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Remarkably Stable Iron Porphyrins Bearing Nonheteroatom-Stabilized Carbene or (Alkoxycarbonyl)carbenes: Isolation, X-ray Crystal Structures, and Carbon Atom Transfer Reactions with Hydrocarbons

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Abstract: Reactions of [Fe(TPFPP)] (TPFPP = *meso*-tetrakis(pentafluorophenyl)porphyrinato dianion) with diazo compounds $N_2C(Ph)R$ (R = Ph, CO_2Et, $CO_2CH_2CH=CH_2$) afforded [Fe(TPFPP)(C(Ph)R)] (R = Ph (**1**), CO_2Et (**2**), $CO_2CH_2CH=CH_2$ (**3**)) in 65−70% yields. Treatment of **1** with *N*-methylimidazole (MeIm) gave the adduct [Fe(TPFPP)(CPh$_2$)(MeIm)] (**4**) in 65% yield. These new iron porphyrin carbene complexes were characterized by NMR and UV−vis spectroscopy, mass spectrometry, and elemental analyses. X-ray crystal structure determinations of **1**·0.5C$_6$H$_6$·0.5CH$_2$Cl$_2$ and **4** reveal Fe=CPh$_2$ bond lengths of 1.767(3) (**1**) and 1.827(5) Å (**4**), together with large ruffling distortions of the TPFPP macrocycle. Complexes **2** and **4** are reactive toward styrene, affording the corresponding cyclopropanes in 82 and 53% yields, respectively. Complex **1** is an active catalyst for both intermolecular cyclopropanation of styrenes with ethyl diazoacetate and intramolecular cyclopropanation of allylic diazoacetates. Reactions of **2** and **4** with cyclohexene or cumene produced allylic or benzylic C−H insertion products in up to 83% yield.

Introduction

The fact that cytochrome P-450 enzymes in biological systems bear iron porphyrin active sites makes iron porphyrins unique candidates for model compounds of these enzymes. Numerous efforts have been directed to oxoiron porphyrins and their oxygen atom transfer reactions with alkenes or alkanes to afford epoxidation or C−H insertion (i.e. hydroxylation) products,[1] mainly to mimic the corresponding hydrocarbon oxidation reactivity of the putative oxoiron species of cytochrome P-450 enzymes.[2] The carbon analogues of oxoiron porphyrins, namely, iron porphyrin carbene complexes, have also received much attention[3−7] due mainly to the possible formation of carbene complexes of cytochrome P-450 enzymes in reductive metabolism of polyhalogenated compounds or oxidative metabolism of benzodioxole derivatives[3] and in the propylene epoxidation by cytochrome P-450.[6] However, the carbon atom transfer reactions of iron porphyrin carbene complexes with alkenes to form cyclopropanes are rarely studied,[8,9] and *no iron porphyrin carbene complexes have been found to react with hydrocarbons to form C−H insertion products*.

Moreover, despite the report of a large number of iron porphyrin carbene complexes in the literature (the predominant of which are halocarbene complexes [Fe(Por)(CX$_2$)], [Fe(Por)(C(X)X′)], or [Fe(Por)(C(R)X)] first prepared by Mansuy and co-workers[3]), there are extremely few (if any) iron porphyrins bearing nonheteroatom-stabilized carbenes CR$_2$ and C(R)R′ or

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(1) For reviews on iron porphyrin-catalyzed epoxidation or hydroxylation reactions that are generally believed to involve oxoiron porphyrin intermediates, see: (a) Ellis, P. E., Jr.; Lyons, J. E. *Coord. Chem. Rev.* **1990**, *105*, 181. (b) Meunier, B. *Chem. Rev.* **1992**, *92*, 1411. (c) Collman, J. P.; Zhang, X.; Lee, V. J.; Uffelman, E. S.; Brauman, J. I. *Science* **1993**, *261*, 1404. (d) Mansuy, D. *Coord. Chem. Rev.* **1993**, *125*, 129. For examples of observed oxoiron porphyrins and their oxygen atom transfer reactions with hydrocarbons, see: (e) Groves, J. T.; Haushalter, R. C.; Nakamura, M.; Nemo, T. E.; Evans, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 2884. (f) Tsuchiya, S. *J. Chem. Soc., Chem. Commun.* **1991**, 716. (g) Yamaguchi, K.; Watanabe, Y.; Morishima, I. *J. Chem. Soc., Chem. Commun.* **1992**, 1721. (h) Fujii, H. *J. Am. Chem. Soc.* **1993**, *115*, 4641. (i) Groves, J. T.; Gross, Z.; Stern, M. K. *Inorg. Chem.* **1994**, *33*, 5065. (j) Traylor, T. G.; Kim, C.; Richards, J. L.; Xu, F.; Perrin, C. L. *J. Am. Chem. Soc.* **1995**, *117*, 3468. (k) Gross, Z.; Nimri, S. *J. Am. Chem. Soc.* **1995**, *117*, 8021. (l) Goh, Y. M.; Nam, W. *Inorg. Chem.* **1999**, *38*, 914.
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(alkoxycarbonyl)carbenes C(R)CO$_2$R′ (R/R′ = H, alkyl, or aryl). These types of iron porphyrin carbene complexes, such as the arylcarbene complex [Fe(TTP)(CH(2,4,6-Me$_3$C$_6$H$_2$))][5,8] and the (alkoxycarbonyl)carbene complexes [Fe(Por)(CHCO$_2$-Et)],[7] have been proposed by Kodadek, Woo, and their co-workers to be the active cyclopropanating agents in the iron porphyrin-catalyzed cyclopropanation of alkenes with aryldi-azomethane or alkyl diazoacetate[8] but are usually highly unstable and in no cases have been isolated and fully characterized. In particular, the putative (alkoxycarbonyl)carbene complexes [Fe(Por)(CHCO$_2$Et)] have not been observed directly,[7] probably owing to their extreme instability.

We report here several iron porphyrin α-phenyl-substituted aryl- or (alkoxycarbonyl)carbene complexes [Fe(TPFPP)-(C(Ph)R)] (R = Ph (**1**), CO$_2$Et (**2**), CO$_2$CH$_2$CH=CH$_2$ (**3**); TPFPP = *meso*-tetrakis(pentafluorophenyl)porphyrinato dianion) and [Fe(TPFPP)(CPh$_2$)(MeIm)] (**4**, MeIm = *N*-methylimida-zole). These nonheteroatom-stabilized carbene or (alkoxycar-bonyl)carbene complexes of iron porphyrins are remarkably stable and can be isolated in spectroscopically and analytically pure forms. Both the arylcarbene complexes **1** and **4** have been characterized by X-ray crystallography, which are so far the only examples of structurally characterized iron porphyrin (nonhalo)carbene or nonheteroatom-stabilized carbene com-plexes.[10] In contrast to the isolable iron porphyrin halocarbene complexes whose alkene cyclopropanations were reported by Suslick and co-workers[4,8] to occur only after photolytic cleavage of their Fe−carbene bonds, complex **4** and the (ethoxycarbonyl)-carbene complex **2** can react with styrenes to form cyclopro-panes without photolysis, serving as the sole examples of *isolated* iron porphyrin carbene complexes that can cyclopro-panate alkenes under such conditions.[8] Even more interesting is that complexes **2** and **4** can react with cyclohexene and cumene to selectively form allylic or benzylic C−H insertion products, contributing the first isolated *monocarbene* metal complexes that can undergo intermolecular carbon atom transfer into saturated C−H bonds of unfunctionalized alkenes.[11]

Results and Discussion

Isolation and Spectral Features of [Fe(TPFPP)(C(Ph)R)] (1−3) and [Fe(TPFPP)(CPh$_2$)(MeIm)] (4). Reactions of [Fe(TPFPP)] with diazo compounds N$_2$C(Ph)R (R = Ph,

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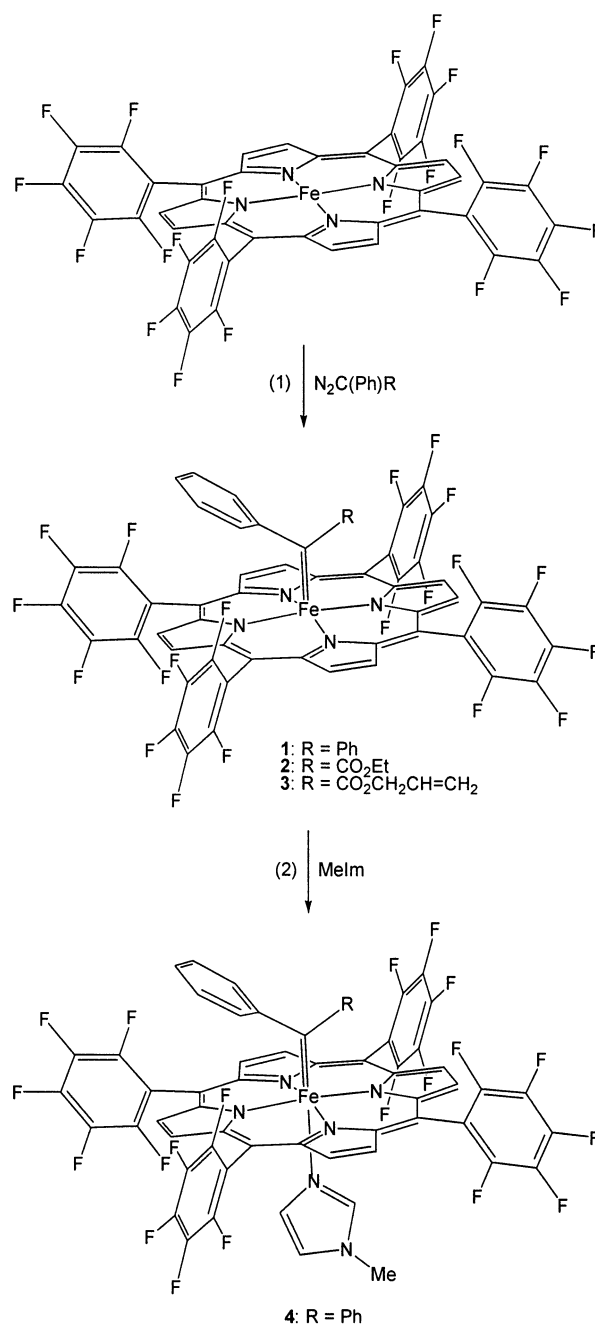
(8) In 1995, Kodadek, Woo, and their co-workers reported that iron porphyrins are active catalysts for cyclopropanation of alkenes with ethyl diazoacetate. The active species in the catalytic carbon atom transfer reactions are assumed to be iron porphyrin carbene complexes.[7] Shortly after, Suslick and co-workers demonstrated that photolysis of several halocarbene iron porphyrins gives free halocarbenes, which can be trapped by alkenes to form cyclopropanes.[4] Recently, Woo and co-workers reported iron por-phyrin-catalyzed alkene cyclopropanations with aryldiazomethane and observed the carbene complexes [Fe(TTP)(CHR)] (R = SiMe$_3$, 2,4,6-Me$_3$C$_6$H$_2$; TTP = *meso*-tetrakis(*p*-tolyl)porphyrinato dianion) by ^{1}H NMR spectroscopy; these two iron porphyrin carbene complexes, which were contaminated by [Fe(TTP)], can react with alkenes to form cyclopropanes without photolysis.[5]

(9) This contrasts with the case of non-porphyrin iron carbene complexes, whose carbon atom transfer reactions with alkenes to form cyclopropanes have been investigated extensively. See for example: Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411.

(10) Although many iron porphyrin carbene complexes have been isolated, only the dichlorocarbene complex, [Fe(TPP)(CCl$_2$)(H$_2$O)] (TPP = *meso*-tetraphenylporphyrinato dianion), has been characterized by X-ray crystallography.[3b] A few other iron porphyrins containing Fe=C double bonds, such as vinylidene or μ_2-carbide complexes, have also been structurally characterized; see: (a) Goedken, V. L.; Deakin, M. R.; Bottomley, L. A. *J. Chem. Soc., Chem. Commun.* **1982**, 607. (b) Mansuy, D.; Battioni, J. P.; Lavallee, D.; Fischer, J.; Weiss, R. *Inorg. Chem.* **1988**, *27*, 1052. (c) Beck, W.; Knauer, W.; Robl, C. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 318.

Scheme 1

1: R = Ph
2: R = CO$_2$Et
3: R = CO$_2$CH$_2$CH=CH$_2$

4: R = Ph

CO$_2$Et, CO$_2$CH$_2$CH=CH$_2$) in benzene under an inert atmosphere afforded complexes **1−3** in 65−70% yields (reaction 1 in Scheme 1). All these complexes are stable enough to be handled at room temperature and can be purified by chromatography on silica gel column. The arylcarbene complex **1** even exhibits a high stability toward attack by moist air and can crystallize from solutions exposed to the atmosphere at room temperature. However, the (alkoxycarbonyl)carbene complexes **2** and **3** are unstable to moist air both in solution and in the solid state. For example, when a dichloromethane solution of **2** exposed to the atmosphere was stirred for 12 h at room temperature, the

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(11) We previously isolated osmium porphyrin monocarbene complex [Os-(TPFPP)(CPh$_2$)(MeOH)] and bis(carbene) complex [Os(TPFPP)(CPh$_2$)$_2$]. Only the bis(carbene) complex can undergo carbon atom transfer into the saturated C−H bonds of unfunctionalized alkenes; see: (a) Li, Y.; Huang, J.-S.; Zhou, Z.-Y.; Che, C.-M. *J. Am. Chem. Soc.* **2001**, *123*, 4843. (b) Che, C.-M.; Huang, J.-S. *Coord. Chem. Rev.* **2002**, *231*, 151.

complex was converted to a mixture of [Fe(TPFPP)(OH)] and {[Fe(TPFPP)]$_2$O},[12] accompanied by formation of the carbene coupling product EtO$_2$CC(Ph)=C(Ph)CO$_2$Et and the ketone PhCOCO$_2$Et in 80 and 14% yields, respectively.

The preparation of iron porphyrin carbene complexes from reactions of [Fe(Por)] with diazoacetates (such as reaction 1 for **2** and **3**) is unprecedented in the literature. Previous methods of preparing iron porphyrin carbene complexes include (i) reaction of [Fe(Por)] with halo compounds in the presence of reductants,[3a−d,f] (ii) reaction of [Fe(Por)] with iodonium ylide,[3g] diazoketone,[3g] or diazoalkane,[5] (iii) reaction of [Fe(Por)(C(R)-Cl)] with alcohol or thiol,[3e] and (iv) reduction of an Fe−N-bridged carbene complex with Zn−Hg,[3h] almost all of which were developed by Mansuy and co-workers. The formation of [Fe(TPFPP)(C(Ph)CO$_2$Et)] (**2**) from [Fe(TPFPP)] and N$_2$C(Ph)-CO$_2$Et provides support for the possible involvement of the [Fe-(TPFPP)(CHCO$_2$Et)] intermediate in [Fe(TPFPP)Cl]-catalyzed cyclopropanation of alkenes with ethyl diazoacetate (EDA).[7]

Since the species [Fe(TPFPP)(CHCO$_2$Et)] was not observed directly,[7] the stability of **1**−**3** might stem from the presence of α-phenyl substituent in their carbene ligands. The electron-deficient nature of the TPFPP macrocycle may also play a role in stabilizing **1**−**3**, because our attempts to extend reaction 1 to simple porphyrin ligands such as TPP[10] did not result in isolation of the corresponding iron porphyrin carbene complexes. Previously we found that a bis(carbene)osmium complex with TPFPP is also significantly stabler than its analogue with simple porphyrin ligand TTP.[11]

Like the halocarbene complex [Fe(TPP)(CCl$_2$)][3a,10] which can bind donor solvent or organic base (such as pyridine) to form six-coordinate species [Fe(TPP)(CCl$_2$)(L)],[3b,c,10] complex **1** rapidly reacted with MeIm to afford **4** in 65% isolated yield (reaction 2 in Scheme 1). This six-coordinate arylcarbene complex is unstable toward moist air at room temperature, *suggesting that coordination of MeIm to **1** significantly destabilizes its Fe=CPh$_2$ bond.* We have also examined the reactions of **2** or **3** with MeIm and the reactions of **1**−**3** with pyridine, but in these cases, the corresponding MeIm or pyridine adducts were not isolated in pure form. A prolonged reaction (~20 h) of **2** with pyridine in dichloromethane led to formation of the bis(pyridine) complex [Fe(TPFPP)(Py)$_2$].[13]

The UV−vis spectra of **1**−**4** each show a Soret band at ~403 nm and two Q-bands at about 522 and 556 nm, similar to the Soret (408 nm) and Q-bands (525, 550 nm) of [Fe(TPP)-(CCl$_2$)].[3a] The mass spectra of **1**−**3** exhibit prominent cluster peaks (M$^+$) at m/z = 1194, 1190, and 1202, respectively, which can be attributed to the corresponding parent ions. Complex **4** gives no parent-ion peaks (M$^+$) in its mass spectrum but shows peaks attributable to M$^+$ − MeIm, suggesting that the coordinated MeIm ligand in **4** is rather labile under the mass spectrometry conditions.

In the ^{13}C NMR spectra of **1**−**4**, the Fe=C(carbene) signals are located at δ = 358.98 (**1**), 327.47 (**2**), 325.67 (**3**), and 385.44 (**4**). These signals are substantially downfield from that of [Fe(TPP)(CCl$_2$)] (δ = 224.7)[3a] but are comparable to those of [Fe(TPP)(C(R)Cl)] ($\delta \approx$ 310).[3d] Compared to the (alkoxycarbonyl)carbene complexes **2** and **3**, the arylcarbene complexes

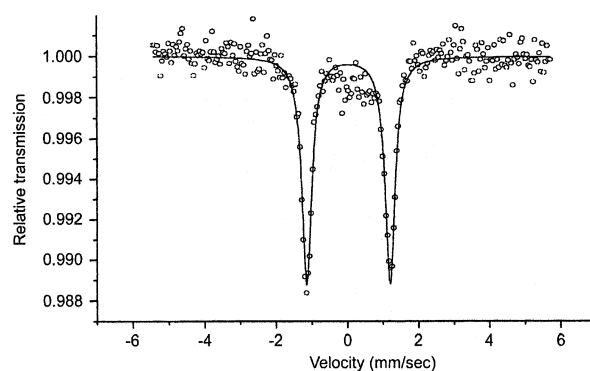**Figure 1.** Mössbauer spectrum of [Fe(TPFPP)(CPh$_2$)] (**1**) at 288 K.

1 and **4** give markedly downfield Fe=C(carbene) signals. Notably, coordination of MeIm to **1** downfield shifts its Fe=C(carbene) signal by ~26 ppm.

A comparison of the ^{19}F NMR spectra of **1**−**3** (see Experimental Section) reveals that the influence of the carbene groups CPh$_2$, C(Ph)CO$_2$Et, and C(Ph)CO$_2$CH$_2$CH=CH$_2$ on the signals of the *meso*-C$_6$F$_5$ groups in TPFPP is very small. For each of **1**−**3**, two sets of signals were observed for either *ortho*- or *meta*-fluorine atoms in the *meso*-C$_6$F$_5$ groups, in agreement with the lack of equatorial plane symmetry in these five-coordinate iron porphyrins.

With regard to the ^{1}H NMR spectra, complex **1** shows the pyrrole proton (H$_\beta$) signal at δ = 8.31 and the CPh$_2$ phenyl proton signals at δ = 6.42 (H$_p$), 6.00 (H$_m$), and 3.13 (H$_o$). Replacement of one of the CPh$_2$ phenyl group in **1** by an alkoxycarbonyl group to form **2** or **3** downfield shifts the above signals to $\delta \approx$ 8.56 (H$_\beta$), 6.74 (H$_p$), 6.09 (H$_m$), and 3.40 (H$_o$). When **1** binds MeIm to form **4**, a slight upfield shift ($\Delta\delta \leq$ 0.08 ppm) was observed for the H$_\beta$, H$_p$, and H$_m$ signals. Note that the spectrum of **4** was recorded in the presence of free MeIm to prevent a significant dissociation of the complex in solution. The signals of coordinated MeIm groups were not located, probably arising from a rapid exchange between the coordinated and free MeIm ligands on the NMR time scale, as similarly rationalized for the absence of the signals of the coordinated Pr^{i}NHOH group in the ^{1}H NMR spectrum of [Fe(TPP)(Pr^{i}NO)-(Pr^{i}NHOH)].[14]

The appearance of the ^{1}H NMR signals of **1**−**4** at normal fields indicates that these iron porphyrin carbene complexes are diamagnetic, like previously reported iron porphyrins bearing other carbene groups.[3,5] Consequently, these types of iron porphyrins can be considered as low-spin iron(II) species.[3] A closely related diamagnetic non-porphyrin iron carbene complex, [Fe(tmtaa)(CPh$_2$)][15] (H$_2$tmtaa = tetramethyldibenzotetraazaan-nulene), is also considered as an iron(II) species on the basis of extended Hückel calculations and the correlation between the out of plane distance of the metal and its d^n configuration.

To provide further information about the electron density at the iron nucleus in an iron porphyrin nonheteroatom-stabilized carbene complex, we conducted Mössbauer studies on complex **1**. Figure 1 shows the Mössbauer spectrum of this complex at 288 K, which features a symmetrical and well-resolved doublet. Interestingly, the isomer shift and quadrupole splitting for **1** were

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(15) Klose, A.; Solari, E.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *Chem. Commun.* **1997**, 2297.
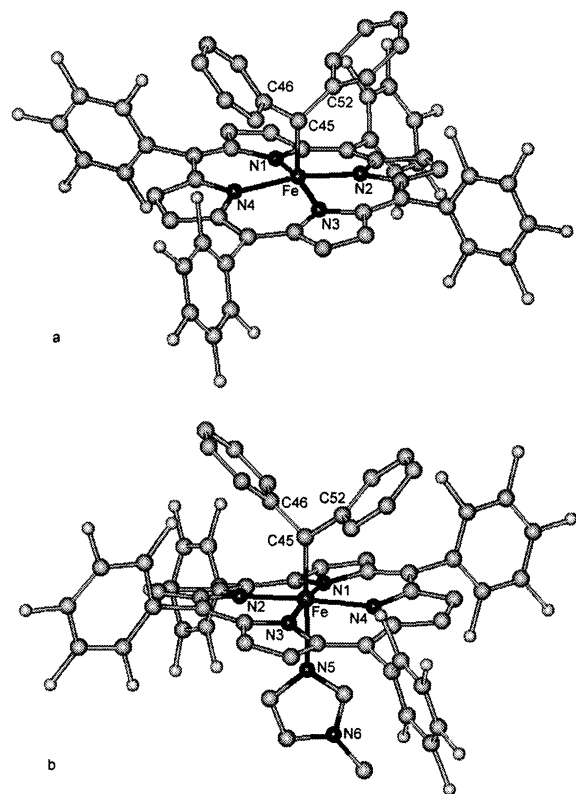
Figure 2. Ball and stick drawings of the structures of (a) [Fe(TPFPP)-(CPh₂)]·0.5C₆H₆·0.5CH₂Cl₂ (**1**·0.5C₆H₆·0.5CH₂Cl₂) and (b) [Fe(TPFPP)-(CPh₂)(MeIm)] (**4**). The solvent molecules and/or hydrogen atoms are not shown.

Table 1. Crystal Data and Structure Refinements for [Fe(TPFPP)(CPh₂)] (**1**) and [Fe(TPFPP)(CPh₂)(MeIm)] (**4**)

param	1·0.5C₆H₆·0.5CH₂Cl₂	4
empirical formula	C₅₇H₁₈F₂₀N₄Fe· 0.5C₆H₆·0.5CH₂Cl₂	C₆₁H₂₄F₂₀N₆Fe
fw	1276.12	1276.71
cryst syst	monoclinic	rhombohedral
space group	$P2_1/n$	$R\bar{3}$
a, Å	14.962(3)	42.299(4)
b, Å	16.406(3)	42.299(4)
c, Å	23.782(5)	17.367(2)
α, deg	90.00	90.00
β, deg	106.844(3)	90.00
γ, deg	90.00	120.00
V, Å³	5587(2)	26911(5)
Z	4	18
$F(000)$	2544	11 484
D(calcd), Mg/m³	1.517	1.418
abs coeff, mm⁻¹	0.429	0.358
index ranges	$-19 \le h \le 19$, $-10 \le k \le 21$, $-30 \le l \le 30$	$-54 \le h \le 54$, $-41 \le k \le 54$, $-22 \le l \le 22$
no. of reflcns collcd	37 229	61 815
no. of indepdt reflcns	12 809	13 740
abs corr	SADABS	SADABS
max/min transm	0.9584/0.9268	0.9651/0.9383
data/restraints/params	12809/92/780	13740/361/1000
final R indices ($I > 2\sigma(I)$)	R1 = 0.077, wR2 = 0.167	R1 = 0.069, wR2 = 0.159
goodness-of-fit	1.09	1.10
largest diff peak/hole, e Å⁻³	0.658/−0.559	0.681/−0.486

found to be 0.03 and 2.34 mm/s, respectively, similar to those observed for iron(IV) rather than low-spin iron(II) porphyrins.[16] Prior to this work, Mössbauer studies on iron porphyrin carbene complexes were reported only for the diamagnetic halocarbene species [Fe(TPP)(CCl₂)],[16] whose isomer shift (0.10 mm/s) and quadrupole splitting (2.28 mm/s) also fall in the region of iron-(IV) porphyrins.

X-ray Crystal Structures of [Fe(TPFPP)(CPh₂)] (1) and [Fe(TPFPP)(CPh₂)(MeIm)] (4). Upon obtaining diffraction-quality crystals of **1**·0.5C₆H₆·0.5CH₂Cl₂ and **4** (see Experimental Section), we determined their structures by X-ray crystallography, which are depicted in Figure 2. The crystal data and structure refinements for the two crystals are summarized in Table 1, whereas the selected bond lengths and angles are given in Table 2.

As shown in Figure 2a, the arylcarbene complex **1** contains a five-coordinate iron center, unlike the structurally characterized halocarbene complex [Fe(TPP)(CCl₂)(H₂O)] (whose iron atom is six-coordinate).[3b] A comparison of the metrical parameters of **1** and [Fe(TPP)(CCl₂)(H₂O)] reveals several interesting structural features of the arylcarbene complex. First, the Fe−C(carbene) distance of 1.767(3) Å in **1** is considerably shorter than that in [Fe(TPP)(CCl₂)(H₂O)] (1.83(3) Å). Second, the porphyrin ring of **1** exhibits a marked ruffling distortion (Figure 3, inset) with a mean deviation of 0.138 Å from the mean plane of the 24 component atoms, in contrast to the essentially planar porphyrin ring (mean deviation: ∼0.03 Å) of [Fe(TPP)(CCl₂)(H₂O)]. Third, the iron atom in **1** is 0.294 Å

(16) English, D. R.; Hendrickson, D. N.; Suslick, K. S. *Inorg. Chem.* **1983**, *22*, 368.

out of the mean porphyrin plane toward the carbene group, whereas that in [Fe(TPP)(CCl₂)(H₂O)] is not significantly displaced from the porphyrin plane. Despite the above differences in the structures of **1** and [Fe(TPP)(CCl₂)(H₂O)], the average Fe−N(pyrrole) distances in these two complexes (1.966-(3) and 1.984(4) Å, respectively) are similar.

Notice that the Fe=CPh₂ bond in **1** is even shorter than that in the five-coordinate non-porphyrin carbene complex [Fe(tmtaa)(CPh₂)]·PhCH₃, which is reported to show a particularly short Fe−C(carbene) bond of 1.794(3) Å.[15] Both **1** and [Fe(tmtaa)(CPh₂)] have a distorted square pyramidal FeN₄C core. The displacement of the iron atom from the mean N₄ plane in **1** is 0.238 Å, smaller than that of 0.335 Å in [Fe(tmtaa)-(CPh₂)].[15]

The coordination of MeIm to **1** to form six-coordinate aryl-carbene complex **4** (Figure 2b) lengthens the Fe=CPh₂ bond of **1** to 1.827(5) Å, which is now similar to the Fe−CCl₂ distance in [Fe(TPP)(CCl₂)(H₂O)]. The Fe−N(MeIm) distance of 2.168(4) Å and the C−Fe−N(MeIm) angle of 176.6(2)° in **4** are also similar to the Fe−O(H₂O) distance (2.13(3) Å) and the C−Fe−O(H₂O) angle (177.1(1.5)°) in [Fe(TPP)(CCl₂)-(H₂O)], respectively. Furthermore, complex **4** exhibits a considerably smaller displacement of the iron atom from the mean plane of the porphyrin ring (0.122 Å toward the CPh₂ group), along with slightly longer Fe−N(pyrrole) bonds (average 1.973(4) Å), than complex **1**. However, the porphyrin ring in **4** shows a more severe ruffling distortion (Figure 3, inset): the mean deviation of the 24 component atoms from their mean plane reaches 0.198 Å.

The large *ruffling* distortions of the porphyrin macrocycle in the iron porphyrins **1** and **4** are unusual. In the crystal structure of {[Fe(TPFPP)]₂O},[17a] the porphyrin ring displays a moderate *doming* distortion with a mean deviation of 0.0721 Å from the mean porphyrin plane. Although [Fe(TPP)(CO)(MeIm)] also has

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [Fe(TPFPP)(CPh₂)] (**1**) and [Fe(TPFPP)(CPh₂)(MeIm)] (**4**)

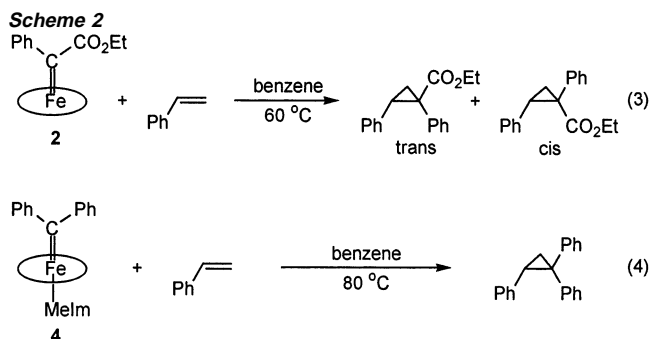|	1	4		1	4
Fe−N1	1.961(3)	1.972(3)	Fe−C45	1.767(3)	1.827(5)
Fe−N2	1.967(3)	1.963(4)	C45−C46	1.482(4)	1.489(6)
Fe−N3	1.964(3)	1.987(3)	C45−C52	1.484(5)	1.499(7)
Fe−N4	1.973(3)	1.970(4)	Fe−N5		2.168(4)
Fe−C45−C46	126.1(3)	124.8(4)	Fe−C45−C52	122.3(2)	124.2(4)
C46−C45−C52	111.5(3)	111.0(4)	C45−Fe−N5		176.6(2)
C45−Fe−N1	96.0(1)	92.8(2)	C45−Fe−N2	95.6(1)	91.5(2)
C45−Fe−N3	99.4(1)	94.8(2)	C45−Fe−N4	96.9(1)	92.4(2)
N1−Fe−N2	89.5(1)	89.9(2)	N2−Fe−N3	89.6(1)	89.6(2)
N3−Fe−N4	88.8(1)	90.2(2)	N4−Fe−N1	88.8(1)	89.8(1)
N1−Fe−N3	164.6(1)	172.4(2)	N2−Fe−N4	167.5(1)	176.1(2)
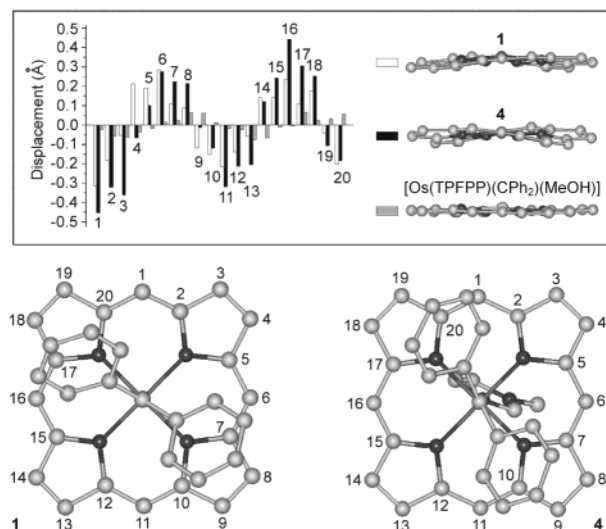
Figure 3. Orientations of the carbene axial ligands in [Fe(TPFPP)(CPh₂)] (**1**) and [Fe(TPFPP)(CPh₂)(MeIm)] (**4**) with respect to the porphyrin ligands. The inset shows the perpendicular displacements of the porphyrin ring carbon atoms from the mean plane of the 24 component atoms (including four pyrrole nitrogens) observed for **1**, **4**, and the closely related osmium analogue [Os(TPFPP)(CPh₂)(MeOH)] reported in ref 11, together with the side views of the porphyrin rings in these monocarbene complexes. The perpendicular displacements of the porphyrin ring nitrogen atoms from the mean plane of the 24 component atoms average 0.058 Å for **1**, 0.049 Å for **4**, and 0.041 Å for [Os(TPFPP)(CPh₂)(MeOH)].

a substantially puckered porphyrin ligand in its crystal structure,[17b] the porphyrin macrocycle in this carbonyl complex exhibits a *saddle* rather than ruffling distortion, and the mean deviation from the mean porphyrin plane is 0.147 Å, smaller than that found in **4**. The large ruffling distortion of the TPFPP macrocycle in **1** and **4** also contrasts with the small *saddle* distortion of the same porphyrin ligand (mean deviation: 0.0382 Å) in the monocarbene osmium porphyrin [Os(TPFPP)(CPh₂)(MeOH)][11] (Figure 3, inset) but is comparable to the ruffling distortion in the bis(carbene)osmium porphyrin [Os(TPFPP)(CPh₂)₂] (mean deviation: 0.197 Å).[11]

For both **1** and **4**, the sum of the angles at the coordinated carbene carbon (**1**, 359.9(3)°; **4**, 360.0(4)°) is almost identical to 360°, consistent with the sp² hybridization of this carbon atom. In the structure of either **1** or **4**, the carbene plane lies close to a pair of diagonal Fe−N(pyrrole) bonds, as depicted in Figure 3, with dihedral angles of about 14° (**1**) and 19° (**4**)

(17) (a) Gold, A.; Jayaraj, K.; Doppelt, P.; Fischer, J.; Weiss, R. *Inorg. Chim. Acta* **1988**, *150*, 177. (b) Salzmann, R.; Ziegler, C. J.; Godbout, N.; McMahon, M. T.; Suslick, K. S.; Oldfield, E. *J. Am. Chem. Soc.* **1998**, *120*, 11323.

Scheme 2

between the Ph−C(carbene) bonds and the closest Fe−N(pyrrole) bonds.

The structure determinations on both the five- and six-coordinate iron complexes **1** and **4** bearing the same carbene and porphyrin ligands make it practical to *directly* assess the influence of a trans donor ligand on the metal−carbene bond. Prior to this work, quite a few other metalloporphyrin carbene complexes have been structurally characterized (some are five-coordinate;[18d] the others are six-coordinate[3b,11,18a−c]) but no pair of these five- and six-coordinate complexes contain the same [M(Por)(carbene)] entity. *The considerable lengthening of the Fe−C(carbene) bond of **1** upon coordination with MeIm is parallel to the decreased stability observed for **4** as mentioned above and to the higher reactivity of **4** than **1** described below.*

Stoichiometric Cyclopropanation of Alkenes by [Fe-(TPFPP)(C(Ph)CO₂Et)] (2) and [Fe(TPFPP)(CPh₂)(MeIm)] (4). Treatment of **2** with excess styrene in benzene at 60 °C for 15 h afforded 1,2-diphenylcyclopropanecarboxylic acid ethyl ester[19] in 82% yield with a trans:cis ratio of 2.0:1 (reaction 3[20] in Scheme 2). This serves as a good evidence for [Fe(TPFPP)-(CHCO₂Et)] as a cyclopropanating agent in [Fe(TPFPP)Cl]-catalyzed cyclopropanation of styrene with EDA,[7] since the CHCO₂Et complex is expected to be more reactive than **2** due to the lack of α-phenyl substituent in the carbene ligand. The lower diastereoselectivity in reaction 3 compared to that in the catalytic reaction (trans:cis = 6.0[7]) probably results from a smaller difference in steric bulk between the phenyl and

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(19) Huisgen, R.; Sustmann, R.; Bunge, K. *Chem. Ber.* **1972**, *105*, 1324.
(20) The iron porphyrin product from the reaction is extremely air-sensitive. Workup of the reaction mixture only led to isolation of {[Fe(TPFPP)]₂O} contaminated by [Fe(TPFPP)(OH)].
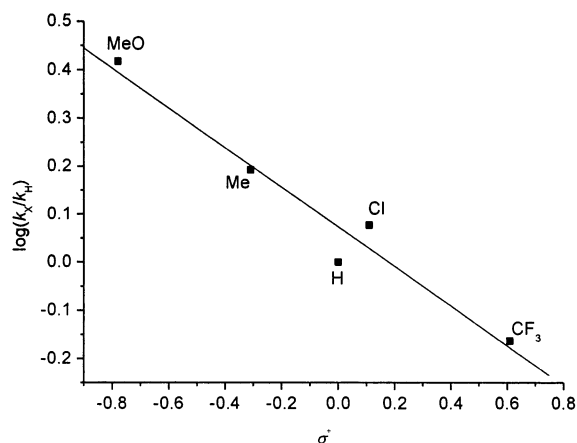
Figure 4. Plot of $\log(k_X/k_H)$ vs σ^+ for the reactions of [Fe(TPFPP)(C(Ph)-CO_2Et)] (**2**) with p-XC_6H_4CH=CH_2 (X = MeO, Me, H, Cl, CF_3).

CO_2Et groups in C(Ph)CO_2Et than that between the H and CO_2Et groups in CHCO_2Et,[7,18d] which leads to a smaller difference in energy between the transition states corresponding to the trans and cis cyclopropyl esters in reaction 3.
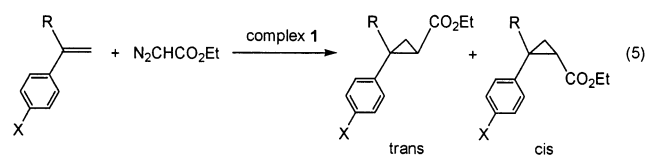
When **2** was treated with a 1:1 (molar ratio) mixture of styrene and its derivative p-XC_6H_4CH=CH_2 at 60 °C for 15 h, the molar ratios of the cyclopropyl esters derived from p-XC_6H_4CH=CH_2 and styrene were found to be 2.6 (X = MeO), 1.6 (X = Me), 1.2 (X = Cl), and 0.69 (X = CF_3). These ratios can be taken as the k_X/k_H ratios,[18d] i.e., the ratios between the cyclopropanation rates of p-XC_6H_4CH=CH_2 and styrene. Plotting $\log(k_X/k_H)$ values against the Hammett constants (σ^+) of the *para*-substituents gave a linearity with $R = 0.98$ and $\rho = -0.41 \pm 0.05$ (Figure 4).

Prior to this work, no Hammett plots were reported for the reactions of isolated iron porphyrin carbene complexes with alkenes. The ρ value obtained for the reactions between the isolated carbene complex **2** and p-XC_6H_4CH=CH_2 (X = H, MeO, Me, Cl, CF_3) is comparable to that of -0.68 ± 0.07 found for the [Fe(TTP)]-catalyzed cyclopropanation of the same alkenes with EDA.[7] This further supports the intervention of the [Fe(Por)(CHCO_2Et)] species in the EDA cyclopropanation of alkenes catalyzed by iron porphyrins and is consistent with the proposed electrophilic nature of these transient carbene species and some carbocationic character of the alkene carbons in the transition states.[7]

The arylcarbene complex **1** is inactive toward stoichiometric styrene cyclopropanations. We once treated **1** with excess styrene in benzene at 80 °C for 24 h but detected no cyclopropanation products in the reaction mixture. Interestingly, when a solution of **1** and styrene in benzene containing ~2 equiv of 2,6-dichloropyridine (2,6-Cl_2Py) was stirred at 80 °C for 10 h, 1,1,2-triphenylcyclopropane[11] was obtained in 56% yield. We speculated that 2,6-Cl_2Py and other donor reagents (L) can activate the coordinated CPh_2 group in **1** by formation of six-coordinate complex [Fe(TPFPP)(CPh_2)(L)]. This is the main reason we studied the binding behavior of **1** toward donor reagents such as MeIm and pyridine, which eventually led to the isolation of the MeIm adduct **4**.

Indeed, **4** has a considerably longer Fe=CPh_2 bond and is less stable than **1**, as described above. Treatment of **4** with excess styrene at 80 °C for 12 h gave 1,1,2-triphenylcyclopropane in 53% yield (reaction 4[20] in Scheme 2).

Table 3. Intermolecular Cyclopropanation of Alkenes with EDA Catalyzed by [Fe(TPFPP)(CPh_2)] (1)[a]

	alkene		conversn of	yield (%)[b]	ratio of
entry	R	X	EDA (%)	(trans + cis)	trans:cis[c]
1	H	H	100	83	6.6:1
2[d]	H	H	91	97	7.0:1
3	H	Me	100	85	4.5:1
4	H	Cl	100	86	6.3:1
5	Me	H	100	54	1.5:1

[a] Reaction conditions: CH_2Cl_2, rt, 5 h; **1**:EDA:alkene molar ratio = 1:1000:20 000. [b] Based on consumed EDA. [c] Determined by GC-MS. [d] EDA was added over 20 h; **1**:EDA:alkene molar ratio = 1:5000:100 000.

The activation of coordinated carbene groups by trans donor ligands has also been proposed in the cases of osmium[21] and ruthenium[18d] porphyrins. However, in those cases, this remains to be proved owing to the lack of well-identified five- *and* six-coordinate complexes of the same [M(Por)(carbene)] entities.

Taking into account the dramatically enhanced reactivity of **4** (relative to that of **1**) toward alkene cyclopropanations, the coordination of donor solvents to putative [Fe(Por)(CHCO_2Et)] species described above may also promote their cyclopropanation of alkenes and result in a lower diastereoselectivity in the catalytic reactions. Such an effect of donor solvents may compete with an opposite effect proposed in the literature;[7] that is, the coordination of donor solvents to [Fe(Por)(CHCO_2Et)] to form [Fe(Por)(CHCO_2Et)(solv)] adducts would render the carbene group less electrophilic and thus retard their cyclopropanation of alkenes (which would enhance the diastereoselectivity in the catalysis). The answer to the question about which of the two effects is dominating should depend on the electronic/steric properties of both the carbene ligands and the solvents involved.
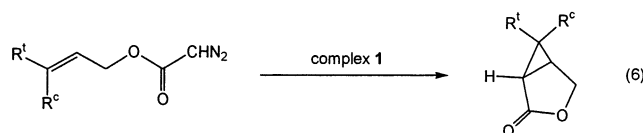
Catalytic Cyclopropanations by [Fe(TPFPP)(CPh_2)] (1). **(i) Intermolecular Cyclopropanation of Alkenes with EDA.** Although complex **1** was unable to cyclopropanate styrene stoichiometrically, it can catalyze intermolecular cyclopropanation of styrenes with EDA (reaction 5 in Table 3), providing a precedent for alkene cyclopropanation catalyzed by iron porphyrin *carbene* complex. The reactions were performed under the conditions similar to those employed for the [Fe(TPFPP)Cl]-catalyzed cyclopropanations.[7] The trans:cis ratios observed for the cyclopropanation of styrene (6.6:1) and α-methylstyrene (1.5:1) (see entries 1 and 5 in Table 3) by employing 0.1 mol % **1** are similar to those (6.0:1 and 1.1:1, respectively) found for the cyclopropanation of the same alkenes catalyzed by [Fe(TPFPP)Cl].[7] With a lower loading of **1** (0.02 mol %) and a slower addition of EDA, the cyclopropanation of styrene afforded a slightly higher trans:cis ratio of 7.0:1 (entry 2 in Table 3) and a high catalyst turnover number of 4410; the latter is similar to the 4200 catalyst turnovers reported for the [Fe(TPFPP)Cl]-catalyzed cyclopropanations.[7]

(ii) Intramolecular Cyclopropanation of Allylic Diazoacetates. Because there are much less reports on intramolecular

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Table 4. Intramolecular Cyclopropanation of Allylic Diazoacetates Catalyzed by [Fe(TPFPP)(CPh$_2$)] (**1**)[a]

$$R^t\!-\!C(R^c)\!=\!CH\!-\!CH_2\!-\!O\!-\!CO\!-\!CHN_2 \xrightarrow{\text{complex } \mathbf{1}} \text{bicyclic lactone} \quad (6)$$

entry	substrate R^c	R^t	additive	conversn (%)	yield[b] (%)
1	Ph	H		21	49
2	Ph	H	2,6-Cl$_2$Py	100	76
3	Me	Me	2,6-Cl$_2$Py	100	92
4	Et	H	2,6-Cl$_2$Py	100	62
5[c]	Me$_2$C=CH(CH$_2$)$_2$	Me	2,6-Cl$_2$Py	84	73
6	Me	Me$_2$C=CH(CH$_2$)$_2$	2,6-Cl$_2$Py	100	58

[a] Reaction conditions: CH$_2$Cl$_2$, 40 °C, 13 h; **1**:substrate = 1:200 or **1**:2,6-Cl$_2$Py:substrate = 1:1:200 (molar ratio). [b] Based on consumed substrate. [c] Molar ratio of **1**:2,6-Cl$_2$Py:substrate = 1:1:1000.

cyclopropanation of alkenes catalyzed by metalloporphyrins than by non-porphyrin metal complexes,[18d] we tested the catalytic behavior of **1** toward an intramolecular alkene cyclopropanation by examining the decomposition of a series of allylic diazoacetates N$_2$CHCO$_2$CH$_2$CH=CR^{c}R^t in the presence of 0.5 or 0.1 mol % complex **1**.
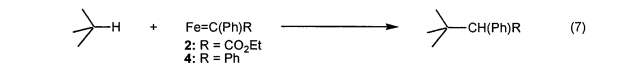
When a solution of the allylic diazoacetate with R^c = Ph and R^t = H in dichloromethane was slowly added to a solution of **1** in the same solvent at 40 °C, the corresponding bicyclic lactone[22] (see reaction 6 in Table 4) was obtained in 49% yield with substrate conversion of 21% (entry 1 in Table 4). Remarkably, addition of 2,6-Cl$_2$Py increased the yield of the lactone to 76% and resulted in complete substrate conversion (entry 2 in Table 4).

Treatment of other allylic diazoacetates with **1** in the presence of 2,6-Cl$_2$Py gave the respective lactones[22] in good-to-excellent yields (entries 3–6). The best result was obtained for N$_2$CHCO$_2$CH$_2$CH=CMe$_2$, whose decomposition afforded the corresponding lactone in 92% yield with 100% substrate conversion (entry 3 in Table 4).

The above decomposition of allylic diazoacetates catalyzed by **1** constitutes the first intramolecular alkene cyclopropanation catalyzed by iron porphyrin. Previously, we reported enantioselective intramolecular cyclopropanations of several allylic or homoallylic diazoacetates catalyzed by a chiral ruthenium porphyrin,[18d] which afford bicyclic lactones in up to 65% yield.

Stoichiometric C–H Insertion Reaction of [Fe(TPFPP)-(C(Ph)CO$_2$Et)] (2) or [Fe(TPFPP)(CPh$_2$)(MeIm)] (4) with Hydrocarbons. We examined the reactions of **2** or **4** with saturated C–H bonds of several types of hydrocarbons, including cyclohexene, cumene, and tetrahydrofuran (which can be considered as an activated hydrocarbon). All these reactions were found to effect insertion of the carbene group of **2** or **4** into a C–H bond of the organic substrates (reaction 7[20] in Table 5). The major byproducts in the reactions are the respective carbene coupling product EtO$_2$CC(Ph)=C(Ph)CO$_2$Et or Ph$_2$C=CPh$_2$.

Our previous work demonstrates that the bis(carbene)osmium porphyrin [Os(TPFPP)(CPh$_2$)$_2$] reacts with cyclopentene or

Table 5. Stoichiometric C–H Insertion Reactions of [Fe(TPFPP)(C(Ph)CO$_2$Et)] (**2**) or [Fe(TPFPP)(CPh$_2$)(MeIm)] (**4**) with Alkenes or Tetrahydrofuran

$$\text{(CH$_3$)$_3$C–H} + \text{Fe=C(Ph)R} \longrightarrow \text{(CH$_3$)$_3$C–CH(Ph)R} \quad (7)$$
2: R = CO$_2$Et **4**: R = Ph

entry	complex	alkene	temperature (°C)	reaction time (h)	product	yield (%)
1	2	cyclohexene	80	24	cyclohexenyl-CH(Ph)R	64[a]
2	4	cyclohexene	80	36		24
3	2	tetrahydrofuran	65	24	THF-CH(Ph)CO$_2$Et	88[b]
4	2	cumene	80	15	cumyl-CH(Ph)R	83
5	2	cumene	60	24		67
6	2	cumene	25	48		15
7	4	cumene	80	20		59

[a] A mixture of two diastereomers in a molar ratio of 1.2:1. [b] A mixture of two diastereomers in a molar ratio of 2:1.

cyclohexene at 80 °C for 24 h to form allylic C–H insertion product 3-(diphenylmethyl)cyclopentene or -cyclohexene in ∼80% yield.[11] In this work, we found that reaction of the monocarbene iron porphyrin **2** with cyclohexene under similar conditions afforded the corresponding allylic C–H insertion product as a 1.2:1 mixture of two diastereomers[23] in 64% yield (entry 1 in Table 5). Complex **4** can also react with cyclohexene at 80 °C, but the reaction gave the 3-(diphenylmethyl)cyclohexene in a lower yield of 24% after 36 h (entry 2 in Table 5).

Treatment of **2** with tetrahydrofuran at 65 °C for 24 h resulted in a regiospecific insertion of the C(Ph)CO$_2$Et carbene group into the α-C–H bond of tetrahydrofuran, similar to the C–H insertion reaction of tungsten arylcarbene (CHPh and CH(*p*-C$_6$H$_4$Me)) complexes with the same organic substrate.[24] The C–H insertion product[25] was isolated in 88% yield as a 2:1 mixture of two diastereomers (entry 3 in Table 5), and the major and minor diastereomers show their C*H*(Ph)CO$_2$Et proton resonance at δ = 2.52 and 2.62, respectively. Such a diastereoselectivity is the inverse of that observed for the rhodium complex-catalyzed C–H insertion of C(Ph)CO$_2$Me into the α-C–H bond of tetrahydrofuran,[26] which features a diastereoselectivity of 1:2.3 (the major diastereomer shows the C*H*(Ph)-CO$_2$Me proton resonance at δ = 2.62).

It is interesting that both **2** and **4** are reactive toward cumene at 80 °C, leading to transfer of their carbene groups into a benzylic C–H bond, with 3-methyl-2,3-diphenylbutyric acid ethyl ester and cumyldiphenylmethane[27] obtained in 83 and 59% yields, respectively (entries 4 and 7 in Table 5). The yield of the C–H insertion product markedly decreased whereas that of the carbene coupling product increased when the reaction was carried out at lower temperatures. For example, treating **2** with cumene at 60 and 25 °C gave 3-methyl-2,3-diphenylbutyric acid ethyl ester in 67 and 15% yields (entries 5 and 6), accompanied by formation of EtO$_2$CC(Ph)=C(Ph)CO$_2$Et in 23 and 67% yields, respectively (at 80 °C, the yield of EtO$_2$CC-(Ph)=C(Ph)CO$_2$Et was 12%).

The benzylic C–H bond of cumene is apparently more reactive than the allylic C–H bonds of cyclohexene toward the carbene group of **2** or **4** (compare entries 1 and 4 or 2 and 7 in

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(23) Yadav, V. K.; Balamurugan, R.; Parvez, M.; Yamdagni, R. *J. Chem. Soc., Perkin Trans. 1* **2001**, 323.
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(26) Davies, H. M. L.; Hansen, T. *J. Am. Chem. Soc.* **1997**, *119*, 9075.
(27) Okamoto, A.; Snow, M. S.; Arnold, D. R. *Tetrahedron* **1986**, *42*, 6175.

Table 5). However, it is surprising that no significant amounts of C−H insertion products were detected in the reaction of **2** or **4** with ethylbenzene, which also contains benzylic C−H bonds. This reflects a high substrate selectivity (cumene vs ethylbenzene) in the C−H insertion reactions of **2** and **4**.[28] To our knowledge, besides complexes **2** and **4**, no other isolated metal carbene complexes have been reported to undergo *benzylic* C−H insertion reactions with *unfunctionalized* alkenes.

Conclusion

We have isolated and fully characterized a remarkably stable iron porphyrin nonheteroatom-stabilized carbene complex [Fe-(TPFPP)(CPh$_2$)] (**1**) and its MeIm adduct [Fe(TPFPP)(CPh$_2$)-(MeIm)] (**4**). The X-ray crystal structure determinations of **1** and **4** provide a direct measure of the trans influence of the MeIm ligand on the Fe=CPh$_2$ bond. We have also isolated and well characterized two additional iron porphyrin carbene complexes, [Fe(TPFPP)(C(Ph)CO$_2$Et)] (**2**) and [Fe(TPFPP)-(C(Ph)CO$_2$CH$_2$CH=CH$_2$)] (**3**); these α-phenyl-substituted (alkoxy-carbonyl)carbene complexes are far more stable than the putative [Fe(TPFPP)(CHCO$_2$Et)] intermediates in iron porphyrin-catalyzed cyclopropanation of alkenes with ethyl diazoacetate. The formation of **2** and **3** from [Fe(TPFPP)] and respective diazoacetates represents a convenient route to iron porphyrin (alkoxycarbonyl)carbene complexes. Our observations that reactions of [Fe(TPFPP)] with diazo compounds N$_2$C(Ph)R (R = Ph, CO$_2$Et) form the carbene complexes **1** and **2** and that **2** and **4** can react with styrenes to form cyclopropanes provide support for the intervention of [Fe(Por)(CHR)] or [Fe(Por)-(CHCO$_2$Et)] in the iron porphyrin-catalyzed cyclopropanations reported by Kodadek, Woo, and their co-workers.[5,7] The reactions of **2** and **4** with cyclohexene and cumene to form C−H insertion products create precedents for iron porphyrin-mediated carbon atom transfer into C−H bonds of hydrocarbons. More-over, this work contributes the first examples of (i) structurally characterized iron porphyrin (nonhalo)carbene or nonheteroatom-stabilized carbene complexes, (ii) isolated and fully characterized iron porphyrin carbene complexes that can cyclopropanate alkenes without photolysis, (iii) iron porphyrin carbene complexes that can catalyze alkene cyclopropanations, (iv) iron porphyrins that can catalyze intramolecular cyclopropanations, and (v) isolated monocarbene metal complexes that can undergo intermolecular carbon atom transfer into saturated C−H bonds of unfunctionalized alkenes.

Experimental Section

General Methods. All reactions were performed under an argon atmosphere unless otherwise specified. [Fe(TPFPP)Cl], pyridine, 2,6-dichloropyridine, and ethyl diazoacetate were purchased from Aldrich. The solvents (AR grade) were predried according to standard procedures. Styrene, 4-methylstyrene, 4-chlorostyrene, 4-methoxystyrene, 4-trifluoromethylstyrene, cyclohexene, cumene, and *N*-methylimidazole (all from Aldrich) were purified by distillation. N$_2$C(Ph)R (R = Ph,[29] CO$_2$Et, CO$_2$CH$_2$CH=CH$_2$[22,30]) and other allylic diazoacetates[22] were prepared by literature methods. [Fe^{II}(TPFPP)] was prepared in situ by reduction of [Fe^{III}(TPFPP)Cl] with Zn/Hg amalgam in benzene.[7] UV−

(28) The higher reactivity of cumene than that of ethylbenzene toward the C−H insertion reactions might stem from a higher activity of the tertiary benzylic C−H bond in the former than the secondary benzylic C−H bonds in the latter.
(29) Miller, J. B. *J. Org. Chem.* **1959**, *24*, 560.
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visible spectra were recorded on a HP 8453 diode array spectrophotometer; IR spectra on a Bio-Rad FTS165 spectrometer. FAB and ES (electrospray) mass spectra were measured on a Finnigan MAT 95 and a Finnigan LCQ quadrupole ion trap mass spectrometer, respectively. ^{1}H, ^{13}C, and ^{19}F NMR spectra were obtained on a Bruker DPX-300 FT-NMR spectrometer; chemical shifts were recorded relative to tetramethylsilane (^{1}H and ^{13}C) or CF$_3$COOH (^{19}F, δ −76.5). Mössbauer spectrum was measured on an Austin S-600 Mössbauer spectrometer at 288 K by placing the sample in a ^{57}Co radiation source, with the transmittances of the 14.4 keV γ-ray collected continuously over >48 h. GC-MS measurements were conducted on a HP G1800C GCD Series II spectrometer. Elemental analyses were carried out by the Institute of Chemistry, the Chinese Academy of Sciences.

Preparation of [Fe(TPFPP)(C(Ph)R)] (R = Ph, CO$_2$Et, CO$_2$-CH$_2$CH=CH$_2$). To a solution of [Fe(TPFPP)] (0.05 mmol) in benzene (100 mL) was added a solution of N$_2$C(Ph)R (0.10 mmol) in the same solvent (10 mL). The mixture was stirred for 10 h at room temperature and then evaporated to dryness in vacuo. The residue was purified by chromatography on a silicon gel column with benzene−hexane (1:1, v/v) as eluent, affording the desired product as a red solid.

[Fe(TPFPP)(CPh$_2$)] (1). Yield: 70%. Anal. Calcd for C$_{57}$H$_{18}$F$_{20}$N$_4$-Fe·0.5C$_6$H$_{14}$: C, 58.23; H, 2.04; N, 4.53. Found: C, 58.28; H, 2.37; N, 4.44. ^{1}H NMR (CDCl$_3$): δ 8.31 (s, 8H), 6.42 (t, *J* = 7.4 Hz, 2H), 6.00 (t, *J* = 7.7 Hz, 4H), 3.13 (d, *J* = 7.5 Hz, 4H). ^{13}C NMR (CDCl$_3$): δ 358.98 (Fe=C). ^{19}F NMR (CDCl$_3$): δ −135.53 (dd), −136.16 (dd), −151.50 (t), −160.95 (dt), −161.03 (dt). UV−vis (1.12 × 10^{-5} M, CH$_2$Cl$_2$): λ_{max} (log ϵ) 404 (5.07), 524 (4.00), 557 nm (4.14). FAB MS: *m/z* 1194 (M$^+$), 1028 ([M − CPh$_2$]$^+$).

[Fe(TPFPP)(C(Ph)CO$_2$Et)] (2). Yield: 67%. Anal. Calcd for C$_{54}$H$_{18}$F$_{20}$N$_4$O$_2$Fe·0.5CH$_2$Cl$_2$ (a product recrystallized from CH$_2$Cl$_2$/C$_6$H$_{14}$): C, 53.09; H, 1.55; N, 4.54. Found: C, 52.83; H, 1.53; N, 4.94. ^{1}H NMR (CDCl$_3$): δ 8.56 (s, 8H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.09 (t, *J* = 7.6 Hz, 2H), 3.40 (d, *J* = 7.9 Hz, 2H), 2.62 (q, *J* = 7.1 Hz, 2H), 0.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (CDCl$_3$): δ 327.47 (Fe=C). ^{19}F NMR (CDCl$_3$): δ −136.34 (dd), −137.00 (dd), −151.92 (t), −161.56 (dt), −161.66 (dt). UV−vis (5.97 × 10^{-6} M, CH$_2$Cl$_2$): λ_{max} (log ϵ) 402 (5.11), 521 (4.02), 555 nm (4.12). FAB MS: *m/z* 1190 (M$^+$), 1028 ([M − C(Ph)CO$_2$Et]$^+$).

[Fe(TPFPP)(C(Ph)CO$_2$CH$_2$CH=CH$_2$)] (3). Yield: 65%. Anal. Calcd for C$_{55}$H$_{18}$F$_{20}$N$_4$O$_2$Fe·1.5C$_6$H$_6$·0.5CH$_2$Cl$_2$ (a product recrystallized from benzene/CH$_2$Cl$_2$/C$_6$H$_{14}$): C, 56.87; H, 2.07; N, 4.11. Found: C, 56.91; H, 2.23; N, 3.86. ^{1}H NMR (CDCl$_3$): δ 8.55 (s, 8H), 6.75 (t, *J* = 7.4 Hz, 1H), 6.08 (t, *J* = 7.9 Hz, 2H), 4.92−4.81 (m, 1H), 4.64−4.60 (dd, *J* = 10.4, 1.1 Hz, 1H), 4.45−4.39 (dd, *J* = 17.1, 1.4 Hz, 1H), 3.39 (d, *J* = 7.5 Hz, 2H), 3.04 (d, *J* = 5.9 Hz, 2H). ^{13}C NMR (CDCl$_3$): δ 325.67 (Fe=C). ^{19}F NMR (CDCl$_3$): δ −136.22 (dd), −137.00 (dd), −151.88 (t), −161.53 (dt), −161.65 (dt). UV−vis (7.98 × 10^{-6} M, CH$_2$Cl$_2$): λ_{max} (log ϵ) 402 (5.03), 521 (3.91), 555 nm (4.01). ES MS: *m/z* 1202 (M$^+$), 1028 ([M − C(Ph)CO$_2$CH$_2$CH=CH$_2$]$^+$).

Preparation of [Fe(TPFPP)(CPh$_2$)(MeIm)] (4). A solution of **1** (50 mg, 0.04 mmol) in dichloromethane (5 mL) containing MeIm (8.2 mg, 0.1 mmol) was stirred for 15 min at room temperature. Addition of hexane (15 mL) to the solution followed by evaporation of the mixture in vacuo led to formation of a red precipitate. The precipitate was collected by filtration, washed with hexane, and dried. Yield: 65%. Anal. Calcd for C$_{61}$H$_{24}$F$_{20}$N$_6$Fe: C, 57.39; H, 1.89; N, 6.58. Found: C, 57.67; H, 1.95; N, 6.14. ^{1}H NMR (CDCl$_3$): δ 8.23 (s, 8H), 6.36 (t, *J* = 7.4 Hz, 2H), 6.06 (t, *J* = 7.7 Hz, 4H), 3.13 (d, *J* = 7.3 Hz, 4H) (measured in the presence of free MeIm). ^{13}C NMR (CDCl$_3$): δ 385.44 (Fe=C) (measured in the presence of free MeIm). UV−vis (8.85 × 10^{-6} M, CH$_2$Cl$_2$): λ_{max} (log ϵ) 403 (5.24), 524 (4.20), 557 nm (4.29). FAB MS: *m/z* 1194 ([M − MeIm]$^+$).

Stoichiometric Cyclopropanation of Styrene by [Fe(TPFPP)-(C(Ph)CO$_2$Et)] (2) or [Fe(TPFPP)(CPh$_2$)(MeIm)] (4). A solution of **2** or **4** (0.015 mmol) and styrene (1.0 g, 9.6 mmol) in benzene (2 mL) was stirred at 60 °C for 15 h (**2**) or at 80 °C for 12 h (**4**). The resultant

mixture was then evaporated to dryness in vacuo. The crude cyclo-propanation product thus obtained was purified by chromatography on a silica gel plate with ethyl acetate/hexane (1:9, v/v).

Competitive Cyclopropanation of Styrene and *Para*-Substituted Styrene by [Fe(TPFPP)(C(Ph)CO$_2$Et)] (2). A mixture of **2** (18.0 mg, 0.015 mmol), styrene (416.6 mg, 4.0 mmol), and *para*-substituted styrene (4.0 mmol) was stirred at 60 °C for 15 h. The mixture was then evaporated to dryness in vacuo. After chromatography of the residue on a silica gel plate with ethyl acetate/hexane (1:9, v/v), the ratio of the cyclopropyl esters derived from *para*-substituted styrene and styrene was determined by GC-MS and ^{1}H NMR spectroscopy.

Intermolecular Cyclopropanation of Alkenes with EDA Catalyzed by [Fe(TPFPP)(CPh$_2$)] (1). Complex **1** (3.0 mg, 2.5 μmol) and alkene (50.4 mmol) were dissolved in dichloromethane (1 mL). To this solution was added a solution of ethyl diazoacetate (287.4 mg, 2.52 mmol) in dichloromethane (10 mL) using a syringe pump over 4 h at room temperature. The reaction mixture was stirred for 1 h and then evaporated to dryness in vacuo. The crude cyclopropyl esters thus obtained were purified by chromatography on a silica gel column with diethyl ether/hexane (1:5, v/v) as eluent.

Intramolecular Cyclopropanation of Allylic Diazoacetates Catalyzed by [Fe(TPFPP)(CPh$_2$)] (1). Complex **1** (3.0 mg, 2.5 μmol) and 2,6-dichloropyridine (0.37 mg, 2.5 μmol) were dissolved in dichloromethane (1 mL). To this solution was added a solution of allylic diazoacetate (0.50 mmol) in dichloromethane (10 mL) using syringe pump over 12 h at 40 °C. The reaction mixture was stirred for 1 h and then evaporated to dryness in vacuo. The bicyclic lactone thus obtained was purified by chromatography on a silica gel column with diethyl ether/hexane (1:5, v/v) as eluent.

Typical Procedures of Stoichiometric C–H Insertion Reaction of [Fe(TPFPP)(C(Ph)CO$_2$Et)] (2) or [Fe(TPFPP)(CPh$_2$)(MeIm)] (4) with Hydrocarbons. A mixture of **2** or **4** (0.015 mmol) and cumene (1.0 mL) was stirred at 80 °C for 15 or 20 h. The mixture was then

evaporated to dryness in vacuo. The products were separated by chromatography on a silica gel plate with ethyl acetate/hexane (1:9, v/v).

X-ray Crystal Structure Determinations. A diffraction-quality crystal of **1** in the form **1**·0.5C$_6$H$_6$·0.5CH$_2$Cl$_2$ (0.10 × 0.16 × 0.18 mm, red prism) was grown from a slow evaporation of a solution of **1** in dichloromethane/benzene/hexane exposed to the atmosphere at room temperature, whereas that of **4** (0.10 × 0.12 × 0.18 mm, dark red prism) was grown from a solution of **4** in dichloromethane/hexane at −5 °C under nitrogen. The data were collected at 294(2) K in the θ range of 1.7−27.5° (**1**·0.5C$_6$H$_6$·0.5CH$_2$Cl$_2$) or 1−27.5° (**4**) on a Bruker CCD SMART system by using graphite-monochromatized Mo Kα source (λ = 0.710 73 Å). The structures were refined by full-matrix least squares on F^2 by employing the SHELXL programs.

Supporting Information Available: Text providing characterization of cyclopropanation and C–H insertion products, tables of final coordinates, bond lengths, bond angles, and anisotropic displacement parameters for **1**·0.5C$_6$H$_6$·0.5CH$_2$Cl$_2$ and **4**, and ORTEP drawings of **1**·0.5C$_6$H$_6$·0.5CH$_2$Cl$_2$ and **4** with the atom-numbering schemes (Figures S1 and S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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