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Communication

Iron Olefin Metathesis: Unlocking Reactivity and Mechanistic Insights

Zachary S. Lincoln and Vlad M. Iluc*

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ABSTRACT: Olefin metathesis catalyzed by iron complexes has garnered substantial interest due to iron's abundance and nontoxicity relative to ruthenium, yet its full potential remains untapped, largely because of the propensity of iron carbenes to undergo cyclopropanation instead of cycloreversion from a metallacycle intermediate. In this report, we elucidate the reactions of [{PC(sp^2)P}Fe(L)(N$_2$)], ([PC(sp^2)P] = bis[2-(diisopropylphosphino)phenyl]methylene) with strained olefins, unveiling their capability to yield metathesis-related products. Our investigations led to the isolation of a structurally characterized metallacyclobutane during the reaction with norbornadiene derivatives, ultimately leading to a ring-opened iron alkylidene. These findings provide compelling evidence that iron complexes adhere to the Chauvin olefin metathesis mechanism.

Iron presents an enticing prospect for olefin metathesis because of its unparalleled abundance, cost effectiveness, and low toxicity in comparison to ruthenium, the conventional choice for this reaction. Nevertheless, the development of iron-based catalysts has faced challenges, primarily due to the proclivity of iron carbenes to engage in carbene transfer events.[1−6]

Multiple theoretical studies offered several avenues to explore iron-based metathesis catalysts.[7,8] These strategies include augmenting the strength of the iron−carbene bond by incorporation of neutral σ-donating ligands[6,9] as well as stabilizing the singlet state of both the alkylidene and metallacycle by employing strong-field anionic ligands within high-valent complexes.[6] Despite a focus on high-valent Fe(IV) complexes as targets for metathesis catalysts, certain theoretical investigations have shown the feasibility of low-valent iron-catalyzed olefin metathesis.[9,10] Additionally, studies suggest that the application of rigid chelating ligands may effectively govern the spatial arrangement of both the alkylidene and metallacycle species, favoring the singlet state for both entities.[6,9,11]

On the experimental end, iron-catalyzed cycloadditions have been reported,[12,13] and recent studies by Bukhryakov[14] and Milstein and Takebayashi[15] offered glimpses of the potential of iron complexes in the ring-opening polymerization of norbornene (Figure 1). Notably, several iron carbenes[16−21] address some theoretical strategies, including the tridentate pincer iron carbene complexes reported by Chirik,[22] Wolczanski,[23,24] and Milsmann.[25] However, these compounds exhibited no reactivity with olefins. Building upon this foundation of experimental and theoretical strategies, we have harnessed a pincer system to synthesize a PC(sp^2)P[26] iron carbene, denoted as [{PC(sp^2)P}Fe(PMe$_3$)(N$_2$)] (**1-PMe$_3$**), which has previously exhibited intriguing $2\pi + 2\pi$ cycloadditions with alkynes, resulting in a novel η^3-vinyl iron carbene, a crucial step in iron enyne metathesis.[27] Furthermore, this η^3-vinyl carbene can undergo a second $2\pi + 2\pi$ cycloaddition to yield a new iron carbene, thus serving as a model system for iron-based alkyne polymerizations.

Motivated by these promising alkyne reactions, we embarked on exploring the reactivity of PC(sp^2)P iron carbene with various strained cyclic olefins. In this study, we present unprecedented $2\pi + 2\pi$ cycloadditions of olefins to iron carbenes, resulting in the formation of metallacyclobutanes. Norbornadiene (NBDE) derivatives led to the isolation of a structurally characterized metallacyclobutane that subsequently undergoes cycloreversion, producing a ring-opened alkylidene. These findings offer compelling evidence that these iron complexes follow the Chauvin olefin metathesis mechanism.

Having established that **1-PMe$_3$** and **2-N$_2$** react stoichiometrically with diphenylacetylene[27] to produce the vinyl carbenes **2-N$_2$** and **3**, respectively (Figure 1D), we sought to react **1-PMe$_3$** with olefins to explore its viability in olefin metathesis. We hypothesized that by using a ring-strained olefin, we might avoid unproductive metathesis pathways. Unfortunately, under no conditions did **1-PMe$_3$** and NBDE, or more strained NBDE derivatives, react. We initially assumed that the strong Fe−PMe$_3$ bond likely prevents dissociation of trimethylphosphine and access to an active species capable of the desired reactivity. Consequentially, the reaction of [{PC(sp^2)P}Fe(NC^{t}Bu)(N$_2$)] (**1-NC^{t}Bu**),[27] which contains the more labile pivalonitrile, with NBDE and its derivatives led to the isolation of metallacyclobutane complexes **4-L**, **5-L**, and **6-L** (Figure 2). Specifically, when 1,4-dihydro-1,4-methanonaphthalene (benzonorbornadiene, BZNBDE) was used, a mixture of diamagnetic **5-N$_2$** and **5-NC^{t}Bu** and paramagnetic **8**

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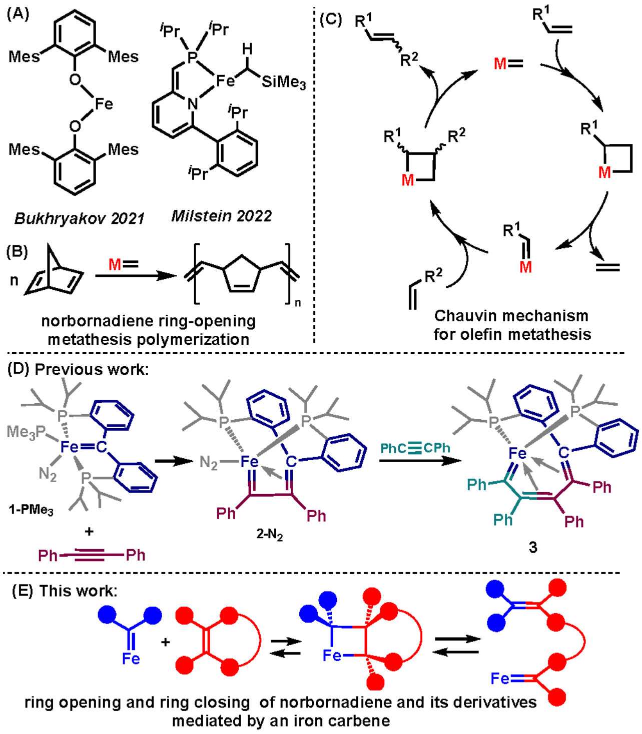

Figure 1. Iron complexes and olefin metathesis. (A) Recently reported iron catalysts for the ring-opening metathesis polymerization (ROMP) of norbornene. (B) ROMP of norbornadiene. (C) Accepted mechanism for olefin metathesis. (D) Iron carbenes undergo [2 + 2] cycloadditions with alkynes to yield η^3-vinyl carbenes. (E) [2 + 2] cycloaddition of a strained cyclic olefin to yield an isolable metallacyclobutane, which can be further converted to a ring-opened carbene.

was obtained. Similarly, when 2,3-diphenylnorbornadiene (DPNBDE) was used, a mixture of diamagnetic **6-N$_2$** and **6-NC^{t}Bu** was obtained. We found early on that the crude mixture of **5-N$_2$**, **5-NC^{t}Bu**, and **8** could be coalesced to a single diamagnetic product by the addition of 1 equiv of 2,6-dimethylbenzonitrile, assigned as **5-NCAr** by NMR spectroscopy. The high solubility of **5-N$_2$**, **5-NC^{t}Bu**, or the derivative **5-NCAr** in aliphatic solvents prevented us from obtaining single crystals. Spectroscopic characterization of **5-NCAr** is consistent with the presence of a metallacyclobutane ring (see below). However, unlike **5-NCAr**, the analogous **6-NCAr**, $[\{PC(sp^3)(-C(sp^3)^{dpnbde}H-C(sp^3)^{dpnbde}H-)P\}Fe(NCAr)]$, was insoluble in aliphatic solvents and only sparingly soluble in diethyl ether, and its solid-state molecular structure showed a five-coordinate distorted trigonal-bipyramidal Fe(II) center with a singular 2,6-dimethylbenzonitrile ligand (Figure 2B).

The Fe−C(1) and Fe−C(3) distances of 2.046(2) and 2.050(2) Å are consistent with those of other iron−carbon single bonds, and the C(1)−C(2) and C(2)−C(3) distances of 1.560(3) and 1.550(2) Å are slightly elongated from idealized C−C single bonds; these parameters are consistent with those of other isolated metallacyclobutanes of first-row transition metals.[28−30] The *exo* isomer of **6-NCAr** is the only species observed in both the solid state and NMR spectroscopy, with a consequence being the observation of an agostic interaction between the iron center and the hydrogen atoms on the bridge of the norbornadiene moiety. This agostic interaction could be characterized by ^{1}H NMR spectroscopy: one of the bridged hydrogens resonates at −9.0 ppm as a doublet of doublets by coupling through the inequivalent phosphines (Figure S22). Formally, this agostic interaction occupies the sixth coordination site of a pseudo-octahedral complex.

The identities of compounds **4**−**6** were assigned based on the diagnostic signal in ^{1}H NMR at *ca.* −9 ppm due to the agostic interaction with the bridgehead methylene group. This signal was observed in each spectrum, and in the case of the mixtures of **4-N$_2$/NC^{t}Bu**, **5-N$_2$/NC^{t}Bu**, and **6-N$_2$/NC^{t}Bu**, two signals were noted at this upfield position, while **5-NCAr** and **6-NCAr** exhibit only one (Table S1 and Figure S2). In addition, several studies have highlighted the correlation between the ^{1}H and ^{13}C NMR resonances of the α and β groups of metallacyclobutanes and metathesis activity,[31,32] and thus, we analyzed whether the isolated **6-NCAr** as well as the observed species **4**, **5**, and **6** followed this trend. In all cases, the H$_\alpha$ proton was located between 4.2 and 4.7 ppm, while H$_\beta$ was located between 3.0 and 3.7 ppm (Table S1), which falls in the wide range (−2.2 to 3.2 ppm) for other reported metathesis-active metallacyclobutanes.[33,34] Analysis of the ^{13}C NMR spectra of **5-NCAr** and **6-NCAr** identified the C$_\alpha$ resonances between 45 and 60 ppm and the C$_\beta$ resonances between 13 and 24 ppm, all of which are consistent with metathesis-active metallacyclobutanes (Table S2).

Once **5-N$_2$**, **5-NC^{t}Bu**, and **6-NCAr** were characterized, we turned our attention to **8**, which was isolated by handling the reaction between **1-NC^{t}Bu** and benzonorbornadiene under an argon atmosphere. Single crystals of **8** revealed a four-coordinate ring-opened iron alkylidene, $[\{PC(=CH\text{-}C_9H_{14}-C(sp^2)H)P\}Fe]$ (Figure 3A). The Fe−C(3) distance of 1.847(1) Å is consistent with an Fe=C interaction, notably shorter than in the parent iron carbene **1-NC^{t}Bu** (1.898(2) Å) but elongated compared to iron vinyl carbenes obtained from reactions of **1-PMe$_3$** and alkynes (1.818−1.820 Å).[27,35] The ring opening of the olefin is evident, with a C(2)−C(3) distance of 2.905(2) Å, coinciding with the formation of a new C=C bond of 1.435(2) Å between the carbene carbon, C(1), and one of the olefin carbons, C(2), consistent with an alkene that is coordinated to the iron center (Figure 3A). **8** is in a distorted tetrahedral geometry and as such is paramagnetic with an effective magnetic moment corresponding to S = 1, suggesting a high-spin Fe(0) or intermediate-spin Fe(II) center, adding **8** to the limited library of paramagnetic iron carbene complexes.[19,22,25,36]

Structurally, **8** is consistent with the proposed intermediate in the polymerization of norbornene using $[(Ph_3P)Cl_2Ru(=C(H)-CH=C(Ph)_2)]$.[37] The coordination of the newly formed alkene in **8** results in a tethered alkylidene that is structurally similar to an intermediate proposed in the ring-expansion polymerization of norbornene.[38] The characterization of **8** provides crucial insight into the potential of iron-based ring-opening metathesis polymerizations, particularly as the ring-opening process appears to be reversible in the presence of an external ligand.

When 1 equiv of trimethylphosphine is added to **8** under a dinitrogen atmosphere, a retro-2π + 2π cycloaddition followed by cycloreversion of the resulting metallacyclobutane results in nearly quantitative conversion to **1-PMe$_3$** and benzonorbornadiene, as evidenced by ^{1}H and ^{31}P NMR spectroscopy (Figure 3B). In general, the ring-opening metathesis reaction is driven forward by relief of ring strain, and therefore, the ring closing of the newly opened ring is thermodynamically unfavorable.[30] Furthermore, ring-closing metathesis typically generates cyclic olefins of low strain,[34,39] and in cases where bicyclic olefins are

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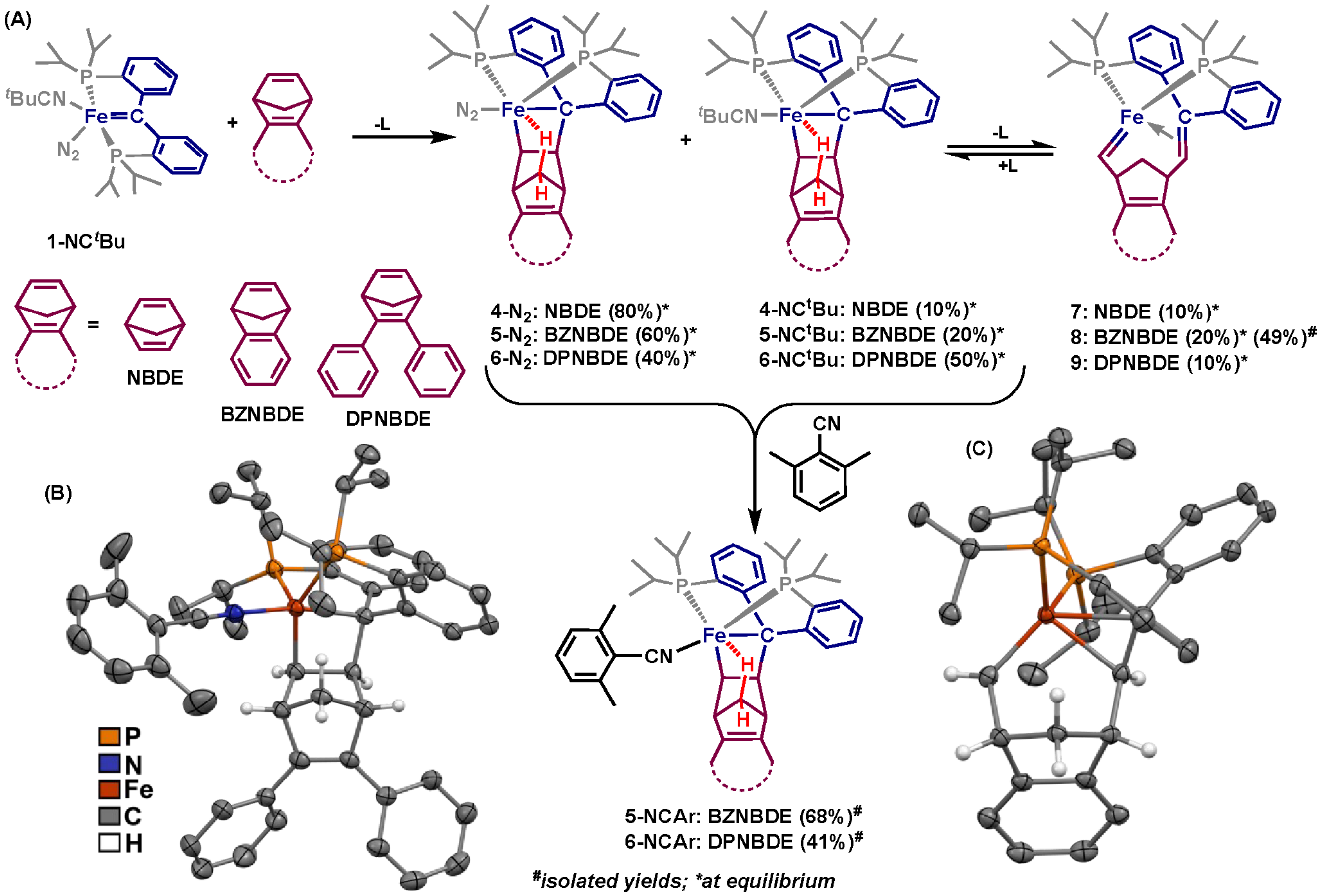

Figure 2. Iron carbenes for ring opening of norbornadiene derivatives. (A) Synthetic scheme for the [2 + 2] cycloaddition between **1-NC^{t}Bu** and norbornadiene derivatives to form **4**–**6**, which undergo subsequent ring opening upon removal of an ancillary ligand to yield **7**–**9**. (B) Solid-state molecular structure of $[\{PC(sp^3)(-C(sp^3)^{dpnbde}H-C(sp^3)^{dpnbde}H-)P\}Fe(NCAr)]$ (**6-NCAr**) with thermal ellipsoids at the 50% probability level; most hydrogen atoms have been omitted for clarity. (C) Solid-state molecular structure of $[\{PC(=CH-C_9H_{14}-C(sp^2)H)P\}Fe]$ (**8**) with thermal ellipsoids at the 50% probability level; most hydrogen atoms have been omitted for clarity.

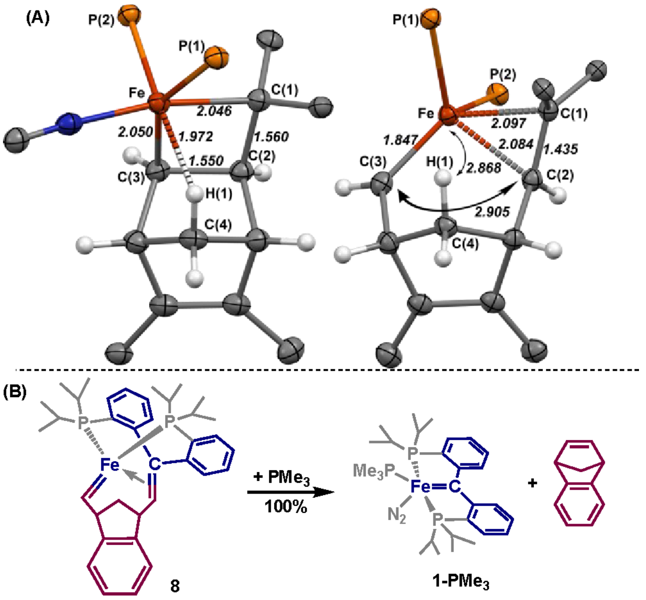

Figure 3. (A) Comparison of the relevant parameters in the solid-state molecular structures of **6-NCAr** and **8**. (B) Ring closing of the ring-opened alkylidene **8** by addition of trimethylphosphine under a N_2 atmosphere to form **1-PMe$_3$**.

formed through ring closing, they typically contain heteroatoms that reduce the strain considerably.[40,41] The ring-closing reaction is also entropically driven by release of ethylene,[34] which cannot be the case in the ring closure observed for the reaction of **8** with PMe_3. It is important to note that in both **8** and **6-NCAr** the dihedral angles between the two phenyl rings of the pincer ligand are 68.42° and 52.56°, respectively, compared to 39.22° in **1-PMe$_3$**. This deviation from coplanarity creates a strain that might contribute to the favorable ring-closing reaction observed for this particular system.

Reversible ring-opening metathesis is a known process for monomers of low ring strain, namely cyclohexene, where the monomer is favored at equilibrium[42] and requires specialized catalysts to undergo ring-opening metathesis polymerization.[43−45] Norbornadiene and derivatives, in contrast, exhibit a significant ring strain (∼35 kcal/mol for norbornadiene)[46] and are typically excellent monomers for ring-opening reactions, as the equilibrium heavily favors the polymer.[47] The reversibility of this ring-opening/ring-closing process explains the observed lack of reactivity of **1-PMe$_3$** toward norbornadiene derivatives. Notably, this process does not occur with all external ligands; only trimethylphosphine initiates the extrusion of benzonorbornadiene from **8**, whereas nitriles and dinitrogen induce the formation of the metallacyclobutanes **4**–**6** from the corresponding carbenes **7**–**9**.

Weakly coordinating ligands such as THF, pyridine, and 4-(dimethylamino)pyridine do not coordinate to **8**, suggesting that the ligand strength dictates this reversible process. Therefore, the addition of norbornadiene derivatives to **1-NC^{t}Bu** results in a 2π + 2π cycloaddition leading to the formation of a metallacyclobutane, which undergoes a cycloreversion upon loss of a ligand to yield a new iron carbene, **8**. These results provide direct evidence for iron carbene complexes behaving according to the Chauvin mechanism. Although well-characterized examples of metathesis-active metallacyclobutanes are known for titanium, molybdenum, and tungsten metallacyclobutanes,[32,48−50] to the best of our knowledge, only *in situ* evidence for this mechanism has been observed with ruthenium carbenes.[33]

In conclusion, this study sheds light on the reactivity of iron carbenes and their potential as alternatives to the traditional, well-established ruthenium catalysts. The formation of ring-opened product **8** showcases the ability of iron complexes to engage in olefin metathesis. Furthermore, the isolation and cycloreversion of a metallacyclobutane during the reaction with norbornadiene derivatives offer evidence that iron complexes adhere to the Chauvin olefin metathesis mechanism. These findings open new avenues for the development of iron-based catalysts in olefin metathesis reactions and provide a deeper understanding of their reactivity and mechanisms.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.4c04356.

Experimental details, NMR spectra, and X-ray crystallography structural details (PDF)

Accession Codes

CCDC 2327758 and 2327759 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

Vlad M. Iluc − *Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556, United States;* orcid.org/0000-0001-6880-2470; Email: viluc@nd.edu

Author

Zachary S. Lincoln − *Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556, United States;* orcid.org/0000-0001-7630-3196

Complete contact information is available at: https://pubs.acs.org/10.1021/jacs.4c04356

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Notes

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