JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Article
pubs.acs.org/JACS

An Iron(II) Ylide Complex as a Masked Open-Shell Iron Alkylidene Species in Its Alkylidene-Transfer Reactions with Alkenes

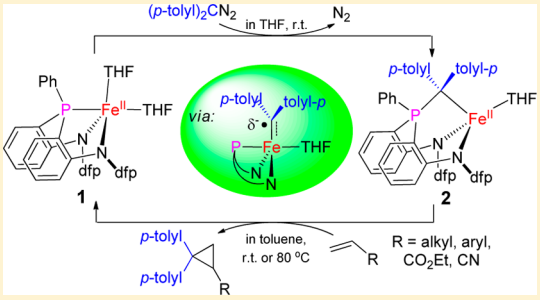
Jian Liu,[†,§] Lianrui Hu,[‡,§] Lei Wang,[†] Hui Chen,*[,‡] and Liang Deng*[,†]

[†]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, P. R. China

[‡]Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China

Supporting Information

ABSTRACT: Transition-metal alkylidenes are important reactive organometallic intermediates, and our current knowledge on them has been mainly restricted to those with closed-shell electronic configurations. In this study, we present an exploration on open-shell iron alkylidenes with a weak-field tripodal amido-phosphine-amido ligand. We found that a high-spin (amido-phosphine-amido)iron(II) complex can react with $(p\text{-tolyl})_2CN_2$ to afford a high-spin (amido-ylide-amido)iron(II) complex, **2**, which could transfer its alkylidene moiety to a variety of alkenes, either the electron-rich or electron-deficient ones, to form cyclopropane derivatives. The reaction of **2** with *cis*-β-deuterio-styrene gave deuterated cyclopropane derivatives with partial loss of the stereochemical integrity with respect to the *cis*-styrene. Kinetic study on the cyclopropanation reaction of **2** with 4-fluorostyrene disclosed the activation parameters of $\Delta H^{\ddagger} = 23 \pm 1$ kcal/mol and $\Delta S^{\ddagger} = -20 \pm 3$ cal/mol/K, which are comparable to those of the cyclopropanation reactions involving transition-metal alkylidenes. However, the cyclopropanation of *para*-substituted styrenes by **2** shows a nonlinear Hammett plot of $\log(k_X/k_H)$ vs σ_p. By introduction of a radical parameter, a linear plot of $\log(k_X/k_H)$ vs $0.59\sigma_p + 0.55\sigma_c^{\bullet}$ was obtained, which suggests the "nucleophilic" radical nature of the transition state of the cyclopropanation step. In corroboration with the experimental observations, density functional theory calculation on the reaction of **2** with styrene suggests the involvement of an open-shell (amido-phosphine-amido)iron alkylidene intermediate that is higher in energy than its (amido-ylide-amido)iron(II) precursor and an "outer-sphere" radical-type mechanism for the cyclopropanation step. The negative charge distribution on the alkylidene carbon atoms of the open-shell states ($S = 2$ and 1) explains the high activity of the cyclopropanation reaction toward electron-deficient alkenes. The study demonstrates the unique activity of open-shell iron alkylidene species beyond its closed-shell analogues, thus pointing out their potential synthetic usage in catalysis.



INTRODUCTION

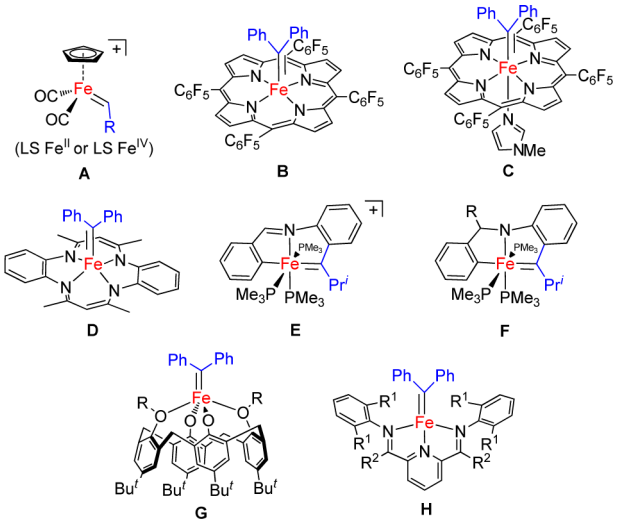
Transition-metal alkylidene/carbene species[1] in the form of $L_nM(CR^1R^2)$ (R^1, R^2 = H, alkyl, and aryl) are recognized as the key intermediates of many important transition-metal-mediated organic transformations, e.g., alkene cyclopropanation, C−H alkylation, and alkene metathesis.[2] Therefore, with the aim of developing new iron catalysts as alternatives to the known precious metal catalysts, there has been great interest in iron alkylidene complexes.[3] Among the reported iron alkylidene complexes, the closed-shell diamagnetic complexes are the best studied ones. Complexes of this type include the cyclopentadienyliron complexes $[CpFeL_2(CR^1R^2)]^+$ (R^1, R^2 = H, alkyl and aryl; L = CO, phosphine, **A** in Chart 1),[4] the porphyrin iron complexes [(TPFPP)Fe(CPhR)] (R = Ph (**B**), CO_2Et, $CO_2CH_2CH{=}CH_2$; TPFPP = *meso*-tetrakis(pentafluorophenyl)porphyrinato)[5] and $[(TPFPP)Fe(Im^{Me})(CPh_2)]$ (Im^{Me} = *N*-methylimidazole, **C**),[5] the (tetrazaannulene)iron complex $[(tmtaa)Fe(CPh_2)]$ (tmtaa = tetramethyldibenzotetrazaannulene, **D**),[6] and also Wolczanski's six-coordinate formal iron(IV) complexes bearing chelating alkylidene ligands (**E** and **F**).[7] Theoretical studies suggest that these closed-shell alkylidene complexes are better to be viewed as low-spin iron(II) complexes featuring singlet carbene ligands $[{:}CR^1R^2]^0$.[6−8] Therefore, they are electrophilic, and some of them, the 18e$^-$ cyclopentadienyliron and porphyrin iron alkylidene complexes **A** and **C**, can react with alkenes to form cyclopropanes.[2b,5]

In contrast to plenty of studies on closed-shell iron alkylidene complexes, the chemistry of their open-shell congeners is rarely known. Floriani reported the preparation of the (calix[4]-arene)iron alkylidene complexes $[(calix[4]\text{-}arene)Fe(CPh_2)]$ (**G**) from the reaction of the iron(II) precursors with Ph_2CN_2.[9] Magnetic property studies indicated an $S = 2$ ground spin-state for these complexes.[9] Probably due to steric shielding by calix[4]-arenes, they are highly thermal stable and kinetically inert. Chirik synthesized four-coordinate iron diphenylidene complexes $[(PDI)Fe(CPh_2)]$ (**H**) via the reactions of

Received: January 16, 2017
Published: February 21, 2017

DOI: 10.1021/jacs.7b00484
J. Am. Chem. Soc. 2017, 139, 3876−3888

Chart 1. Examples of Isolable Iron Alkylidene Complexes



(bisimidopyridine)iron dinitrogen complexes with Ph_2CN_2.[10] Spectroscopic characterization and theoretical studies established the open-shell (S = 1) nature of these 16e$^-$ iron alkylidene complexes that contain a high-spin iron(II) center antiferromagnetically coupled with bis(imino)pyridine and carbene radicals. The (bisiminopyridine)iron alkylidene complexes are unreactive toward alkenes.[10] In addition, Shaik's recent theoretical study[11] revealed the open-shell singlet ground state of the iron alkylidene species [(por)Fe(SMe)-$(CHCO_2Et)]^-$ that has the two antiferromagnetically coupled electrons residing on the low-spin iron(III) center and the carbene ligand. NBO charge analysis indicated the electrophilic nature of the carbene moiety in $[(por)Fe(SMe)(CHCO_2Et)]^-$ at its open-shell singlet state.[11]

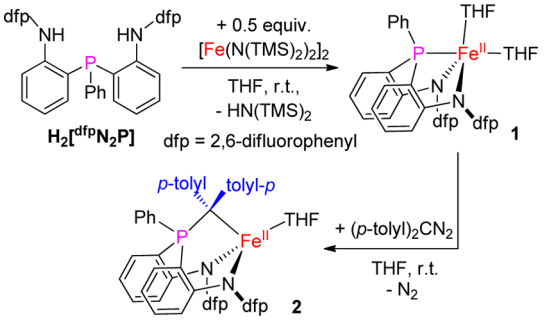
The limited knowledge on open-shell iron alkylidenes forms a sharp contrast to the rich chemistry of open-shell iron imido and oxo complexes,[1c,12] and also that of open-shell cobalt alkylidene complexes.[13−15] Aiming to explore the chemistry of open-shell iron alkylidenes, we envisioned the use of weak-field tripodal ligands to access open-shell iron alkylidene species.[16] In this context, we report herein the study with a tripodal amido-phosphine-amido ligand,[17] bis(*N*-(2,6-difluorophenyl)-*o*-aminophenyl)phenylphosphine $[^{dfp}N_2P]^{2-}$, which led to the preparation of a "masked" iron alkylidene complex, a high-spin (amido-ylide-amido)iron(II) complex, from the reaction of an (amido-phosphine-amido)iron(II) complex with $(p\text{-tolyl})_2CN_2$. Intriguingly, the "masked" iron alkylidene complex effects alkylidene transfer to both electron-rich and electron-deficient alkenes to form cyclopropanes. Kinetic and theoretical studies on the cyclopropanation reaction suggest the involvement of open-shell (amido-phosphine-amido)iron alkylidene intermediate, and that the open-shell iron alkylidene intermediate supported by the tripodal amido-phosphine-amido ligand shows "nucleophilic" alkylidene radical character, showcasing a distinct reactivity of open-shell iron alkylidene species over its closed-shell congeners that are usually electrophilic.[2b,4−6]

RESULTS AND DISCUSSION

Preparation and Characterization of the "Masked" Iron Alkylidene Complex. Previously, we found that the interaction of organic azides with the iron(II) complex [(κ-*N,N,P*-$^{mes}N_2P$)Fe(OEt_2)] containing the tripodal ligand bis(*N*-mesityl-*o*-aminophenyl)phenylphosphine led to facile C−H amination reactions on the benzylic position of the ligand.[16] To avoid similar C−H activation reaction by the desired iron alkylidene species, the new ligand incorporating *N*-2,6-difluorophenyl substituents, bis(*N*-(2,6-difluorophenyl)-*o*-aminophenyl)phenylphosphine $H_2(^{dfp}N_2P)$, was prepared. As shown below, this amido-phosphine-amido ligand also functions as a tripodal ligand when coordinating with iron.

Treatment of $[Fe(N(SiMe_3)_2)_2]_2$ with $H_2(^{dfp}N_2P)$ (2 equiv) in THF at room temperature gave a yellow suspension. After workup and recrystallization, the iron(II) complex [(κ-*N,N,P*-$^{dfp}N_2P$)Fe($THF)_2$] (**1**) was isolated as yellow crystals in 71% yield (Scheme 1). A single-crystal X-ray diffraction

Scheme 1. Synthesis of the Iron(II) Ylide Complex



study revealed the facial coordination mode of the dianionic amido-phosphine-amido chelate $[^{dfp}N_2P]^{2-}$ to the iron center that is further coordinating with two THF molecules to form a trigonal bipyramidal geometry (Figure S1). The long Fe−P (2.424(2) Å), Fe−O (2.138(3) and 2.198(3) Å), and Fe−N (2.030(2) Å) separations observed in the structure are typical of high-spin ferrous complexes. The measured solution magnetic moment (μ_{eff} = 4.4(1) μ_B in C_6D_6) and zero-field ^{57}Fe Mössbauer data (isomer shift δ = 0.94 mm/s, quadrupole splitting $|\Delta E_Q|$ = 2.46 mm/s at 80 K, Figure S2) corroborate the high-spin (S = 2) ground spin-state for **1**.

Complex **1** can readily react with $(p\text{-tolyl})_2CN_2$ at room temperature to produce a yellow solution, from which the iron(II) ylide complex [(κ-*N,N,C*-$^{dfp}N_2PC(tolyl\text{-}p)_2$)Fe(THF)] (**2** in Scheme 1), rather than the desired alkylidene complex (κ-*N,N,P*-$^{dfp}N_2P$)Fe(C(tolyl-*p*)$_2$)(THF), was isolated as a yellow crystalline solid in 81% yield. Complex **2** was characterized by ^{1}H NMR spectroscopy (Figure S13), solution magnetic susceptibility measurement, single-crystal X-ray diffraction study, zero-field ^{57}Fe Mössbauer spectroscopy, and elemental analysis. The Mössbauer data (δ = 0.77 mm/s, $|\Delta E_Q|$ = 3.38 mm/s at 80 K, Figure S3) and magnetic moment (4.7(1) μ_B in C_6D_6 at room temperature) support the high-spin ferrous nature of **2**. As shown in Figure 1, the iron(II) center in **2** is coordinating with a tripodal amido-ylide-amido ligand and a THF molecule, forming a tetrahedral geometry with pyramidal distortion (τ_4 = 0.35).[18] The newly formed ylide side arm has the Fe−C distance of 2.138(4) Å, being slightly longer than those of the reported ylide complexes $[Fe(CO)_4(CH_2PPh_3)]$ (2.122(3) Å)[19] and $[(Cp^*)Fe(CO)_2(CH_2PPh_3)][BF_4]$ (2.11(1) Å).[20] Its P−CPh_2 bond (1.784(4) Å) is longer than its congener in CH_2PPh_3 (1.661(8) Å),[21] and locates on the long end of the P−C bonds of the reported phosphonium ylide metal complexes, e.g., $[Co(PPh_3)(CH_2PPh_3)Cl_2]$ (1.739 Å),[22] $[Fe(CO)_4(CH_2PPh_3)]$ (1.755(3) Å),[19] [{κ-*C,C*-(NHC-

DOI: 10.1021/jacs.7b00484
J. Am. Chem. Soc. 2017, 139, 3876−3888

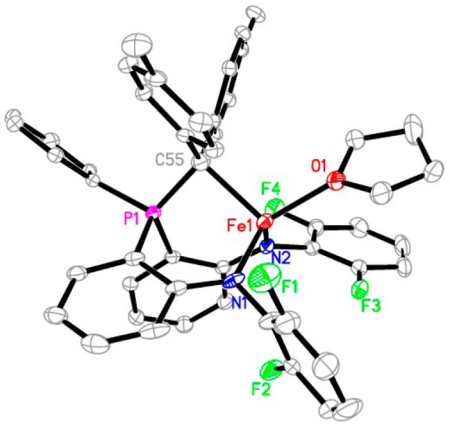
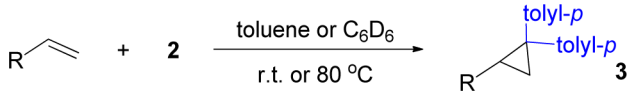


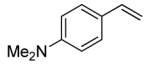
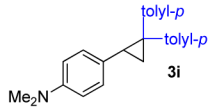
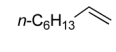
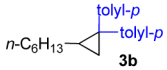
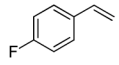
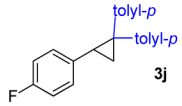
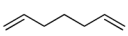
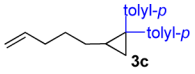
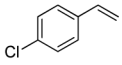
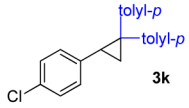
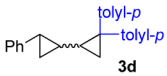
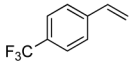
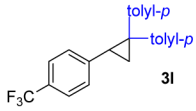
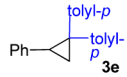
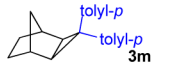
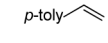
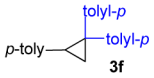
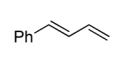
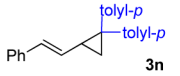
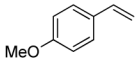
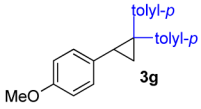
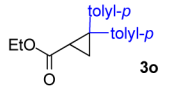
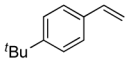
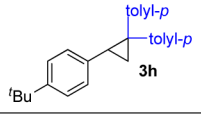
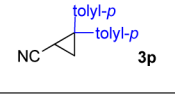
Figure 1. Molecular structure of **2**, showing 30% probability ellipsoids and the partial atom numbering scheme. Selected distances (Å) and angles (deg): Fe(1)−C(55) 2.138(4), Fe(1)−N(1) 2.002(4), Fe(1)−N(2) 1.985(4), Fe(1)−O(1) 2.011(4), P(1)−C(55) 1.784(4), Fe(1)−C(55)−P(1) 90.9(2).

PPh_2CH_2)}Pd(C_3H_5)][OTf] (1.72(1) Å),[23] [(Cp*)Fe(CO)$_2$-(CH_2PPh_3)][BF_4] (1.78(1) Å),[20] [{κ-*P,C*-(Bu^t_2PCH_2CH_2P-(Bu^t)$_2$CH(dmp))}Ni][BAr^F_4] (1.811(4) Å).[24] The Fe−C−P angle (90.9(2)°) in **2** is acute and smaller than those of the reported ylide complexes, which span the range 100−140°.[25] Alongside the small Fe−C−P angle, the Fe···P separation (2.81 Å) in **2** is merely longer than that of **1** by 0.42 Å. The long P−C bond and acute Fe−C−P angle reflect geometry constraint within the molecule.

The attainment of **2** from the reaction of **1** with the diazo compound implicates the high reactivity of the iron alkylidene intermediate (κ-*N,N,P*-$^{dfp}N_2$P)Fe(C(tolyl-*p*)$_2$)(THF), which, once formed, could undergo migratory insertion with the phosphine ligand to form the iron ylide complex **2**. The transformation is reminiscent of the one-electron oxidation-triggered conversion of the nickel(II) alkylidene complex [(dtbpe)Ni(CHdmp)] to the ylide complex [{κ-*P,C*-(Bu^t_2P-CH_2CH_2P(Bu^t)$_2$CH(dmp))}Ni][BAr^F_4].[24] As the bulky amine-phosphine-amine ligand $H_2(^{dfp}N_2P)$ proved unreactive toward (*p*-tolyl)$_2CN_2$ at ambient conditions, the alternative mechanism

Table 1. Cyclopropanation Reactions of the Iron(II) Ylide Complex with Alkenes[a]



entry	substrate	temp.	time	product	yield [b]	entry	substrate	temp.	time	product	yield [b]
1		r.t.	30 min	 **3a**	(77%)	9		80 °C	9 h	 **3i**	88% (39%)
2		80 °C	6 h	 **3b**	(66%)	10		80 °C	10 h	 **3j**	91% (79%)
3		80 °C	6 h	 **3c**	(76%)	11		80 °C	8 h	 **3k**	94% (67%)
4		80 °C	12 h	 **3d**	(70%)	12		80 °C	4 h	 **3l**	90% (66%)
5		80 °C	14 h	 **3e**	90% (81%)	13		80 °C	30 min	 **3m**	(83%)
6		80 °C	14 h	 **3f**	90% (60%)	14		80 °C	3 h	 **3n**	(97%)
7		80 °C	10 h	 **3g**	89% (57%)	15		80 °C	7 h	 **3o**	88% (61%)
8		80 °C	11 h	 **3h**	96% (72%)	16		80 °C	9 h	 **3p**	22% (16%)

[a] **2** with 3 equiv of alkene. [b] NMR yields (isolated yields) based on **2** with 1,3,5-trimethoxybenzene as the internal standard.

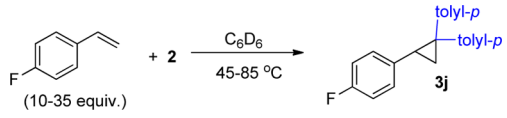
DOI: 10.1021/jacs.7b00484
J. Am. Chem. Soc. 2017, 139, 3876−3888

accounting for the formation of **2**, which involves the direct nucleophilic attack of the phosphine moiety to the diazo compound, seems less likely.

Alkylidene-Transfer Reactions of 2 with Alkenes. The novel structure features of the iron(II) ylide complex, long P−C separation, and acute Fe−C−P angle, hint its potential to perform alkylidene-transfer reactions. Noted this, the reactions of **2** with alkenes were examined. Indeed, complex **2** can react with various alkenes to produce cyclopropanation products **3** in good to excellent yields (Table 1), along with **1** as the iron-containing product (Figure S4). An important feature of the cyclopropanation reaction is its broad scope of alkenes as not only electron-rich alkenes but also electron-deficient alkenes can be applied. The reactions of **2** with alkenes bearing alkyl (entries 2−4 and 13), aryl (entries 5−12), alkenyl (entry 14), and ester (entry 15) groups gave the corresponding cyclopropanation products in comparable yields despite their differentiated rates (*vide infra*). In spite of the coordinating nature of cyano group, the trial with acrylonitrile could still afford the cyclopropanation product in 22% yield (entry 16). The cyclopropanation reaction is affected by the steric property of alkenes. The interaction of **2** with the smallest alkene, ethylene, took place at room temperature and completed in 0.5 h (entry 1). The reactions with substituted alkenes required higher temperature (80 °C) and longer reaction times (entries 2−16). The internal alkenes, cyclohexene and *cis*-stilbene, are unreactive with **2** either at room temperature or 80 °C. For disubstituted alkenes, the only successful trial is the one with norbornene, which gave the *exo*-addition product in 83% yield (entry 13). In contrast to these iron-mediated cyclopropanation reactions, phosphonium ylides alone are known unreactive toward nonactivated alkenes.[26]

The cyclopropanation reaction of **2** shows a close resemblance to those of transition-metal alkylidene complexes. Such reactivity, however, is atypical for phosphonium yildes. Aiming to throw light on their reaction mechanisms, the reactions of **2** with styrenes were examined in detail by kinetic studies. Monitoring the increase of the ^{19}F NMR signal of 2-(*p*-fluorophenyl)-1,1-di(*p*-tolyl)cyclopropane formed in the reaction of **2** with excess amount of 4-fluoro-styrene (10−35 equiv) in C_6D_6 at 60 °C (Scheme 2) revealed the *pseudo*-first-order

Scheme 2. Cyclopropanation of 4-Fluoro-styrene by 2



kinetics of the reaction. As a representative example, Figure 2 shows the change of yield versus time for the reaction employing 35 equiv of 4-fluoro-styrene. The linear dependence of the observed pseudo-first-order rate constants, k_{obs}, on the alkene concentration indicates that the reaction is also first-order in 4-fluoro-styrene (inset in Figure 2). The rate constants acquired in the temperature range 45−85 °C under the pseudo-first-order conditions using 20 equiv of 4-fluoro-styrene are shown in Table S2. The Eyring plot (Figure 3) gave the activation parameters $\Delta H^{\ddagger}$ = 23 ± 1 kcal/mol and $\Delta S^{\ddagger}$ = −20 ± 3 cal/mol/K. The large and negative entropy change indicates an associative mechanism for the cyclopropanation reaction. These activation parameters can be compared with those of cyclopropanation reactions by transition-metal

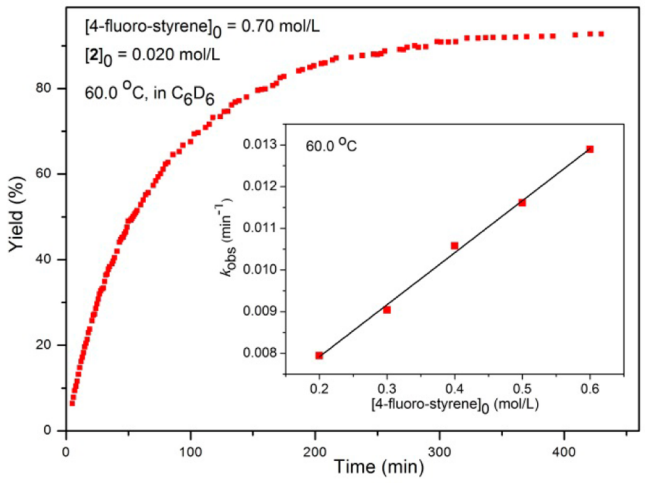


Figure 2. Representative plot for the change of the yield of the cyclopropanation product versus time for the reaction of **2** with 4-fluoro-styrene in C_6D_6 at 60 °C. Inset: the linear dependence of the observed pseudo-first-order rate constants, k_{obs}, versus alkene concentration.

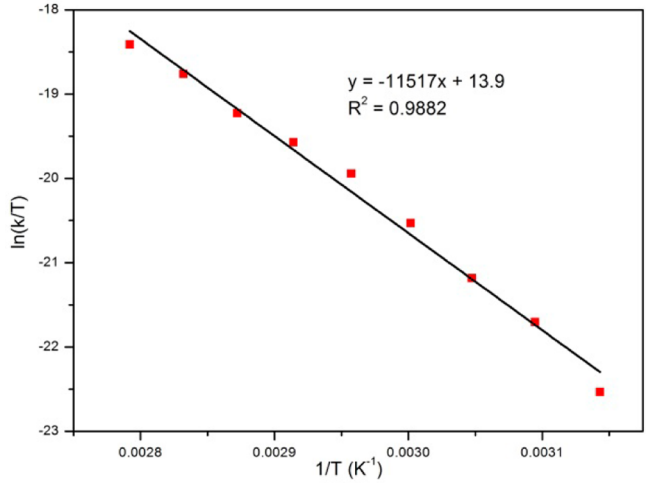


Figure 3. Erying plot for the cyclopropanation of 4-fluoro-styrene by **2** in C_6D_6 at the temperature range 45−85 °C.

alkylidene species. For examples, the reaction of the tungsten complex $W(CO)_5(CHC_6H_4\text{-}OMe\text{-}p)$ with vinyl acetate has $\Delta H^{\ddagger}$ = 10 kcal/mol and $\Delta S^{\ddagger}$ = −34 cal/mol/K,[27] that of Warren's copper alkylidene [(nacnac)Cu(CPh_2)] with styrene has $\Delta H^{\ddagger}$ = 10 kcal/mol and $\Delta S^{\ddagger}$ = −32 cal/mol/K,[28] and the copper(I) triflate-catalyzed cyclopropanation of 1-hexene by ethyl diazoacetate has $\Delta H^{\ddagger}$ = 19 kcal/mol and $\Delta S^{\ddagger}$ = −9 cal/mol/K.[29]

In order to probe the nature of the reactive species in the cyclopropanation reaction, the relative rates of the cyclopropanation of a series of *para*-substituted styrenes by the ylide complex **2** were measured by competition experiments (Scheme 3). As listed in Table 2, the styrene derivatives with either electron-donating or electron-withdrawing substituents on the *para*-position are found more reactive than styrene. Interestingly, the electron-rich styrene derivatives only show slight rate-acceleration, whereas the electron-withdrawing substitutes exhibit apparently rate acceleration. Plotting log-(k_X/k_H) versus σ_p gave a nonlinear plot (Figure 4a) that is in striking difference to the linear plots of many of the reported

DOI: 10.1021/jacs.7b00484
J. Am. Chem. Soc. 2017, 139, 3876−3888

Scheme 3. Competition Reactions

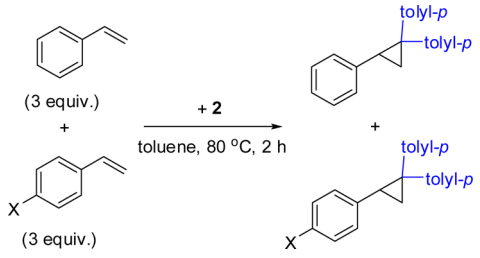


Table 2. Relative Rates $\log(k_X/k_H)$ with σ_p and $\sigma_c^\bullet$ Scales for the Cyclopropanation of *Para*-Substituted Styrenes by 2[a]

substituent	k_X/k_H	$\log(k_X/k_H)$	σ_p	$\sigma_c^\bullet$
Me_2N	1.28	0.11	−0.83	0.90
MeO	1.24	0.093	−0.27	0.24
Bu^t	1.18	0.072	−0.20	0.13
CH_3	1.16	0.060	−0.17	0.11
F	1.25	0.099	0.06	−0.08
Cl	1.88	0.274	0.23	0.12
CF_3	3.12	0.49	0.54	0.08

[a] σ_p are Hammett constants measured on *para*-substituented aryl derivatives.[33] $\sigma_c^\bullet$ are Creary's constants.[34]

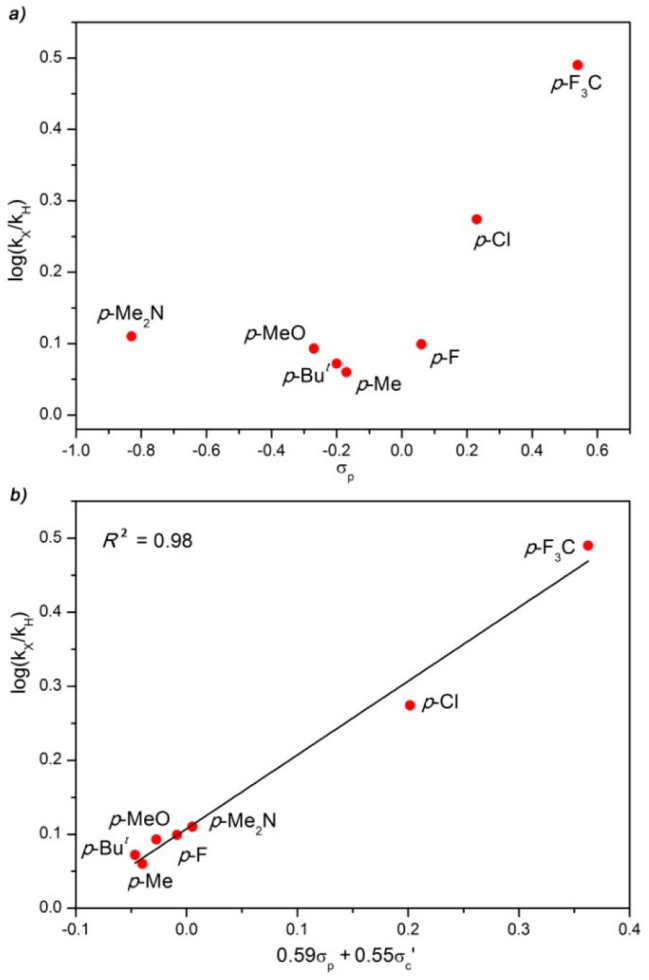


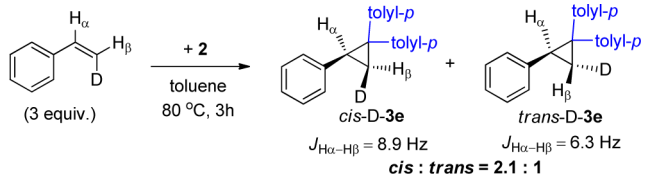
Figure 4. Linear-free-energy correlation of $\log(k_X/k_H)$ vs σ_p (a) and vs $0.59\sigma_p + 0.55\sigma_c^\bullet$ (b) for the cyclopropanation of *para*-substituted styrene derivatives by **2**.

transition-metal-mediated or -catalyzed cyclopropanation reactions, e.g., the reaction of *para*-substituted styrenes with [(TPFPP)Fe(CPhCOOEt)] (ρ = −0.41),[5] the (TTP)Fe-catalyzed cyclopropanation of styrenes with ethyl diazoacetate (ρ = −0.68),[30] myoglobin-catalyzed cyclopropanation of styrenes with ethyl diazoacetate (ρ = −0.34),[31] and Pérez's copper-catalyzed cyclopropanation reaction (ρ = −0.85).[32] In the latter cases, the negative ρ values suggest the electrophilic nature of the metal carbene intermediates.

In group-transfer reactions, nonlinear Hammett plots have been observed on the alkene epoxidation by *trans*-dioxoruthenium(VI) porphyrins,[35a] amine-accelerated osmylation of substituted styrenes,[35b] alkene aziridation by bis(tosylimido)ruthenium(VI) porphyrins,[35c] alkene aziridation by organic azides catalyzed by ferrous dipyrrinato complexes,[35d] and alkene aziridation by PhINTs catalyzed by copper(I) tris(pyrazolyl)borate.[32] The nonlinearity was thought to hint the existence of intermediates that have significant radical character. Noted this, spin-delocalization effect of the substituents was taken into account using the dual parameter equation $\log(k_X/k_H) = \rho^X\sigma^X + \rho^\bullet\sigma^\bullet$.[36] While the multiple linear regression for the equation using Jiang's σ_{mb} and $\sigma_{JJ}^\bullet$ scales[36] gave poor linear correlation (R^2 = 0.55), an appreciably better linearity (R^2 = 0.98) was achieved when the Hammett constant σ_p[33] and Creary's radical scale $\sigma_c^\bullet$[34] were applied, resulting in ρ_p and $\rho_c^\bullet$ values of 0.59 and 0.55, respectively (Figure 4b). The positive ρ_p value implies that the attack toward the alkenes is "nucleophilic", being distinct from the reactions of the aforementioned electrophilic metal carbene species with styrenes.[2b,5,31,32] The positive ρ_p value, on the other hand, accounts for the failure of using σ_{mb} and $\sigma_{JJ}^\bullet$ scales to achieve good linear fitting as these scales were obtained from reactions involving electrophilic radicals.[36] The $\rho_p/\rho_c^\bullet$ ratio of 1.07 indicates that both polar and spin effects are important in the iron-mediated cyclopropanation reaction. Notably, the scales σ_p and $\sigma_c^\bullet$ have proved successful for the dual parameter correlation analysis of a bromo-abstraction reaction by a nucleophilic silyl radical.[37]

To gain insights into the stereochemistry of the cyclopropanation reaction, the reaction of **2** with the stereospecifically labeled styrene *cis*-β-deuterio-styrene was tested. As seen in Scheme 4 and Figures S48−S50, the reaction yields a mixture

Scheme 4. Reaction of 2 with *cis*-β-Deuterio-styrene



of *cis*- and *trans*-products with a ratio of 2.1:1 according to ^1H and ^2H NMR spectra. The partial loss of stereospecifity is different from the cyclopropanation reactions by $[CpFeL_2(CR^1R^2)]^+$ and $[W(CO)_5(CHPh)]$, which show high stereochemical integrity,[2b] whereas a similar situation (loss of stereospecifity) is known in alkene cyclopropanation, epoxidation, and aziridation by certain porphyrin-metal carbene,[38a] oxo,[38b] and imido species.[35c] The scrambling of the deuterium label implies the involvement of a stepwise pathway for the C−C bond formation steps of the cyclopropanation reaction. The low percentage of the *trans*-product apparently suggests a rapid

DOI: 10.1021/jacs.7b00484
J. Am. Chem. Soc. 2017, 139, 3876−3888

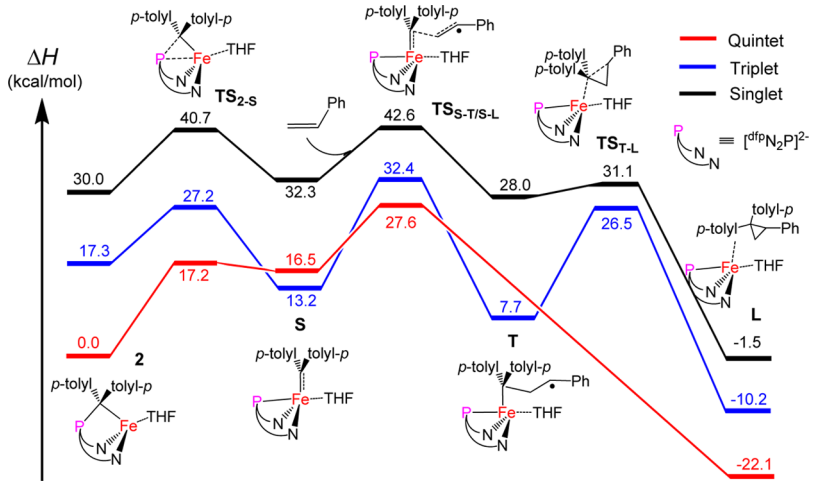


Figure 5. Calculated pathways for the cyclopropanation reaction of **2** with styrene.

ring-closure step in a stepwise pathway. In addition to a stepwise pathway, the high percentage of the *cis*-product suggests that the involvement of a concerted pathway in the cyclopropanation step could not be excluded. Notably, these understandings also provide explanation to the observation of the absence of the ring-opening product in the reaction of **2** with the cyclopropyl ethene (entry 4 in Table 1).

Theoretical Study on the Mechanism of the Reaction of 2 with Styrene. As the aforementioned results collectively point out that the cyclopropanation reaction of **2** with the substituted styrenes probably involves the attack of a nucleophilic iron alkylidene intermediate toward the alkenes with a spin-delocalized transition state, DFT calculations on the reaction of ($^{dfp}N_2PC$(tolyl-*p*)$_2$)Fe(THF) (**2**) with styrene were performed to evaluate the possibility.

The computed reaction profiles show that the interaction of the iron alkylidene intermediate ($^{dfp}N_2P$)Fe(C(tolyl-*p*)$_2$)(THF) (**S**) with styrene in an "outer-sphere" manner indeed could be responsible for the formation of the cyclopropanation product (Figure 5). The transformation from the ylide complex **2** to the iron alkylidene **S** on the quintet energy surface has to surmount an activation barrier of 17.2 kcal/mol. The alkylidene intermediate **S** has a triplet (S = 1) ground state that is higher in energy than the reactant ($^{dfp}N_2PC$(tolyl-*p*)$_2$)Fe(THF) (**2**) in its quintet (S = 2) ground spin-state by 13.2 kcal/mol. The higher energy of **S** than **2** explains the failure of detecting the iron alkylidene intermediate in our experimental studies. Following the formation of the alkylidene intermediate, the interaction of its alkylidene moiety with the C=C double bond of styrene via either a concerted manner ($\mathbf{TS}_{S\text{-}L}$) on the quintet surface or a stepwise way ($\mathbf{TS}_{S\text{-}T}$) on the triplet or singlet surface could result in the formation of the cyclopropanation product. Along each surface, the transition states of the reactions between **S** and styrene ($\mathbf{TS}_{S\text{-}L}$ or $\mathbf{TS}_{S\text{-}T}$) lay the highest on the energy surfaces, being 27.6, 32.4, and 42.6 kcal/mol higher than the reactants (**2** and styrene) on the quintet, triplet, and singlet energy surfaces, respectively. Among these three barriers, the lower one (27.6 kcal/mol) on the quintet surface is more comparable to the experimental activation enthalpy $\Delta H^{\ddagger}$ = 23 ± 1 kcal/mol acquired from the cyclopropanation of 4-fluoro-styrene. However, the relatively close energies of $^5\mathbf{TS}_{S\text{-}L}$ (quintet) and $^3\mathbf{TS}_{S\text{-}T}$ (triplet) imply that they can both be viable in the cyclopropanation reaction, therefore indicating the possibility of involving both the concerted and the stepwise mechanisms of cyclopropanation, as inferred by the experimental stereochemical result of *cis*-β-deuterio-styrene (Scheme 4). As a result, there could be a two-state reactivity scenario operative in cyclopropanation reactions.[39] Alternative to "outer-sphere" mechanism, we also explored the corresponding "inner-sphere" mechanism of cyclopropanation reaction between **2** and styrene (Figure S61). Compared to the corresponding transition states ($\mathbf{TS}_{S\text{-}L}$ and $\mathbf{TS}_{S\text{-}T}$) in "outer-sphere" mechanism, the higher-lying transition states of interaction between alkylidene moiety with the C=C double bond of styrene in "inner-sphere" mechanism do not support this mechanism for cyclopropanation reaction. These calculations, along with the results of kinetic studies, suggest that "outer-sphere" pathway is more likely to be involved in the cyclopropanation reactions under study.

Noting the limited knowledge on open-shell iron alkylidene species, the open-shell nature of ($^{dfp}N_2P$)Fe(C(tolyl-*p*)$_2$)(THF) (**S**) is noteworthy. Benefited from the weak-field nature of the tripodal amido-phosphine-amido ligand, the alkylidene species has a triplet ground state, with the quintet state lying slightly higher by only 3.3 kcal/mol, but being substantially lower in energy than the closed-shell singlet state by 19.1 kcal/mol. The iron centers in the structures of both open-shell states display trigonal bipyramidal geometry with the alkylidene carbon atoms sitting on the equatorial position. Figure 6 shows the structure of **S** at the triplet state. The Fe−C(alkylidene) distances (1.935 and 2.001 Å for that of the triplet and quintet states, respectively) locate between its congeners in the low-spin iron alkylidene complexes, e.g., [CpFe(dppe)(CHMe)][CF_3SO_3] (1.787(8) Å),[4] [(TPFPP)Fe(CPh_2)] (1.767(3) Å),[5] and [(tmtaa)Fe(CPh_2)] (1.794(3) Å),[6] and five-coordinate high-spin iron(II)-*N*-heterocyclic carbene complexes (ca. 2.10 Å),[40] implying certain multiple bond nature of Fe−C(alkylidene) interaction, at least in the triplet structure. Indeed, the Fe−C(alkylidene) bonds in the triplet and quintet structures have the Wiberg bond orders of 0.96 and 0.80, respectively, which are higher than those of the Fe−N bonds (0.47 and 0.45) in the same molecules.

Notably, in spite of the formal iron(IV) nature of **S**, the compositions of the frontier molecular orbitals (Figures S62 and S63) indicate that **S** at the triplet state should be best described as an intermediate-spin iron(III) species bearing an antiferromagnetically coupled carbene radical [C(tolyl-*p*)$_2$]$^{\bullet-}$ with an overlap of 0.55 for the two corresponding orbitals

DOI: 10.1021/jacs.7b00484
J. Am. Chem. Soc. 2017, 139, 3876−3888

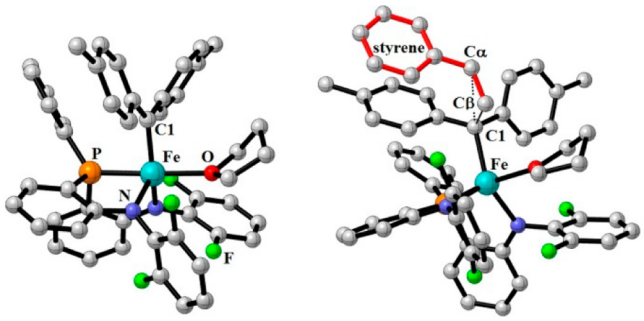


Figure 6. Calculated structures of ($^{dfp}N_2P$)Fe(C(tolyl-*p*)$_2$)(THF) (**S**) (left), and the transition state $\mathbf{TS_{S\text{-}L/S\text{-}T}}$ (right) at their triplet and quintet states, respectively. Selected bond distances (Å) for ^{5}**S**: Fe−C1 2.001, Fe−P 2.410, P−C1 2.928; for ^{3}**S**: Fe−C1 1.935, Fe−P 2.262, P−C1 2.852; for $^5\mathbf{TS_{S\text{-}L}}$: Fe−C1 2.197, Fe−P 2.423, P−C1 3.264, C1−Cβ 2.076, C1−Cα 2.791, Cα−Cβ 1.394; and for $^3\mathbf{TS_{S\text{-}T}}$: Fe−C1 2.053, Fe−P 2.326, P−C1 3.093, C1−Cβ 2.109, C1−Cα 2.918, Cα-Cβ 1.406.

(implying certain π-bonding nature of the Fe−C(alkylidene) interaction), and that **S** at the quintet state could be described as an high-spin iron(II) species bearing an singlet carbene [C(tolyl-*p*)$_2$]^0 ligand. This assignment is also reflected by the spin-density distribution as the iron and the alkylidene carbon atoms in the triplet structure have the corresponding spin density population values of 2.926 and −0.703, whereas the four unpaired spins in the quintet structure locate essentially on the iron center (Table 3). The antiferromagnetic coupling of

Table 3. Selected Structure Parameters of the Calculated Structures ($^{dfp}N_2P$)Fe(C(tolyl-*p*)$_2$)(THF) (S) and the Transition States of the Cyclopropanation Step

	S = 1		*S* = 2	
	^{3}**S**	$^3\mathbf{TS_{S\text{-}T}}$	^{5}**S**	$^5\mathbf{TS_{S\text{-}L}}$
bond order of				
Fe−C1	0.96	0.73	0.80	0.47
spin density[a] on				
Fe	2.926	3.129	3.678	3.593
C1	−0.703	−0.543	0.059	−0.079
Cα		−0.546		0.364
charge[b] on				
Fe	0.465	0.522	0.597	0.612
C1	−0.163	−0.258	−0.174	−0.260
Cα		−0.058		−0.048

[a]Mulliken spin density. [b]Mulliken charge.

iron center with carbene radical in **S** at its triplet state shows reminiscence to that of Chirik's open-shell iron alkylidene species [(PDI)Fe(CPh$_2$)],[7a] Shaik's iron porphyrin carbene [(por)Fe(SMe)(CHCO$_2$Et)]$^-$,[11] Zhang and de Bruin's cobalt porphyrin carbenes [(por)Co(CRCO$_2$Et)],[13] and Groysman's cobalt carbene complex [Co(OCBu$^t_2$Ph)$_2$(CPh$_2$)].[15]

The interaction of the iron alkylidene intermediate **S** with styrene gives rise to the cyclopropanation product. The spin and charge distributions of the transition states ($^3\mathbf{TS_{S\text{-}T}}$ and $^5\mathbf{TS_{S\text{-}L}}$) give explanations to the linear-free-energy correlation of the relative rates of the cyclopropanation of *para*-substituted styrenes by **2** versus the substituent constants (Figure 4). In the transition states, there are high spin density on the α-carbon of the styrene moiety (−0.546 and 0.364 in $^3\mathbf{TS_{S\text{-}T}}$ and $^5\mathbf{TS_{S\text{-}L}}$, respectively), revealing the radical addition character of the C−C bond formation step (Table 3). Moreover, negative charges are discerned on the alkylidene carbon atoms (−0.163, −0.174, −0.258, and −0.260 in ^{3}**S**, ^{5}**S**, $^3\mathbf{TS_{S\text{-}T}}$, and $^5\mathbf{TS_{S\text{-}L}}$, respectively), as well as the α-carbon of the styrene moiety (−0.058 and −0.048 in $^3\mathbf{TS_{S\text{-}T}}$ and $^5\mathbf{TS_{S\text{-}L}}$, respectively). The negative charge distribution on the carbene atom resembles the Schrock carbene species and differs from Fischer carbene species that have positive charge on the carbene carbon,[13g] hinting the "nucleophilic" character of the open-shell iron alkylidene species ^{3}**S** and ^{5}**S**. Thus, while both electron-donating and electron-withdrawing substituents on styrene could stabilize the transition states that have radical character on the α-carbon of the styrene moiety, the "nucleophilic" character of the open-shell iron alkylidene species renders further stabilization on the transition state of the reaction with more electron-deficient alkenes, whereas that of the reactions with the more electron-rich alkenes might be destabilized. Consequently, introduction of electron-withdrawing substituents on styrene could result in larger rate acceleration for the cyclopropanantion reaction by **2**, whereas rate acceleration in the reactions with styrene bearing electron-donating substituents is modest. Noted this, one could reason that the absence of the ring-opening product in the reaction of **2** with the cyclopropyl ethene (entry 4 in Table 1) could suggest a concerted mechanism for the formation of the cyclopropane (^{5}**S** to ^{5}**L via** $^5\mathbf{TS_{S\text{-}L}}$ in Figure 5) or a fast rate of the second C−C bond formation step (^{3}**T** to ^{3}**L via** $^3\mathbf{TS_{T\text{-}L}}$ in Figure 5) exceeding that of the ring-opening of cyclopropylmethyl radical (8.6×10^7 s^{-1} at 298 K).[41] The high activity of the open-shell iron alkylidene species **S** toward electron-deficient alkenes forms a sharp contrast to many of the closed-shell metal carbene species that usually exhibit high activity toward electron-rich alkenes. While whether this is a common reactivity feature of open-shell transition-metal carbene species or not has to wait for more studies, we note that Zhang and de Bruin's cobalt porphyrin carbene radicals [(por)Co(CRCO$_2$Et)] indeed show higher activity toward electron-deficient alkenes,[13] and that U-shaped Hammett plots were observed in the catalytic cyclopropanation reaction of diazo compound with styrenes using (terpyridine)iron(II)/cobalt(II) catalysts.[42] On the other hand, the failure of observing cyclopropanation products in the reactions of Chirik's iron complex [(PDI)Fe(CPh$_2$)][7a] and Groysman's cobalt complex [Co(OCBu$^t_2$Ph)$_2$(CPh$_2$)][15] with alkenes might be due to steric hindrance.

CONCLUSION

We found that the reaction of a high-spin iron(II) complex supported by a tripodal amido-phosphine-amido ligand with the diazo compound (*p*-tolyl)$_2$CN$_2$ affords a high-spin (amido-ylide-amido)iron(II) complex that displays alkylidene-transfer reactivity toward alkenes. The reactions of the iron(II) ylide complex with alkenes furnish cyclopropane derivatives in good to excellent yields. These alkylidene-transfer reactions are atypical for phosphonium ylides, but show similarity to reactions of transition-metal alkylidene complexes. Notably, the cyclopropanation reaction by the ylide complex could be applied to alkenes bearing either electron-donating or electron-withdrawing groups, unlike the common cyclopropanation reactions by electrophilic transition-metal alkylidene complexes, which usually occur only on electron-rich alkenes.

The activation parameters obtained from the kinetic studies on the reaction of the iron ylide complex with 4-fluoro-styrene

DOI: 10.1021/jacs.7b00484
J. Am. Chem. Soc. 2017, 139, 3876−3888

($\Delta H^{\ddagger}$ = 23 ± 1 kcal/mol and $\Delta S^{\ddagger}$ = −20 ± 3 cal/mol/K) are comparable to those of the cyclopropanation reactions catalyzed or mediated by transition-metal alkylidene species. Competition reactions of the cyclopropanation of *para*-substituted styrenes versus styrene, however, revealed a linear plot of $\log(k_X/k_H)$ vs $0.59\sigma_p + 0.55\sigma_c^{\bullet}$, hinting at the "nucleophilic" radical character of the cyclopropanation step. DFT calculation on the reaction of the iron(II) ylide complex with styrene indicated that the conversion of the iron(II) ylide complex to open-shell iron alkylidene intermediate is energetically feasible, and that the cyclopropanation step occurs via an "outer-sphere" radical-type mechanism between the open-shell iron alkylidene intermediates (S = 2 or 1) and styrene, corroborating the experimental observations. These results prove the capability of tripodal ligands in supporting open-shell iron alkylidene species and also point out the potential application of nonheme iron catalyst for new alkylidene-transfer reactions, which might be beyond those based on their closed-shell analogues.

EXPERIMENTAL SECTION

General Procedures. All experiments were performed either under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture using standard Schlenk techniques or in a glovebox. Organic solvents were dried with a solvent purification system (Innovative Technology) and bubbled with dry N_2 gas prior to use. $[Fe(N(TMS)_2)_2]_2$,[43] $(p\text{-tolyl})_2CN_2$,[44] *trans*-1-phenyl-2-vinylcyclopropane,[45] and *cis*-β-deuterio-styrene[46] were synthesized according to literature procedures. All other chemicals were purchased from either Strem or J&K Chemical Co. and used as received unless otherwise noted. ^{1}H, ^{2}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on an Agilent 300, 400, or 600 MHz spectrometers. All chemical shifts were reported in units of ppm with references to the residue of the deuterated solvents for proton and carbon chemical shifts, to external 85% phosphoric acid solution for phosphorus chemical shifts, to CF_3COOH for fluorine chemical shifts, and to $CDCl_3$ for deuterium chemical shifts. Elemental analysis was performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry (CAS). Magnetic moments were measured by the method originally described by Evans with stock and experimental solutions containing a known amount of a $(CH_3)_3SiOSi(CH_3)_3$ standard.[47] Absorption spectra were recorded with a Shimadzu UV-3600 UV−vis−NIR spectrophotometer. IR spectra were recorded with a NICOLET AVATAR 330 FT-IR spectrophotometer.

X-ray Structure Determination. Crystals were coated with Paratone-*N* oil and mounted on a Bruker APEX CCD-based diffractometer equipped with an Oxford low-temperature apparatus. Cell parameters were retrieved with SMART software and refined using SAINT software on all reflections. Data integration was performed with SAINT, which corrects for Lorentz polarization and decay. Absorption corrections were applied using SADABS.[48] Space groups were assigned unambiguously by analysis of symmetry and systematic absences determined by XPREP. All structures were solved and refined using SHELXTL.[49] Metal and first coordination sphere atoms were located from direct-methods E-maps. Non-hydrogen atoms were found in alternating difference Fourier synthesis and least-squares refinement cycles and during final cycles were refined anisotropically. Table S1 summarizes the crystal data and data collection and refinement for the complexes.

^{57}Fe Mössbauer Spectroscopy. All solid samples for ^{57}Fe Mössbauer spectroscopy were run on nonenriched samples of the as-isolated complexes. Each sample was loaded into a Delrin Mössbauer sample cup for measurements and loaded under liquid nitrogen. Low temperature ^{57}Fe Mössbauer measurements were performed using a See Co. MS4 Mössbauer spectrometer integrated with a Janis SVT-400T He/N_2 cryostat for measurements at 80 K. Isomer shifts were determined relative to α-Fe at 298 K. All Mössbauer spectra were fitted using the program WMoss (SeeCo).

Preparation of (2,6-$F_2C_6H_3$)(2-BrC_6H_4)NH. To an oven-dried Schlenk tube was added $Pd_2(dba)_3$ (2.20 g, 2.40 mmol, 6 mol%) and *rac*-BINAP (2.99 g, 4.80 mmol, 12 mol%). The tube was capped with a Teflon screw cap, evacuated, and backfilled with dinitrogen. After the Teflon screw cap was replaced with a rubber septum, toluene (50 mL) was added via syringe under dinitrogen atmosphere. The suspension was heated at 60 °C with stirring for 30 min. After cooling to room temperature, 2,6-F_2-$C_6H_3NH_2$ (5.40 g, 41.8 mmol, 1.1 equiv), 2-Br-C_6H_4I (11.02 g, 39.0 mmol, 1 equiv), and Bu^{t}ONa (4.61 g, 48.0 mmol, 1.2 equiv) were added under dinitrogen atmosphere. The reaction mixture was heated at 110 °C with stirring for 48 h. After filtration and removal of volatiles, the crude product was purified by flash column chromatography (silica gel, *n*-hexane as elute) to give (2,6-$F_2C_6H_3$)(2-BrC_6H_4)NH as a colorless oil (9.81 g, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 295 K): δ (ppm) 7.58−7.48 (m, 1H), 7.22−7.07 (m, 2H), 7.06−6.94 (m, 2H), 6.82−6.72 (m, 1H), 6.70−6.59 (m, 1H), 5.84 (br, 1H, N*H*). ^{13}C NMR (101 MHz, $CDCl_3$, 295 K): δ (ppm) 157.40 (dd, J_{C-F} = 248.6, 5.2 Hz), 141.20 (s), 132.64 (s), 128.21 (s), 124.93 (t, J_{C-F} = 9.6 Hz), 121.09 (s), 118.26 (t, J_{C-F} = 15.5 Hz), 114.56 (t, J_{C-F} = 2.2 Hz), 112.14 (dd, J_{C-F} = 17.9, 5.6 Hz), 111.29 (s). ^{19}F NMR (376 MHz, $CDCl_3$, 295 K): δ (ppm) −119.20 (s). IR (thin film, cm^{-1}): ν = 3393 (w), 3068 (w), 1587 (m), 1509 (s), 1471 (s), 1422 (m), 1312 (m), 1236 (m), 1024 (m), 1000 (s), 887 (w), 774 (m), 738 (s), 699 (m), 665 (w). HRMS (EI) calcd for $C_{12}H_8BrF_2N$ (M^+): 282.9808. Found: 282.9809.

Preparation of H_2(^{dfp}N_2P). To an Et_2O (20 mL) solution of (2,6-$F_2C_6H_3$)(2-BrC_6H_4)NH (4.54 g, 16.0 mmol, 1 equiv) was added Bu^{n}Li (1.6 M in *n*-hexane, 20 mL, 32 mmol, 2 equiv) slowly at −78 °C. The resulting mixture was allowed to warm to room temperature and further stirred for 5 h. To this solution, an Et_2O solution (10 mL) of $PhPCl_2$ (1.42 g, 7.90 mmol, 0.5 equiv) was added at −78 °C. The resulting mixture was allowed to warm to room temperature and further stirred for 24 h. The mixture was then quenched with a saturated aqueous solution of $NaHCO_3$, and extracted with CH_2Cl_2 (30 mL × 3). The combined organic phases were washed with a saturated $NaHCO_3$ aqueous solution and brine, and dried over Na_2SO_4. After filtration and removal of volatiles, the crude product was purified by flash column chromatography (silica gel, 8:1 *n*-hexanes/CH_2Cl_2 as elute) to give H_2(^{dfp}N_2P) as a white solid (2.87 g, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 295 K): δ (ppm) 7.54−7.45 (m, 2H), 7.45−7.40 (m, 3H), 7.32−7.26 (m, 2H), 7.05−6.95 (m, 4H), 6.95−6.86 (m, 6H), 6.78−6.70 (m, 2H), 6.06 (d, J = 3.7 Hz, 2H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$, 302 K): δ (ppm) 156.75 (dd, J_{C-F} = 247.9, 5.6 Hz), 146.80 (d, J_{C-P} = 17.4 Hz), 134.12 (d, J_{C-P} = 3.2 Hz), 133.85 (d, J_{C-P} = 18.8 Hz), 132.99 (d, J_{C-P} = 4.1 Hz), 130.42 (s), 129.43 (s), 129.03 (d, J_{C-P} = 7.3 Hz), 123.36 (t, J_{C-F} = 9.5 Hz), 121.37 (d, J_{C-P} = 2.4 Hz), 121.00 (d, J_{C-P} = 6.2 Hz), 119.36 (t, J_{C-F} = 14.7 Hz), 114.92 (d, J_{C-P} = 1.7 Hz), 111.89 (dd, J_{C-F} = 16.5, 6.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, 295 K): δ (ppm) −120.08 (s). ^{31}P NMR (162 MHz, $CDCl_3$, 295 K): δ (ppm) −30.56 (s). IR (thin film, cm^{-1}): ν = 3353 (w), 3066 (w), 2923 (w), 2853 (w), 1586 (m), 1569 (m), 1496 (s), 1469 (s), 1442 (m), 1300 (m), 1237 (m), 1159 (w), 1000 (s), 931 (w), 878 (w), 778 (s), 743 (s), 697 (s). HRMS (EI) calcd for $C_{30}H_{20}F_4N_2P$ [$(M-H)^+$]: 515.1300. Found: 515.1303.

Preparation of [(κ-*N,N,P*-^{dfp}N_2P)Fe(THF)$_2$] (1). To a THF (10 mL) solution of H_2(^{dfp}N_2P) (266 mg, 0.51 mmol) was added $[Fe(N(TMS)_2)_2]_2$ (195 mg, 0.26 mmol). The resulting mixture was stirred at room temperature for 2 h to afford a yellow suspension. After removal of the solvent under vacuum, the yellow oily residue was washed by *n*-hexane (5 mL) and Et_2O (5 mL) to produce **1** as a yellow solid (259 mg, 71%). Single crystals of **1** suitable for X-ray diffraction study were obtained by standing its saturated THF solution at room temperature for 2 days. ^{1}H NMR (400 MHz, C_6D_6, 295 K): δ (ppm) 43.92 (br), 36.53 (br), 34.43 (br), 31.48 (br), 16.45 (br), 12.36 (br), 3.81 (br), 2.18 (br), 1.09 (br), −2.90 (br), −27.95 (br), −40.49 (br), −49.39 (br). Magnetic susceptibility (C_6D_6, 302 K): μ_{eff} = 4.4(1) μ_B. Absorption spectrum (THF): λ_{max}, nm (ε, M^{-1} cm^{-1}) = 279 (29600), 934 (70). IR (KBr, cm^{-1}): ν = 3049 (w), 2974 (w), 2876 (w), 1583

DOI: 10.1021/jacs.7b00484
J. Am. Chem. Soc. 2017, 139, 3876−3888

(m), 1463 (s), 1433 (m), 1303 (m), 1288 (m), 1233 (m), 1164 (w), 1039 (m), 997 (s), 867 (w), 778 (m), 743 (m), 727 (w), 694 (w). Anal. Calcd for $C_{38}H_{35}F_4FeN_2O_2P$: C 63.88, H 4.94, N 3.92; Found: C 63.34, H 5.08, N 3.74.

Preparation of [(*κ*-*N*,*N*,*C*-^{dfp}N$_2$PC(tolyl-*p*)$_2$)Fe(THF)] (2). To a yellow suspension of **1** (735 mg, 1.0 mmol) in THF (20 mL) was added (*p*-tolyl)$_2$CN$_2$ (234 mg, 1.0 mmol). The color of the suspension changed from yellow to dark brown immediately. The reaction mixture was stirred at room temperature for 12 h, during which time the brown suspension turned into a dark yellow solution. After removal of the solvent under vacuum, the yellow oily residue was washed by *n*-hexane (10 mL) and Et_2O (5 mL) to produce **2** as a yellow solid (695 mg, 81% yield). Single crystals of **2** suitable for X-ray crystallography were obtained by vapor diffusion of *n*-hexane into a benzene solution of **2**. ^{1}H NMR (400 MHz, C_6D_6, 292 K): δ (ppm) 45.26 (br), 31.42 (br), 26.27 (br), 25.85 (br), 25.23 (br), 14.85 (br), 9.74 (br), 8.50 (br), 2.24 (br), −17.64 (br), −19.20 (br), −32.58 (br), −35.86 (br). Magnetic susceptibility (C_6D_6, 292 K): μ_{eff} = 4.7(1) μ_B. Absorption spectrum (THF): λ_{max}, nm (ε, M^{-1} cm^{-1}) = 308 (21300), 1328 (180), 1462 (160). IR (KBr, cm^{-1}): ν = 2970 (w), 2916 (w), 2868 (w), 1583 (m), 1504 (m), 1468 (s), 1432 (s), 1330 (m), 1283 (m), 1236 (w), 1206 (w), 1022 (w), 999 (m), 866 (w), 816 (w), 781 (m), 747 (m), 697 (w). Anal. Calcd for $C_{49}H_{41}F_4FeN_2OP$: C 70.34, H 4.94, N 3.35; Found: C 69.75, H 4.94, N 3.00.

Reaction of 2 with Ethylene. A red solution of **2** (129 mg, 0.15 mmol) in toluene (5 mL) was frozed with liquid N_2, and then ethylene gas (1 atm) was quickly introduced. The mixture was allowed to warm to room temperature and stirred for 30 min, giving a red solution. The reaction mixture was then quenched with wet silica gel. Flash column chromatography separation (silica gel, *n*-hexane as elute) gave 1,1-di-*p*-tolylcyclopropane (**3a**) as a colorless oil (26 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 292 K): δ (ppm) 7.16 (d, J = 8.1 Hz, 4H), 7.11 (d, J = 8.0 Hz, 4H), 2.34 (s, 6H), 1.29 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$, 292 K): δ (ppm) 143.12, 135.51, 129.05, 128.38, 29.26, 21.11, 16.40. IR (thin film, cm^{-1}): ν = 3004 (w), 2920 (w), 1513 (m), 1452 (w), 1115 (w), 1019 (m), 923 (w), 809 (s), 723 (m). HRMS (EI) calcd for $C_{17}H_{18}$ (M$^+$): 222.1409. Found: 222.1412.

Reaction of 2 with 1-Octene. To a toluene (5 mL) solution of **2** (136 mg, 0.16 mmol) was added 1-octene (55 mg, 0.49 mmol). The resulting mixture was stirred at 80 °C for 6 h, providing a red solution. The reaction was then quenched with wet silica gel. Flash column chromatography separation (silica gel, *n*-hexane as elute) gave the cyclopropanation product 2-(*n*-hexyl)-1,1-di(*p*-tolyl)cyclopropane (**3b**) as a colorless oil (33 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 292 K): δ (ppm) 7.22 (d, J = 7.8 Hz, 2H), 7.14−7.07 (m, 4H), 7.04 (d, J = 8.1 Hz, 2H), 2.34 (s, 3H), 2.29 (s, 3H), 1.61−1.51 (m, 1H), 1.50−1.37 (m, 3H), 1.31−1.17 (m, 7H), 1.14 (t, J = 5.2 Hz, 1H), 0.88 (t, J = 6.8 Hz, 3H), 0.82−0.73 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, 292 K): δ (ppm) 145.15, 139.31, 135.62, 135.04, 130.51, 128.93, 127.68, 34.57, 32.01, 31.07, 29.65, 29.33, 26.58, 22.77, 21.22, 21.03, 20.86, 14.24. IR (thin film, cm^{-1}): ν = 2922 (s), 2854 (m), 1513 (s), 1451 (m), 1020 (w), 810 (s), 760 (w), 725 (m). HRMS (EI) calcd for $C_{23}H_{30}$ (M$^+$): 306.2348. Found: 306.2346.

Reaction of 2 with Hepta-1,6-diene. To a toluene (5 mL) solution of **2** (128 mg, 0.15 mmol) was added hepta-1,6-diene (43 mg, 0.60 mmol). The resulting mixture was stirred at 80 °C for 6 h, providing a red solution. The reaction was then quenched with wet silica gel. Flash column chromatography separation (silica gel, *n*-hexane as elute) gave the cyclopropanation product 2-(4′-pentenyl)-1,1-di(*p*-tolyl)cyclopropane (**3c**) as a colorless oil (33 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 292 K): δ (ppm) 7.24 (d, J = 8.0 Hz, 2H), 7.12 (dd, J = 7.8, 5.8 Hz, 4H), 7.07 (d, J = 6.0 Hz, 2H), 5.81 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.05−4.91 (m, 2H), 2.36 (s, 3H), 2.31 (s, 3H), 2.10−2.02 (m, 2H), 1.64−1.46 (m, 4H), 1.25−1.20 (m, 1H), 1.19−1.15 (m, 1H), 0.88−0.78 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, 292 K): δ (ppm) 144.87, 139.05, 139.00, 135.51, 134.94, 130.31, 128.80, 128.76, 127.53, 114.15, 34.47, 33.57, 30.36, 28.83, 26.15, 21.05, 20.87, 20.62. IR (thin film, cm^{-1}): ν = 2996 (w), 2922 (m), 2855 (w), 1640 (w), 1513 (s), 1447 (m), 1113 (w), 1021 (w), 992 (w), 908 (m), 808 (s), 761 (w), 727 (m). HRMS (EI) calcd for $C_{22}H_{26}$ (M$^+$): 290.2035. Found: 290.2029.

Reaction of 2 with (2-Vinylcyclopropyl)benzene. To a toluene (5 mL) solution of **2** (129 mg, 0.15 mmol) was added 1-phenyl-2-vinylcyclopropane (46 mg, 0.32 mmol). The resulting mixture was stirred at 80 °C for 12 h, providing a red solution. The reaction was then quenched with wet silica gel. Flash column chromatography separation (silica gel, *n*-hexane as elute) gave 2-(2′-phenylcyclopropyl)-1,1-di(*p*-tolyl)cyclopropane (**3d**) as a colorless oil (36 mg, 70% yield). The NMR data indicate the presence of both diastereoisomers of 2-(2′-phenylcyclopropyl)-1,1-di(*p*-tolyl)cyclopropane with the ratio of 1:1.6 (denoted as *A* and *B*). Attempts to assign the identity of the isomers on the basis of the NMR data were unsuccessful. ^{1}H NMR (400 MHz, $CDCl_3$, 292 K): δ (ppm) 7.34−7.30 (m, 2H, H_A), 7.29−7.25 (m, 2H, H_B), 7.25−7.20 (m, 2H, H_B), 7.18−7.12 (m, 3H, H_A; 1H, H_B), 7.11−7.04 (m, 6H, H_A; 4H, H_B), 7.00−6.96 (m, 2H, H_B), 6.96−6.92 (m, 2H, H_B), 6.79−6.75 (m, 2H, H_A), 2.34 (s, 3H, H_A), 2.31 (s, 3H, H_A; 3H, H_B), 2.29 (s, 3H, H_B), 1.91−1.85 (m, 1H, H_B), 1.76−1.68 (m, 1H, H_A), 1.57−1.50 (m, 1H, H_B), 1.49−1.42 (m, 1H, H_A), 1.36−1.27 (m, 3H, H_A; 1H, H_B), 1.05−0.98 (m, 2H, H_B), 0.96−0.90 (m, 1H, H_A), 0.84−0.72 (m, 2H, H_B), 0.68−0.60 (m, 1H, H_A). ^{13}C NMR (101 MHz, $CDCl_3$, 292 K): δ (ppm) 144.66, 144.60, 143.34, 143.07, 139.14, 139.07, 135.80, 135.70, 135.15, 130.80, 130.75, 129.10, 128.99, 128.91, 128.18, 127.99, 127.19, 127.16, 125.96, 125.76, 125.28, 125.26, 34.77, 34.75, 30.42, 30.25, 24.33, 23.98, 23.63, 22.98, 21.22, 21.18, 21.02, 20.05, 19.75, 15.73. IR (thin film, cm^{-1}): ν = 3023 (w), 2998 (w), 2920 (w), 1512 (m), 1447 (w), 1264 (w), 1113 (w), 1030 (w), 907 (w), 814 (m), 733 (s), 696 (s). HRMS (EI) calcd for $C_{26}H_{26}$ (M$^+$): 338.2035. Found: 338.2032.

Reaction of 2 with Styrene. To a toluene (5 mL) solution of **2** (117 mg, 0.14 mmol) was added styrene (44 mg, 0.42 mmol). The resulting mixture was stirred at 80 °C for 14 h, providing a red solution. The reaction was then quenched with wet silica gel. Flash column chromatography separation (silica gel, *n*-hexane as elute) gave the cyclopropanation product 2-phenyl-1,1-di(*p*-tolyl)cyclopropane (**3e**) as a white solid (34 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 292 K): δ (ppm) 7.20 (d, J = 8.1 Hz, 2H), 7.15−7.04 (m, 5H), 6.99 (d, J = 8.1 Hz, 2H), 6.91 (dd, J = 14.4, 7.4 Hz, 4H), 2.82 (dd, J = 8.8, 6.7 Hz, 1H), 2.32 (s, 3H), 2.24 (s, 3H), 1.96−1.90 (m, 1H), 1.78 (dd, J = 8.9, 5.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, 292 K): δ (ppm) 144.54, 139.12, 137.47, 135.71, 135.51, 131.01, 129.13, 128.76, 128.08, 127.73, 127.38, 125.57, 38.81, 32.45, 21.19, 21.06, 21.03. IR (thin film, cm^{-1}): ν = 3021 (w), 2917 (w), 1512 (m), 1451 (m), 1112 (w), 1077 (w), 1019 (w), 966 (w), 812 (s), 779 (m), 738 (m), 693 (s). HRMS (EI) calcd for $C_{23}H_{22}$ (M$^+$): 298.1722. Found: 298.1719.

Reaction of 2 with 4-Methylstyrene. To a toluene (5 mL) solution of **2** (50 mg, 0.06 mmol) was added 4-methylstyrene (21 mg, 0.18 mmol). The resulting mixture was stirred at 80 °C for 14 h, providing a red solution. The reaction was then quenched with wet silica gel. Flash column chromatography separation (silica gel, *n*-hexane as elute) gave the cyclopropanation product 1,1,2-tri(*p*-tolyl)cyclopropane (**3f**) as a white solid (11 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 294 K): δ (ppm) 7.16 (d, J = 8.2 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 6.97 (d, J = 8.1 Hz, 2H), 6.94−6.86 (m, 4H), 6.75 (d, J = 8.1 Hz, 2H), 2.74 (dd, J = 9.0, 6.6 Hz, 1H), 2.29 (s, 3H), 2.23 (s, 3H), 2.22 (s, 3H), 1.89−1.83 (m, 1H), 1.73 (dd, J = 9.0, 5.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, 294 K): δ (ppm) 144.69, 137.62, 136.00, 135.61, 135.41, 134.94, 131.04, 129.10, 128.77, 128.48, 127.94, 127.37, 38.54, 32.23, 21.21, 21.15, 21.12, 21.05. IR (thin film, cm^{-1}): ν = 3020 (w), 2919 (w), 2864 (w), 1513 (s), 1448 (m), 1261 (w), 1110 (w), 1040 (w), 1019 (m), 814 (s), 762 (w), 728 (m), 621 (w), 597 (w), 550 (s), 510 (m), 425 (w). HRMS (EI) calcd for $C_{24}H_{24}$ (M$^+$): 312.1878. Found: 312.1884.

Reaction of 2 with 4-Methoxystyrene. To a toluene (5 mL) solution of **2** (125 mg, 0.15 mmol) was added 4-methoxystyrene (60 mg, 0.45 mmol). The resulting mixture was stirred at 80 °C for 10 h, providing a red solution. The reaction was the quenched with wet silica gel. Flash column chromatography separation (silica gel, *n*-hexane/ethyl acetate (15:1) as elute) gave the cyclopropanation product 2-(*p*-methoxyphenyl)-1,1-di(*p*-tolyl)cyclopropane (**3g**) as a

DOI: 10.1021/jacs.7b00484
J. Am. Chem. Soc. 2017, 139, 3876−3888

colorless oil (28 mg, 57% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 294 K): δ (ppm) 7.16 (d, J = 8.2 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 6.97 (d, J = 8.1 Hz, 2H), 6.92 (d, J = 8.0 Hz, 2H), 6.80 (d, J = 8.6 Hz, 2H), 6.65 (d, J = 8.7 Hz, 2H), 3.73 (s, 3H), 2.74 (dd, J = 9.0, 6.7 Hz, 1H), 2.30 (s, 3H), 2.23 (s, 3H), 1.89−1.81 (m, 1H), 1.73 (dd, J = 9.0, 5.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, 294 K): δ (ppm) 157.61, 144.63, 137.63, 135.60, 135.40, 131.15, 131.04, 129.10, 129.01, 128.77, 127.36, 113.23, 55.26, 38.24, 31.84, 21.19, 21.05, 21.01. IR (thin film, cm^{-1}): ν = 3021 (w), 2917 (w), 1512 (m), 1451 (m), 1112 (w), 1077 (w), 1019 (w), 966 (w), 812 (s), 779 (m), 738 (m), 693 (s). HRMS (EI) calcd for $C_{24}H_{24}O$ (M^+): 328.1827. Found: 328.1830.

Reaction of 2 with 4-*tert*-Butylstyrene. To a toluene (5 mL) solution of **2** (54 mg, 0.07 mmol) was added 4-*tert*-butylstyrene (31 mg, 0.19 mmol). The resulting mixture was stirred at 80 °C for 11 h, providing a red solution. The reaction was then quenched with wet silica gel. Flash column chromatography separation (silica gel, *n*-hexane as elute) gave the cyclopropanation product 2-(*p*-*tert*-butylphenyl)-1,1-di(*p*-tolyl)cyclopropane (**3h**) as a white solid (17 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 294 K): δ (ppm) 7.17 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 7.9 Hz, 2H), 6.98 (d, J = 7.8 Hz, 2H), 6.91 (d, J = 7.7 Hz, 2H), 6.78 (d, J = 8.1 Hz, 2H), 2.81−2.65 (m, 1H), 2.29 (s, 3H), 2.23 (s, 3H), 1.82−1.87 (m, 1H), 1.76 (dd, J = 8.9, 5.2 Hz, 1H), 1.24 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$, 294 K): δ (ppm) 148.33, 144.73, 137.67, 136.11, 135.61, 135.39, 131.11, 129.11, 128.73, 127.68, 127.35, 124.62, 38.58, 34.39, 32.22, 31.48, 21.43, 21.22, 21.06. IR (thin film, cm^{-1}): ν = 2963 (w), 2921 (w), 2867 (w), 1512 (m), 1450 (w), 1266 (w), 1108 (w), 1036 (w), 1019 (w), 940 (w), 848 (w), 828 (m), 805 (m), 765 (w), 728 (w), 625 (w), 552 (s), 536 (m). HRMS (EI) calcd for $C_{27}H_{30}$ (M^+): 354.2348. Found: 354.2347.

Reaction of 2 with *N*,*N*-Dimethyl-4-vinylaniline. To a toluene (5 mL) solution of **2** (108 mg, 0.13 mmol) was added *N*,*N*-dimethyl-4-vinylaniline (57 mg, 0.39 mmol). The resulting mixture was stirred at 80 °C for 9 h, providing a red solution. The reaction was then quenched with wet silica gel. Flash column chromatography separation (silica gel, *n*-hexane/ethyl acetate (15:1) as elute) gave the cyclopropanation product 2-(*N*,*N*-dimethyl-*p*-aminophenyl)-1,1-di(*p*-tolyl)cyclopropane (**3i**) as a white solid (17 mg, 39% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 294 K): δ (ppm) 7.15 (d, J = 8.2 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 6.98 (d, J = 7.8 Hz, 2H), 6.92 (d, J = 8.1 Hz, 2H), 6.74 (d, J = 8.3 Hz, 2H), 6.52 (d, J = 8.2 Hz, 2H), 2.85 (s, 6H), 2.69 (dd, J = 8.6, 5.6 Hz, 1H), 2.29 (s, 3H), 2.22 (s, 3H), 1.75−1.84 (m, 1H), 1.70 (dd, J = 8.7, 5.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, 294 K): δ (ppm) 148.82, 144.94, 137.94, 135.43, 135.22, 131.15, 129.05, 128.73, 127.33, 127.25, 112.52, 40.94, 38.00, 32.08, 21.22, 21.09, 21.05. IR (thin film, cm^{-1}): ν = 2963 (w), 1413 (w), 1259 (s), 1085 (s), 1016 (s), 865 (w), 796 (s), 701 (w). HRMS (EI) calcd for $C_{25}H_{27}N$ (M^+): 341.2143. Found: 341.2146.

Reaction of 2 with 4-Fluorostyrene. To a toluene (5 mL) solution of **2** (52 mg, 0.06 mmol) was added 4-fluorostyrene (23 mg, 0.18 mmol). The resulting mixture was stirred at 80 °C for 10 h, providing a red solution. The reaction was then quenched with wet silica gel. Flash column chromatography separation (silica gel, *n*-hexane as elute) gave the cyclopropanation product 2-(*p*-fluorophenyl)-1,1-di(*p*-tolyl)cyclopropane (**3j**) as a colorless oil (15 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 294 K): δ (ppm) 7.21−7.14 (m, 2H), 7.08 (d, J = 8.0 Hz, 2H), 6.99−6.89 (m, 4H), 6.86−6.75 (m, 4H), 2.78 (dd, J = 9.0, 6.5 Hz, 1H), 2.31 (s, 3H), 2.23 (s, 3H), 1.85−1.90 (m, 1H), 1.75 (dd, J = 9.0, 5.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, 294 K): δ (ppm) 161.17 (d, J_{C-F} = 243.4 Hz), 144.28 (s), 137.26 (s), 135.84 (s), 135.60 (s), 134.75 (d, J_{C-F} = 3.0 Hz), 130.96 (s), 129.35 (d, J_{C-F} = 7.8 Hz), 129.16 (s), 128.84 (s), 127.37 (s), 114.56 (d, J_{C-F} = 21.2 Hz), 38.56 (s), 31.62 (s), 21.17 (s), 21.05 (s). ^{19}F NMR (376 MHz, $CDCl_3$, 294 K) δ (ppm) −117.86 (s). IR (thin film, cm^{-1}): ν = 3021 (w), 2921 (w), 2867 (w), 1605 (w), 1510 (s), 1448 (w), 1234 (m), 1159 (m), 1017 (w), 832 (m), 806 (m), 763 (w), 730 (m), 560 (w), 550 (m), 514 (w), 478 (w). HRMS (EI) calcd for $C_{23}H_{21}F$ (M^+): 316.1627. Found: 316.1625.

Reaction of 2 with 4-Chlorostyrene. To a toluene (5 mL) solution of **2** (50 mg, 0.06 mmol) was added 4-chlorostyrene (25 mg, 0.18 mmol). The resulting mixture was stirred at 80 °C for 8 h, providing a red solution. The reaction was then quenched with wet silica gel. Flash column chromatography separation (silica gel, *n*-hexane as elute) gave the cyclopropanation product 2-(*p*-chlorophenyl)-1,1-di(*p*-tolyl)cyclopropane (**3k**) as a colorless oil (13 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 294 K): δ (ppm) 7.16 (d, J = 8.1 Hz, 2H), 7.11−7.03 (m, 4H), 7.01−6.89 (m, 4H), 6.79 (d, J = 8.4 Hz, 2H), 2.76 (dd, J = 8.8, 6.6 Hz, 1H), 2.30 (s, 3H), 2.24 (s, 3H), 1.96−1.82 (m, 1H), 1.78 (dd, J = 8.9, 5.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, 294 K): δ (ppm) 144.16, 137.79, 137.05, 135.96, 135.66, 131.24, 130.95, 129.29, 129.17, 128.94, 127.84, 127.31, 38.97, 31.80, 21.27, 21.20, 21.06. IR (thin film, cm^{-1}): ν = 3022 (w), 2920 (w), 1513 (m), 1494 (s), 1449 (w), 1093 (s), 1040 (w), 1014 (m), 828 (m), 814 (m), 550 (w), 535 (m), 511 (w). HRMS (EI) calcd for $C_{23}H_{21}Cl$ (M^+): 332.1332. Found: 332.1334.

Reaction of 2 with 4-(Trifluoromethyl)styrene. To a toluene (5 mL) solution of **2** (170 mg, 0.20 mmol) was added 4-(trifluoromethyl)styrene (105 mg, 0.60 mmol). The resulting mixture was stirred at 80 °C for 4 h, providing a red solution. The reaction was then quenched with wet silica gel. Flash column chromatography separation (silica gel, *n*-hexane as elute) gave the cyclopropanation product 2-(*p*-trifluoromethylphenyl)-1,1-di(*p*-tolyl)cyclopropane (**3l**) as a colorless oil (49 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 294 K): δ (ppm) 7.35 (d, J = 8.1 Hz, 2H), 7.18 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 7.03−6.88 (m, 6H), 2.83 (dd, J = 8.6, 6.7 Hz, 1H), 2.31 (s, 3H), 2.25 (s, 3H), 1.92−1.99 (m, 1H), 1.85 (dd, J = 8.8, 5.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, 294 K): δ (ppm) 143.97 (s), 143.66 (s), 136.79 (s), 136.18 (s), 135.83 (s), 130.94 (s), 129.23 (s), 129.03 (s), 128.14 (s), 127.68 (q, J_{C-F} = 32.2 Hz), 127.29 (s), 124.61 (q, J_{C-F} = 3.8 Hz), 124.53 (q, J_{C-F} = 271.7 Hz), 39.68 (s), 32.18 (s), 21.70 (s), 21.19 (s), 21.06 (s). ^{19}F NMR (376 MHz, $CDCl_3$, 294 K) δ (ppm) −62.17 (s). IR (thin film, cm^{-1}): ν = 3023 (w), 2923 (w), 2867 (w), 1618 (w), 1513 (m), 1324 (m), 1191 (m), 1163 (s), 1120 (m), 1108 (m), 729 (w), 648 (w), 628 (w), 600 (w), 550 (w) HRMS (EI) calcd for $C_{24}H_{21}F_3$ (M^+): 366.1595. Found: 366.1597.

Reaction of 2 with Norbornene. To a toluene (5 mL) solution of **2** (170 mg, 0.20 mmol) was added norbornene (56 mg, 0.60 mmol). The resulting mixture was stirred at 80 °C for 0.5 h, providing a red solution. The reaction was then quenched with wet silica gel. Flash column chromatography separation (silica gel, *n*-hexane as elute) gave the cyclopropanation product 3,3-di-*p*-tolyltricyclo[3.2.1.0^{2,4}]-octane (**3m**) as a white solid (48 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 292 K): δ (ppm) 7.24 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.2 Hz, 2H), 7.10 (d, J = 7.8 Hz, 2H), 7.01 (d, J = 8.0 Hz, 2H), 2.52 (s, 2H), 2.32 (s, 3H), 2.26 (s, 3H), 1.52−1.47 (m, 2H), 1.46 (s, 2H), 1.36−1.31 (m, 2H), 0.63−0.56 (m, 1H), 0.47−0.41 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, 292 K): δ (ppm) 145.83, 140.03, 135.33, 135.06, 129.67, 129.06, 128.99, 127.85, 36.71, 36.00, 31.87, 31.40, 30.37, 21.26, 20.98. IR (thin film, cm^{-1}): ν = 3005 (w), 2953 (s), 2923 (s), 2863 (m), 1507 (m), 1453 (w), 1109 (w), 1021 (w), 855 (m), 819 (s), 802 (s), 776 (m), 758 (m), 726 (m). HRMS (EI) calcd for $C_{22}H_{24}$ (M^+): 288.1878. Found: 288.1882.

Reaction of 2 with 1-Phenylbuta-1,3-diene. To a toluene (5 mL) solution of **2** (170 mg, 0.20 mmol) was added 1-phenylbuta-1,3-diene (78 mg, 0.60 mmol). The resulting mixture was stirred at 80 °C for 3 h, providing a red solution. The reaction was then quenched with wet silica gel. Flash column chromatography separation (silica gel, *n*-hexane as elute) gave the cyclopropanation product 2-(phenylvinyl)-1,1-di(*p*-tolyl)cyclopropane (**3n**) as a white solid (63 mg, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 292 K): δ (ppm) 7.31 (d, J = 7.9 Hz, 2H), 7.26 (d, J = 7.3 Hz, 2H), 7.24−7.17 (m, 3H), 7.17−7.12 (m, 4H), 7.10 (d, J = 8.0 Hz, 2H), 6.60 (d, J = 15.8 Hz, 1H), 5.54 (dd, J = 15.8, 9.7 Hz, 1H), 2.44−2.38 (m, 1H), 2.37 (s, 3H), 2.33 (s, 3H), 1.74 (dd, J = 8.6, 4.9 Hz, 1H), 1.61−1.54 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, 292 K): δ (ppm) 143.94, 138.67, 137.87, 136.16, 135.48, 132.11, 130.85, 129.18, 129.11, 129.01, 128.54, 127.13, 126.73, 125.88, 37.09, 31.20, 22.96, 21.27, 21.04. IR (thin film, cm^{-1}): ν = 3022 (w), 2919 (w), 1643 (w), 1512 (m), 1446 (m), 1118 (w), 1022 (w), 957 (s), 807 (m), 744 (s), 692 (s). HRMS (EI) calcd for $C_{25}H_{24}$ (M^+): 324.1878. Found: 324.1873.

DOI: 10.1021/jacs.7b00484
J. Am. Chem. Soc. 2017, 139, 3876−3888

Reaction of 2 with Ethyl Acrylate. To a toluene (5 mL) solution of **2** (121 mg, 0.15 mmol) was added ethyl acrylate (43 mg, 0.43 mmol). The resulting mixture was stirred at 80 °C for 7 h, providing a red solution. The reaction was then quenched with wet silica gel. Flash column chromatography separation (silica gel, *n*-hexane/CH_2Cl_2 (3:1) as elute) gave the cyclopropanation product ethyl 2,2-di(*p*-tolyl)-cyclopropylcarboxylate (**3o**) as a colorless oil (26 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 294 K): δ (ppm) 7.22 (d, J = 7.5 Hz, 2H), 7.15 (d, J = 7.6 Hz, 2H), 7.07 (s, 4H), 4.02−3.86 (m, 2H), 2.46−2.55 (m, 1H), 2.29 (s, 6H), 2.08−2.71 (m, 1H), 1.55 (dd, J = 7.2, 5.1 Hz, 1H), 1.06 (t, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 294 K): δ (ppm) 170.99, 142.36, 137.53, 136.49, 136.19, 129.62, 129.21, 129.12, 127.53, 60.55, 39.44, 29.07, 21.27, 21.05, 20.31, 14.23. IR (thin film, cm^{-1}): ν = 2922 (w), 1732 (s), 1514 (m), 1444 (w), 1396 (w), 1379 (m), 1261 (s), 1174 (s), 1090 (s), 1018 (s), 852 (w), 807 (s), 726 (w), 668 (w), 661 (w), 550 (m), 481 (w). HRMS (EI) calcd for $C_{20}H_{22}O_2$ (M^+): 294.1620. Found: 294.1617.

Reaction of 2 with Acrylonitrile. To a toluene (5 mL) solution of **2** (213 mg, 0.25 mmol) was added acrylonitrile (41 mg, 0.76 mmol). The resulting mixture was stirred at 80 °C for 9 h, providing a red solution. The reaction was then quenched with wet silica gel. Flash column chromatography separation (silica gel, *n*-hexane/CH_2Cl_2 (3:1) as elute) gave the cyclopropanation product ethyl 2,2-di(*p*-tolyl)-cyclopropanecarbonitrile (**3p**) as a yellow oil (10 mg, 16% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 294 K): δ (ppm) 7.34 (d, J = 8.0 Hz, 2H), 7.22−7.14 (m, 4H), 7.11 (d, J = 8.0 Hz, 2H), 2.34 (s, 3H), 2.32 (s, 3H), 2.19 (dd, J = 9.1, 5.7 Hz, 1H), 1.96−2.04 (m, 1H), 1.76 (dd, J = 9.1, 5.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, 294 K): δ (ppm) 139.70, 137.61, 137.15, 136.26, 129.61, 129.49, 129.22, 127.68, 119.84, 37.78, 21.23, 21.15, 21.07, 12.26. IR (thin film, cm^{-1}): ν = 3025 (w), 2921 (w), 2237 (m), 1514 (s), 1444 (m), 1311 (w), 1260 (w), 1182 (w), 1112 (w), 1019 (m), 910 (w), 819 (s), 764 (m), 727 (s), 629 (w), 547 (s), 520 (w). HRMS (EI) calcd for $C_{18}H_{17}N$ (M^+): 247.1361. Found: 247.1364.

Reaction of 2 with *cis*-β-Deuterio-styrene. To a toluene (5 mL) solution of **2** (150 mg, 0.18 mmol) was added *cis*-β-deuterio-styrene (54 mg, 0.54 mmol). The resulting mixture was stirred at 80 °C for 3 h, providing a red solution. The reaction was then quenched with wet silica gel. Flash column chromatography separation (silica gel, *n*-hexane as elute) gave the deuterated cyclopropanation product 3-D-2-phenyl-1,1-di(*p*-tolyl)cyclopropane as a white solid. The NMR data indicate the presence of both diastereoisomers of 3-D-2-phenyl-1,1-di(*p*-tolyl)cyclopropane with the ratio of 2.1:1 (*cis*-D-**3e** and *trans*-D-**3e**). ^{1}H NMR (400 MHz, $CDCl_3$, 294 K): δ (ppm) 7.21 (d, J = 7.7 Hz, 2H), 7.17−7.07 (m, 5H), 7.00 (d, J = 7.7 Hz, 2H), 6.88−6.97 (m, 4H), 2.82 (d, J = 8.3 Hz, 1H), 2.33 (s, 3H), 2.25 (s, 3H), 1.94 (d, J = 6.3 Hz, 0.32H), 1.78 (d, J = 8.9 Hz, 0.68H). ^{13}C NMR (101 MHz, $CDCl_3$, 294 K): δ (ppm) 144.52 (s), 139.10 (s), 137.44 (s), 135.71 (s), 135.50 (s), 131.02 (s), 129.13 (s), 128.77 (s), 128.07 (s), 127.72 (s), 127.37 (s), 125.56 (s), 38.73 (s), 32.39 (s), 21.20 (s), 21.06 (s), 20.71 (t, $J_{C\text{-}D}$ = 23.5 Hz). ^{2}H NMR (92 MHz, $CDCl_3$, 298 K): δ (ppm) 1.97, 1.82.

Kinetic Studies on the Reaction of 2 with 4-Fluoro-styrene at Various Temperatures. The kinetic studies monitor the increase of the ^{19}F NMR signal of 2,2-di(*p*-tolyl)-1-(*p*-fluorophenyl)-cyclopropane formed in the reaction of **2** with excess amount of 4-fluoro-styrene (10−35 equiv) in C_6D_6 at certain temperature (85, 80, 75, 70, 65, 60, 55, 50, and 45 °C), using trifluoromethylbenzene as internal standard. These reactions were conducted with general procedure as follows: To a J-Young tube were added **2** (0.025 M in C_6D_6, 400 μL), trifluoromethylbenzene (0.10 M in C_6D_6, 13 μL) and a certain amount of 4-fluoro-styrene (100, 150, 200, 250, 300, and 350 μmol). The reaction mixture was then diluted with C_6D_6 to 500 μL. The measured rate constants are compiled in Table S2, and the plots of $\ln([P]_1/([P]_1 - [P]))$ vs time are shown in Figures S51−S59.

Competition Experiments. To a glass vessel was added **2** (42 mg, 0.05 mmol), styrene (16 mg, 0.15 mmol), a *para*-substituted styrene (0.15 mmol), and 2.0 mL of toluene. The solution were stirred for 2 h at 80 °C. The reaction was then quenched with wet silica gel and extracted by CH_2Cl_2 (20 mL). After removal of volatiles under vacuum, the residue was redissolved in $CDCl_3$ and analyzed by ^{1}H NMR in $CDCl_3$. The ratio of the yield of the 2-(*para*-substituted phenyl)-1,1-di(*p*-tolyl)cyclopropane to the yield of the 2-phenyl-1,1-di(*p*-tolyl)cyclopropane is the relative rate k_X/k_H (Table 2).

Computational Details. All molecular geometries were optimized in the gas phase, employing the B3LYP[50] density functional with def2-SVP basis set[51] for all atoms, and considering Grimme's DFT empirical dispersion correction DFT-D3.[52] Optimized minima and transition states (TSs) were verified by harmonic vibrational analysis to have no and one proper imaginary frequency, respectively. To refine the calculated energy, single-point calculatios with larger basis set were then done based on these optimized structures, by using the B3LYP functional with the def2-TZVP basis set.[51] Solvent effect was modeled in these single point calculations by employing continuum solvation model of SMD,[53] with toluene as the solvent. The reported enthalpies in this work were calculated at the B3LYP/def2-TZVP level, including the thermal correction for enthalpy obtained from vibrational analysis in the gas phase at the reaction temperature, as well as Grimme's DFT empirical dispersion correction DFT-D3 with Grimme's original short-range damping.[52] All geometry optimizations and single-point calculations were performed with Gaussian 09 program.[54]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b00484.

Tables S1 and S2, listing crystallographic data for **1** and **2** and rate constants for reactions of **2** with 4-fluoro-styrene; molecular structure of **1**, ^{57}Fe Mössbauer spectra, NMR spectra, other calculated reaction pathways, and electronic configurations of iron-alkylidene species **S**, including Figures S1−S63; and Cartesian coordinates of the optimized structures and (PDF)

Crystallographic data (CIF)

■ AUTHOR INFORMATION

Corresponding Authors

*chenh@iccas.ac.cn

*deng@sioc.ac.cn

ORCID

Hui Chen: 0000-0003-0483-8786

Liang Deng: 0000-0002-0964-9426

Author Contributions

§J.L. and L.H. contributed equally.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The work was supported by the National Key Research and Development Program (2016YFA0202900), the National Natural Science Foundation of China (Nos. 21690062, 21421091, and 21432001 to L.D., and Nos. 21290194, 21473215, and 21521062 to H.C.), and the Strategic Priority Research Program of the Chinese Academy of Sciences (No. XDB20000000).

■ REFERENCES

(1) (a) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds, The Chemistry of Transition Metal Complexes Containing Oxo, Nitrido, Imido, Alkylidyne Ligands*; Wiley: Canada, 1988. (b) Dörwald, F. Z. *Metal Carbenes in Organic Synthesis*; Wiley-VCH: Weinheim, 1999. (c) Che, C.-M.; Zhou, C.-Y.; Wong, E. L.-M. *Top. Organomet. Chem.* **2011**, 33, 111−138.

DOI: 10.1021/jacs.7b00484
J. Am. Chem. Soc. 2017, 139, 3876−3888

(2) (a) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919−939. (b) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411−432. (c) Chauvin, Y. *Angew. Chem., Int. Ed.* **2006**, *45*, 3740−3747. (d) Schrock, R. R. *Angew. Chem., Int. Ed.* **2006**, *45*, 3748−3759. (e) Grubbs, R. H. *Angew. Chem., Int. Ed.* **2006**, *45*, 3760−3765. (f) Zhu, S.-F.; Zhou, Q.-L. *Natl. Sci. Rev.* **2014**, *1*, 580−603.
(3) For examples, see: (a) Varela-Álvarez, A.; Musaev, D. G. *Chem. Sci.* **2013**, *4*, 3758−3764. (b) Fallah, H.; Horng, F.; Cundari, T. R. *Organometallics* **2016**, *35*, 950−958. (c) de Brito Sá, É.; Rodríguez-Santiago, L.; Sodupe, M.; Solans-Monfort, X. *Organometallics* **2016**, *35*, 3914−3923. (d) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 2605−2612.
(4) For examples, see: (a) Jolly, P. W.; Pettit, R. J. *J. Am. Chem. Soc.* **1966**, *88*, 5044−5045. (b) Brookhart, M.; Nelson, G. O. J. *J. Am. Chem. Soc.* **1977**, *99*, 6099−6101. (c) Mahias, V.; Cron, S.; Toupet, L.; Lapinte, C. *Organometallics* **1996**, *15*, 5399−5408.
(5) Li, Y.; Huang, J.-S.; Zhou, Z.-Y.; Che, C.-M.; You, X.-Z. J. *J. Am. Chem. Soc.* **2002**, *124*, 13185−13193.
(6) Klose, A.; Solari, E.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *Chem. Commun.* **1997**, 2297−2298.
(7) (a) Lindley, B. M.; Swidan, A.; Lobkovsky, E. B.; Wolczanski, P. T.; Adelhardt, M.; Sutter, J.; Meyer, K. *Chem. Sci.* **2015**, *6*, 4730−4736. (b) Lindley, B. M.; Jacobs, B. P.; MacMillan, S. N.; Wolczanski, P. T. *Chem. Commun.* **2016**, *52*, 3891−3894. (c) Jacobs, B. P.; Agarwal, R. G.; Wolczanski, P. T.; Cundari, T. R.; MacMillan, S. N. *Polyhedron* **2016**, *116*, 47−56.
(8) (a) Dazinger, G.; Kirchner, K. *Organometallics* **2004**, *23*, 6281−6287. (b) Meng, Q. X.; Wang, F.; Qu, X. J.; Zhou, J.; Li, M. *J. Mol. Struct.: THEOCHEM* **2007**, *815*, 157−163. (c) Wang, F.; Meng, Q. X.; Li, M. *Int. J. Quantum Chem.* **2008**, *108*, 945−953. (d) Khade, R. L.; Fan, W. C.; Ling, Y.; Yang, L.; Oldfield, E.; Zhang, Y. *Angew. Chem., Int. Ed.* **2014**, *53*, 7574−7578. (e) Khade, R. L.; Zhang, Y. J. *J. Am. Chem. Soc.* **2015**, *137*, 7560−7563.
(9) (a) Giusti, M.; Solari, E.; Giannini, L.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1997**, *16*, 5610−5612. (b) Esposito, V.; Solari, E.; Floriani, C.; Re, N.; Rizzoli, C.; Chiesi-Villa, A. *Inorg. Chem.* **2000**, *39*, 2604−2613.
(10) Russell, S. K.; Hoyt, J. M.; Bart, S. C.; Milsmann, C.; Stieber, S. C. E.; Semproni, S. P.; DeBeer, S.; Chirik, P. J. *Chem. Sci.* **2014**, *5*, 1168−1174.
(11) Sharon, D. A.; Mallick, D.; Wang, B. J.; Shaik, S. J. *J. Am. Chem. Soc.* **2016**, *138*, 9597−9610.
(12) For reviews, please see: (a) Mehn, M. P.; Peters, J. C. *J. Inorg. Biochem.* **2006**, *100*, 634−643. (b) Berry, J. F. *Comments Inorg. Chem.* **2009**, *30*, 28−66. (c) Saouma, C. T.; Peters, J. C. *Coord. Chem. Rev.* **2011**, *255*, 920−937. (d) Zhang, L.; Deng, L. *Chin. Sci. Bull.* **2012**, *57*, 2352−2360. (e) Hohenberger, J.; Ray, K.; Meyer, K. *Nat. Commun.* **2012**, *3*, 720.
(13) For selected examples, please see: (a) Doyle, M. P. *Angew. Chem., Int. Ed.* **2009**, *48*, 850−852. (b) Huang, L. Y.; Chen, Y.; Gao, G.-Y.; Zhang, X. P. *J. Org. Chem.* **2003**, *68*, 8179−8184. (c) Chen, Y.; Zhang, X. P. *J. Org. Chem.* **2007**, *72*, 5931−5934. (d) Chen, Y.; Ruppel, J. V.; Zhang, X. P. *J. Am. Chem. Soc.* **2007**, *129*, 12074−12075. (e) Dzik, W. I.; Xu, X.; Zhang, X. P.; Reek, J. N. H.; de Bruin, B. *J. Am. Chem. Soc.* **2010**, *132*, 10891−10902. (f) Lu, H. J.; Dzik, W. I.; Xu, X.; Wojtas, L.; de Bruin, B.; Zhang, X. P. *J. Am. Chem. Soc.* **2011**, *133*, 8518−8521. (g) Belof, J. L.; Cioce, C. R.; Xu, X.; Zhang, X. P.; Space, B.; Woodcock, H. L. *Organometallics* **2011**, *30*, 2739−2746.
(14) Marquard, S. L.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. *J. Am. Chem. Soc.* **2013**, *135*, 6018−6021.
(15) Bellow, J. A.; Stoian, S. A.; van Tol, J.; Ozarowski, A.; Lord, R. L.; Groysman, S. J. *J. Am. Chem. Soc.* **2016**, *138*, 5531−5534.
(16) Xiao, J.; Deng, L. *Dalton Trans.* **2013**, *42*, 5607−5610.
(17) The amido-phosphine-amido ligand scaffold was originally reported by Fryzuk et al.: MacLachlan, E. A.; Fryzuk, M. D. *Organometallics* **2005**, *24*, 1112−1118.
(18) (a) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. J. *J. Chem. Soc., Dalton Trans.* **1984**, 1349−1356. (b) Vela, J.; Stoian, S.; Flaschenriem, C. J.; Münck, E.; Holland, P. L. *J. Am. Chem. Soc.* **2004**, *126*, 4522−4523.
(19) Toupet, P. L.; Weinberger, B.; Des Abbayes, H.; Grosse, U. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *40*, 2056−2058.
(20) Guerchais, V.; Astruc, D.; Nunn, C. M.; Cowley, A. H. *Organometallics* **1990**, *9*, 1036−1041.
(21) Bart, J. C. J. *J. Chem. Soc. B* **1969**, 350−365.
(22) Pattacini, R.; Jie, S.; Braunstein, P. *Chem. Commun.* **2009**, 890−892.
(23) Canac, Y.; Duhayon, C.; Chauvin, R. *Angew. Chem., Int. Ed.* **2007**, *46*, 6313−6315.
(24) Iluc, V. M.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2014**, *136*, 6479−6488.
(25) (a) Schröder, F. G.; Lichtenberg, C.; Elfferding, M.; Sundermeyer, J. *Organometallics* **2013**, *32*, 5082−5091. (b) Asay, M.; Donnadieu, B.; Baceiredo, A.; Soleilhavoup, M.; Bertrand, G. *Inorg. Chem.* **2008**, *47*, 3949−3951. (c) Fortier, S.; Walensky, J. R.; Wu, G.; Hayton, T. W. J. *J. Am. Chem. Soc.* **2011**, *133*, 6894−6897.
(26) (a) Lennon, P.; Rosan, A. M.; Rosenblum, M. J. *J. Am. Chem. Soc.* **1977**, *99*, 8426−8439. (b) Vicente, J.; Chicote, M. T.; MacBeath, C.; Jones, P. G. *Organometallics* **2003**, *22*, 1843−1848.
(27) Fischer, H.; Mauz, E.; Jaeger, M.; Fischer, R. J. *J. Organomet. Chem.* **1992**, *427*, 63−75.
(28) Dai, X. L.; Warren, T. H. *J. Am. Chem. Soc.* **2004**, *126*, 10085−10094.
(29) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 3300−3310.
(30) Wolf, J. R.; Hamaker, C. G.; Djukic, J.-P.; Kodadek, T.; Woo, L. K. *J. Am. Chem. Soc.* **1995**, *117*, 9194−9199.
(31) Bordeaux, M.; Tyagi, V.; Fasan, R. *Angew. Chem., Int. Ed.* **2015**, *54*, 1744−1748.
(32) Diaz-Requejo, M.; Pérez, P. J.; Brookhart, M.; Templeton, J. L. *Organometallics* **1997**, *16*, 4399−4402.
(33) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165−195.
(34) Creary, X.; Mehrsheikh-Mohammadi, M. E.; McDonald, S. J. *J. Org. Chem.* **1987**, *52*, 3254−3263.
(35) (a) Ho, C.; Leung, W.-H.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **1991**, 2933−2939. (b) Nelson, D. W.; Gypser, A.; Ho, P. T.; Kolb, H. C.; Kondo, T.; Kwong, H.-L.; McGrath, D. V.; Rubin, A. E.; Norrby, P.-O.; Gable, K. P.; Sharpless, K. B. *J. Am. Chem. Soc.* **1997**, *119*, 1840−1858. (c) Au, S.-M.; Huang, J.-S.; Yu, W.-Y.; Fung, W.-H.; Che, C.-M. *J. Am. Chem. Soc.* **1999**, *121*, 9120−9132. (d) Hennessy, E. T.; Liu, R. Y.; Iovan, D. A.; Duncan, R. A.; Betley, T. A. *Chem. Sci.* **2014**, *5*, 1526−1532.
(36) Jiang, X.-K. *Acc. Chem. Res.* **1997**, *30*, 283−289.
(37) Jiang, X.-K.; Ding, W. F.-X.; Zhang, Y.-H. *Tetrahedron* **1997**, *53*, 8479−8490.
(38) For examples, see: (a) Hamaker, C. G.; Djukic, J.-P.; Smith, D. A.; Woo, L. K. *Organometallics* **2001**, *20*, 5189−5199. (b) Zhang, R.; Yu, W.-Y.; Sun, H.-Z.; Liu, W.-S.; Che, C.-M. *Chem. - Eur. J.* **2002**, *8*, 2495−2507.
(39) (a) Schröder, D.; Shaik, S.; Schwarz, H. *Acc. Chem. Res.* **2000**, *33*, 139−145. (b) Shaik, S.; Hirao, H.; Kumar, D. *Acc. Chem. Res.* **2007**, *40*, 532−542.
(40) Käß, M.; Hohenberger, J.; Adelhardt, M.; Zolnhofer, E. M.; Mossin, S.; Heinemann, F. W.; Sutter, J.; Meyer, K. *Inorg. Chem.* **2014**, *53*, 2460−2470.
(41) Bowry, V. W.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, *113*, 5687−5698.
(42) Yeung, C.-T.; Sham, K.-C.; Lee, W.-S.; Wong, W.-T.; Wong, W.-Y.; Kwong, H.-L. *Inorg. Chim. Acta* **2009**, *362*, 3267−3273.
(43) Olmstead, M. M.; Power, P. P.; Shoner, S. C. *Inorg. Chem.* **1991**, *30*, 2547−2551.
(44) Javed, M. I.; Brewer, M. *Org. Lett.* **2007**, *9*, 1789−1792.
(45) Fu, H.; Look, G. C.; Zhang, W.; Jacobsen, E. N.; Wong, C.-H. *J. Org. Chem.* **1991**, *56*, 6497−6500.
(46) Wood, J. T.; Arney, J. S.; Cortes, D.; Berson, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 3855−3860.

DOI: 10.1021/jacs.7b00484
J. Am. Chem. Soc. 2017, 139, 3876−3888

(47) (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003−2005. (b) Sur, S. K. *J. Magn. Reson.* **1989**, *82*, 169−173.
(48) Sheldrick, G. M. *SADABS: Program for Empirical Absorption Correction of Area Detector Data*; University of Göttingen: Göttingen, Germany, 1996.
(49) Sheldrick, G. M. *SHELXTL 5.10 for Windows NT: Structure Determination Software Programs*; Bruker Analytical X-ray systems, Inc.: Madison, WI, 1997.
(50) (a) Becke, A. D. *Phys. Rev. A: At., Mol., Opt. Phys.* **1988**, *38*, 3098−3100. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785−789. (c) Becke, A. D. J. *J. Chem. Phys.* **1993**, *98*, 5648−5652.
(51) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297−3305.
(52) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. J. *J. Chem. Phys.* **2010**, *132*, 154104.
(53) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, *113*, 6378−6396.
(54) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fu-kuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, revision D.01; Gaussian, Inc.: Wallingford, CT, 2009.

DOI: 10.1021/jacs.7b00484
J. Am. Chem. Soc. 2017, 139, 3876−3888