s-trans* (**A–C.**) and *s-cis* (**D–F.**) isomers of (MePDI)Fe(η^4 -diene) complexes, computed using the M06-L level of density functional theory with the ZORA-def2-TZVP(-f) basis set augmented by SARC/J terms for Fe, N, and C atoms in the primary coordination sphere, and the ZORA-def2-SVP basis set augmented with SARC/J terms for all other atoms.^[26,27] Images rendered using CYLview.^[28] Relative free energies listed in kcal/mol calculated at 298 K; relative electronic energies listed in parentheses. Hydrogen atoms, except those on the diene ligand, omitted for clarity. H = white, C = gray, N = blue, Fe = red-orange.

Figure 3.

Variable temperature ^1H NMR measurements established exchange of inequivalent sites on the NMR timescale. (A.) Temperature dependence of representative NMR signals for $(^{\text{Me}}(\text{Et})\text{PDI})\text{Fe}(\eta^4\text{-piperylene})$ collected in $\text{toluene-}d_8$. Rate constants (k) for exchange extracted from lineshape analysis. (B.) Eyring plot of VT NMR rate data. Dotted line indicates the fit to the linear regression shown to afford the activation parameters for diene exchange.

Figure 4.

^1H - ^1H EXSY titrations reveal that diene exchange is inhibited by excess diene. (**A.**) Excerpt of the 2D EXSY spectrum obtained in the absence of exogenous piperylene. Circles highlight the in-phase cross-peaks indicative of exchange between coordinated and free (*E*)-piperylene. (**B.**) Observed first-order rate constant for diene exchange as a function of added (*E*)-piperylene. (**C.**) Plausible mechanism for diene exchange accounting for the inhibitory effect of excess diene.

A. **B.** **Figure 5.**

Time-shifted reaction profiles for trials conducted with the ‘same excess’ of diene and the same catalyst concentration ($[\text{Fe}]_{\text{tot}} = 10.0 \text{ mM}$) but different $[\text{ethylene}]_0$ and $[\text{diene}]_0$ (open markers vs. filled markers). Overlay indicates that neither catalyst death nor product inhibition occurred during the iron-catalyzed cross-[2+2] cycloaddition of ethylene with (A.) butadiene and (B.) (*E*)-piperylene. Grey arrows indicate where values were time-shifted and/or concentration-shifted to correct for the differing initial concentrations.

Figure 6.

Rate profiles for trials conducted with a 'different excess' of ethylene (open markers vs. filled markers) but the same catalyst concentration ($[\text{Fe}]_{\text{tot}} = 10.0 \text{ mM}$) and $[\text{piperylene}]_0$. Overlay of the linear rate vs. [ethylene] curves indicates that the reaction is zero-order in [piperylene] and first-order in [ethylene].

A. Prior Work: [2+2]-Cycloaddition of Butadiene and Ethylene ^[a] **B. Divergent Reactivity with Substituted Dienes** **C. Catalytically Relevant [Fe] Diene Complexes** **Scheme 1.**Substrate-dependent (PDI)Fe-catalyzed cross-reactions between 1,3-dienes and ethylene. ^[a]

Ref. 17g

Scheme 2.

Iron-catalyzed cross-[2+2]-cycloadditions between (*E*)-piperylene and α -olefins. Combined isolated yields of diastereomeric [2+2]-cycloadducts listed for reactions performed on 1 or 3 mmol scale unless noted otherwise. [a] 2.0 M in benzene-*d*₆ [b] with 1.25 mol% [(^{Me}(Et)PDI)Fe(N₂)₂](μ_2 -N₂) [c] yield determined by integration of diagnostic ¹H NMR signals relative to an internal standard [d] with 0.5 mol% [(^{Me}(Et)PDI)Fe(N₂)₂](μ_2 -N₂) [e] with 5 mol% (^{Me}(Et)PDI)Fe(η^4 -butadiene) [f] with 2.5 mol% [(^{Me}(Et)PDI)Fe(N₂)₂](μ_2 -N₂) [g] with 2.5 mol% [(^{Me}PDI)Fe(N₂)₂](μ_2 -N₂) [h] product **8h** was not separated from remaining tributyl(vinyl)stannane (**7h**); conversion (40%) determined from the relative integration of ¹H NMR signals diagnostic of **8h** and **7h**.

Scheme 3.
Synthesis of (^{Me}PDI)Fe(diene) complexes.

Scheme 4.

Synthesis and solid-state structure of (Me(Et)PDI)Fe(η⁴-piperylene), depicted with 30% probability ellipsoids (CCDC #1956377). Hydrogen atoms are omitted for clarity. C = gray, N = blue, Fe = red-orange. Selected bond distances (Å) and angles (deg): Fe1–N1 1.978(4), Fe1–N2 1.844(4), Fe1–N3 1.976(4), Fe1–C28 2.20(3), Fe1–C29 2.082(9), Fe1–C30 2.058(12), Fe1–C31 2.17(4), N1–C9 1.329(6), C9–C12 1.423(6), C12–N2 1.382(6), N2–C16 1.385(6), C16–C17 1.417(7), C17–N3 1.335(6), N1–Fe1–N3 151.99(15), N1–Fe1–N2 78.89(15), N3–Fe1–N2 79.21(16), N1–Fe1–C31 105.7(6), N2–Fe1–C31 101.6(8), N3–Fe1–C31 95.7(8)

Scheme 5.

Relative coordination affinities of diene ligands to pyridine(diimine) iron complexes determined from isodesmic reaction equilibria. Experimental values determined from relative ^1H NMR integrations for equilibrium mixtures in benzene- d_6 at 23 °C. Computational values calculated at 298 K for isodesmic reactions of $(^{\text{Me}}\text{PDI})\text{Fe}(\eta^4\text{-diene})$ and butadiene, isoprene, or (*E*)-piperylene optimized in the gas phase. [26,27]

Scheme 7.

Proposed catalytic cycle for iron-catalyzed cross-[2+2]-cycloadditions with ethylene.

Scheme 8.

Proposed mechanistic basis for diene-controlled divergent chemoselectivity in iron-catalyzed cross-reactions with ethylene.