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Nonheme Iron-Mediated Amination of $C(sp^3)-H$ Bonds. Quinquepyridine-Supported Iron-Imide/Nitrene Intermediates by Experimental Studies and DFT Calculations

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Supporting Information

ABSTRACT: The 7-coordinate complex $[Fe(qpy)(MeCN)_2](ClO_4)_2$ (**1**, qpy = 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine) is a highly active nonheme iron catalyst for intra- and intermolecular amination of $C(sp^3)-H$ bonds. This complex effectively catalyzes the amination of limiting amounts of not only benzylic and allylic $C(sp^3)-H$ bonds of hydrocarbons but also the $C(sp^3)-H$ bonds of cyclic alkanes and cycloalkane/linear alkane moieties in sulfamate esters, such as those derived from menthane and steroids cholane and androstane, using PhI═NR or "$PhI(OAc)_2$ + H_2NR" [R = Ts (*p*-toluenesulfonyl), Ns (*p*-nitrobenzenesulfonyl)] as nitrogen source, with the amination products isolated in up to 93% yield. Iron imide/nitrene intermediates $[Fe(qpy)(NR)(X)]^{n+}$ ($\mathbf{C_X}$, X = NR, solvent, or anion) are proposed in these amination reactions on the basis of experimental studies including ESI-MS analysis, crossover experiments, Hammett plots, and correlation with C−H bond dissociation energies and with support by DFT calculations. Species consistent with the formulations of $[Fe(qpy)(NTs)_2]^{2+}$ ($\mathbf{C_{NTs}}$) and $[Fe(qpy)(NTs)]^{2+}$ (**C**) were detected by high-resolution ESI-MS analysis of the reaction mixture of **1** with PhI═NTs (4 equiv). DFT calculations revealed that the reaction barriers for H-atom abstraction of cyclohexane by the ground state of 7-coordinate $\mathbf{C_{NTs}}$ and ground state of **C** are 15.3 and 14.2 kcal/mol, respectively, in line with the observed high activity of **1** in catalyzing the C−H amination of alkanes under mild conditions.

■ INTRODUCTION

Metal-mediated amination of $C(sp^3)-H$ bonds via reactive metal−imide (or nitrene) intermediates is an appealing methodology for C−N bond formation.[1] Development of iron catalysis[2] for such amination reactions is important because of the natural abundance and biocompatibility of iron. In literature, there have been extensive works on the functionalization of $C(sp^3)-H$ bonds catalyzed by iron-containing enzymes, including alkane hydroxylation by heme iron enzymes, such as cytochrome P-450,[3] and by nonheme iron enzymes, such as methane monooxygenase,[4] both being proposed to involve iron−oxo intermediates. Hydroxylation of $C(sp^3)-H$ bonds using nonheme iron catalysts has also been extensively studied over the past decades.[5] Iron-imide/nitrene complexes are nitrogen analogues of iron-oxo species. However, studies on nonheme iron-catalyzed amination of $C(sp^3)-H$ bonds via nitrogen group insertion are sparse,[6] with the reported examples mostly confined to benzylic C−H bonds. Other types of catalytic nitrogen group transfer reactions such as C═C aziridination via proposed nonheme iron−imide/nitrene intermediates have also been well documented in literature.[7−14] Characterizations of the iron−imide/nitrene intermediates involved in these reported catalytic reactions, however, are scarce.[6d,10] Remarkably, a number of nonheme iron−imide complexes having 3-,[15] 4-,[6d,10,16] and 5-coordination numbers[17] (**I**−**VI**, Figure 1) have been structurally characterized by X-ray crystal analysis,[18] some of which exhibit interesting reactivity.[19−23] For example, a 3-coordinate complex (**I**), or a 4-coordinate complex formed by binding of *tert*-butylpyridine to its 3-coordinate counterpart (**I**), can undergo H-atom abstraction of allylic 2° $C(sp^3)-H$ bonds of cyclic alkenes/dienes,[15c,21a,b] and a 4-coordinate complex (**IV**) aminates the benzylic 1° $C(sp^3)-H$ bond of toluene.[6d] Iron−imide complexes having coordination numbers >5 are also reactive, presumably this is due to the elongated Fe−N(imide) distance resulting from population of electrons in the Fe−N π antibonding orbitals.[24] An example is the 6-coordinate complex (**VII**, Figure 1) which was characterized by spectroscopic methods and examined by DFT calculations.[24] Two proposed reactive 6-coordinate nonheme iron−imide intermediates (**A**[25a] and **B**,[25b] Figure 1) have been reported to convert to iron−amide complexes via intramolecular amination of the $C(sp^2)-H$ bond(s) of pendant phenyl group in their coligands.[26]

Development of nonheme iron catalysts for intermolecular amination of strong $C(sp^3)-H$ bonds of alkanes[27] is a challenge. The amination of cyclohexane $C(sp^3)-H$ bond was first reported in 1982 with synthetic heme iron catalyst[28]

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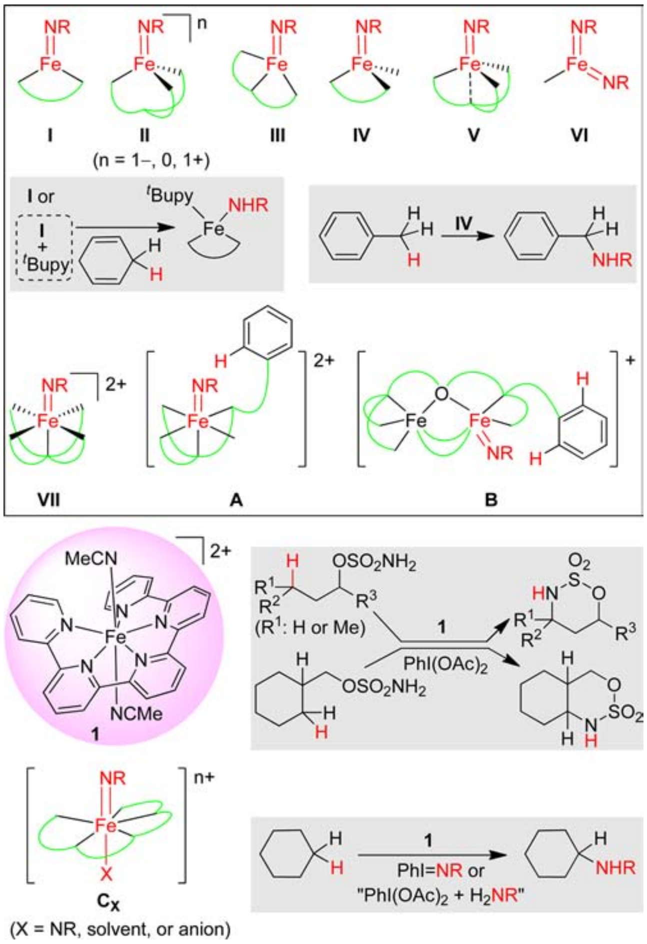


Figure 1. Top: Types of nonheme iron−imide/nitrene complexes reported in literature (**I**−**VI**: structurally characterized, **VII**: characterized by spectroscopic methods; **A** and **B**: proposed) and intermolecular reaction with C(sp^3)−H bonds. Bottom: Findings in this work including amination of C(sp^3)−H bond of cyclohexane catalyzed by 7-coordinate **1**, along with proposed iron−imide/nitrene intermediates $\mathbf{C_X}$ based on experimental studies and DFT calculations. For simplicity, the iron−imide/nitrene coordination is generally depicted as Fe═NR.

and in 1985 with cytochrome P-450 enzyme;[29] subsequently there have been further developments of C(sp^3)−H bond amination catalyzed by heme[6a,30] and heme-like[31] iron complexes. The few literatures on nonheme iron-catalyzed amination of saturated alkanes are in contrast to many studies involving hydroxylation of saturated alkanes, including the typical cycloalkanes catalyzed by nonheme iron complexes.[32]

In our quest for nonheme iron catalysts for amination of C(sp^3)−H bonds of alkanes, we are interested in exploring the possibility of generating highly reactive bis(imide/nitrene) iron species using robust, strongly chelating N-donor ligand systems. Complex [Fe(Ar)(NAd)$_2$] (i.e., **VI** in Figure 1, Ar = 3,5-^{i}Pr$_2$-2,6-(2′,4′,6′-^{i}Pr$_3$C$_6$H$_2$)$_2$-C$_6$H$_1$, Ad = adamantyl),[15a] the sole iron bis(imide) complex in literature, has a low-coordinate iron protected by sterically encumbered anionic monodentate coligand. The reactivity of **VI** has not been documented. A number of isolated reactive 6-coordinate ruthenium bis(imide) complexes supported by dianionic porphyrin ligands have been reported;[33] these complexes aminated benzylic and allylic 2° C(sp^3)−H bonds in good yields, but the yield for amination of C(sp^3)−H bond of cyclohexane was ∼10%.[33a] Use of neutral multidentate coligands would allow formation of highly reactive cationic metal bis(imide/nitrene) species; the cationic charge would enhance electrophilicity of the coordinated imide/nitrene groups.

Inspired by the intriguing oxidation catalysis of the structurally characterized 7-coordinate complex [Fe(qpy)(MeCN)$_2$](ClO$_4$)$_2$[34] (**1**, Figure 1; qpy is a neutral pentadentate ligand 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine)[35] with both [Fe(qpy)O]$^{2+}$ and [Fe(qpy)O$_2$]$^{2+}$ species detected by high-resolution electrospray ionization mass spectrometry (ESI-MS),[36] we examined the utility of **1**, which possesses two labile coordination sites to allow possible formation of iron bis(imide/nitrene) species, in iron imide/nitrene chemistry. Seven-coordinate iron is well documented[37] but remains little explored in the formation of iron imide species. In a recent report, the proposed nitrene transfer from PhI═NR mediated by 7-coordinate iron complex supported by hexadentate tris(2-picolyl)amine ligand 6,6′-(pyridin-2-ylmethylazanediyl)bis(methylene)bis(*N*-*tert*-butylpicolinamide) afforded iron mono(amide) complexes (likely from nitrene transfer with subsequent hydrogen atom abstraction).[38]

Herein we report that **1** is an active nonheme iron catalyst for intermolecular amination of the C(sp^3)−H bond of cycloalkanes (Figure 1) as well as for intramolecular amination of C(sp^3)−H bonds in sulfamate esters, using PhI═NR or "PhI(OAc)$_2$ + H$_2$NR" as nitrogen source. These catalytic C−H amination reactions feature high product yields and a broad substrate scope and hence are of practical interest in organic synthesis. The reactive iron−imide/nitrene intermediate(s) [Fe(qpy)(NR)(X)]$^{n+}$ ($\mathbf{C_X}$, Figure 1) is proposed for the catalysis, and species assignable to [Fe(qpy)(NTs)$_2$]$^{2+}$ ($\mathbf{C_{NTs}}$, Ts = SO$_2$-*p*-MeC$_6$H$_4$) and [Fe(qpy)(NNs)$_2$]$^{2+}$ ($\mathbf{C_{NNs}}$, Ns = SO$_2$-*p*-NO$_2$C$_6$H$_4$) have been detected by high-resolution ESI-MS analysis. The ESI-MS detection of [Fe(qpy)(NR)$_2$]$^{2+}$ ($\mathbf{C_{NR}}$, R = NTs, NNs) and its mono(imide/nitrene) counterparts (**C**), such as [Fe(qpy)(NTs)]$^{2+}$, the further experimental studies and DFT calculations altogether lend support to the intermediacy of $\mathbf{C_X}$ to be responsible for the C−H amination.

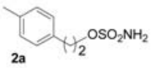
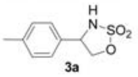
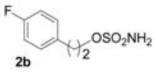
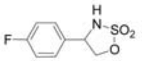
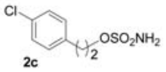
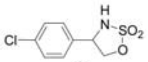
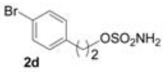
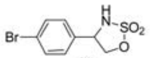
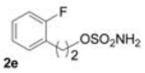
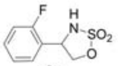
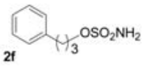
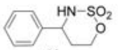
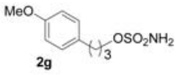
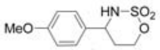
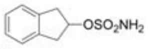
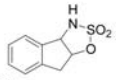
■ RESULTS

Prior to exploring the catalytic activity of **1** toward amination of C(sp^3)−H bonds, we found that **1** can catalyze nitrogen group transfer to alkenes, resulting in aziridination of styrenes with PhI═NTs or "PhI(OAc)$_2$ + H$_2$NR" (up to 89% yield) and intramolecular aziridination of unsaturated sulfonamides with PhI(OAc)$_2$ (up to 97% yield) (Tables S1 and S2). We also observed intramolecular amination of benzylic 2° C(sp^3)−H bonds of three sulfamate esters with PhI(OAc)$_2$ catalyzed by [Fe(Cl$_3$terpy)$_2$](ClO$_4$)$_2$ (Cl$_3$terpy =4,4′,4″-trichloro-2,2′:6′,2″-terpyridine).[6c] Earlier there had been several reports on metal-catalyzed intramolecular amination of sulfamate esters with PhI(OAc)$_2$,[39a,b] since the first examples reported in 2001 using dirhodium catalysts.[39a] A seminal study reported in 1983[6a] on metal-catalyzed intramolecular C−H bond amination employed a PhI═NR substrate prepared from PhI(OAc)$_2$ and H$_2$NR, wherein the R group contains reactive benzylic 3° C(sp^3)−H bond. In 2000 we reported that PhI═NR can be replaced by "PhI(OAc)$_2$ + H$_2$NR" in metal-catalyzed intermolecular C−H amination reactions.[40]

Intramolecular Amination of C(sp^3)−H Bonds of Sulfamate Esters. Using **1** as catalyst, a series of sulfamate ester substrates (**2a**−**p**) underwent intramolecular benzylic (2°) or aliphatic (3° or 2°) C−H amination to result in 100%

substrate conversion and cyclic sulfamidates (**3a**−**p**) in up to 92% isolated yield (Tables 1 and 2; the product turnover number (TON) is up to 18.4). Compared with [Fe(Cl_3terpy)$_2$](ClO_4)$_2$ which was reported to catalyze reaction of **2c**,**f**,**h** to give **3c**,**f**,**h**,[6c] catalyst **1** exhibited broader substrate scope, higher substrate conversions, and higher product yields. For benzylic substrates **2i**−**n** that have allylic (2°) or aliphatic (3°, 2°, or 1°) C(sp^3)−H bonds, the reaction preferentially gave benzylic 2° C−H amination products **3i**−**n** (59−89% isolated yields) that are mainly or completely in a *cis*-configuration; allylic (2°) and 3° C−H bonds were aminated with up to 21% product yield (Table 2). This preference of **1** for benzylic 2° C−H amination [benzylic/3° ratio = 3.2:1 (**3k**/**3k′**), 10:1 (**3l**/**3l′**); benzylic/allylic ratio = 2.8:1 (**3i**/**3i′**)] is different from preferential amination of 3° and allylic (2°) C−H bonds catalyzed by dirhodium [3°/benzylic ratio = up to 14:1 (**3k′**/**3k**)[39e,f]] and diruthenium complexes (allylic/benzylic ratio = 3.3:1),[39f] respectively. A heme-like iron catalyst (iron phthalocyanine complex [Fe(Pc)]$^+$) was recently reported to prefer amination of allylic (2°) C−H bonds over other types of C−H bonds (including benzylic 2° C−H bonds) in the intramolecular amination of sulfamate esters with PhI(OR)$_2$.[31] It is noteworthy that, while the 1° and nonbenzylic 2° C−H bonds in **2j**,**m** remained unfunctionalized, the 1° C−H bond in **2n** was appreciably aminated to give **3n′**, albeit in 6% yield (TON: 1.2).

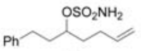
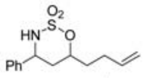
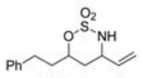
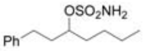
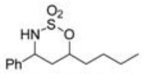
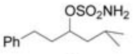
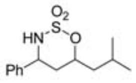
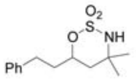
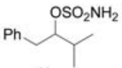
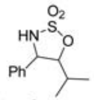
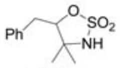
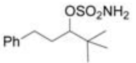
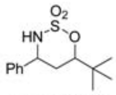
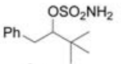
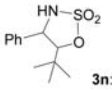
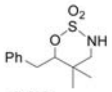
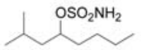
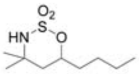
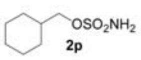
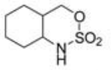
Table 1. Intramolecular Amination of Benzylic C(sp^3)−H Bonds of Sulfamate Esters Catalyzed by 1^a

entry	substrate	product	yield (%)^b
1	 **2a**	 **3a**	84
2	 **2b**	 **3b**	87
3	 **2c**	 **3c**	87
4	 **2d**	 **3d**	87
5^c	 **2e**	 **3e**	81
6	 **2f**	 **3f**	82
7^d	 **2g**	 **3g**	92
8^{d,e}	 **2h**	 **3h**	85

^{a}Reaction conditions: substrate/**1**/PhI(OAc)$_2$/MgO = 1:0.05:1.8:2.5, MeCN, 80 °C, 12 h; substrate conversion: 100%. ^{b}Isolated yield. ^{c}Substrate/**1**/PhI(OAc)$_2$/MgO = 1:0.05:2.1:3.0. ^{d}Substrate/**1**/PhI(OAc)$_2$/MgO = 1:0.05:1.4:2.3. ^{e}40 °C.

The catalytic activity of **1** toward amination of the aliphatic C(sp^3)−H bonds of **2o** and particularly **2p** (both are devoid of benzylic C(sp^3)−H bonds) encouraged us to extend the catalysis to intermolecular amination of cyclohexane and other cyclic alkanes (see below). For the amination of **2o** catalyzed by **1**, only 3° C−H amination product (**3o**) was observed (86% isolated yield, Table 2), and this is different from the formation of a mixture of 3° and 2° C−H amination products [3°/2° ratio = (4.5−20):1] in dirhodium-catalyzed amination of **2o**.[39e] Substrate **2p** was previously converted to 2° C−H amination product (**3p**) in yields of 51% (using a manganese catalyst)[41a] and 5% (using a copper catalyst);[41b] catalyst [Fe(Cl_3terpy)$_2$](ClO_4)$_2$ gave **3p** in 23% yield (*cis*/*trans* 1:1). A higher yield of 79% was obtained for **3p** using catalyst **1** (Table 2, the corresponding 3° C−H amination product was not detected).

Table 2. Intramolecular Amination of Various C(sp^3)−H Bonds of Sulfamate Esters Catalyzed by 1^a

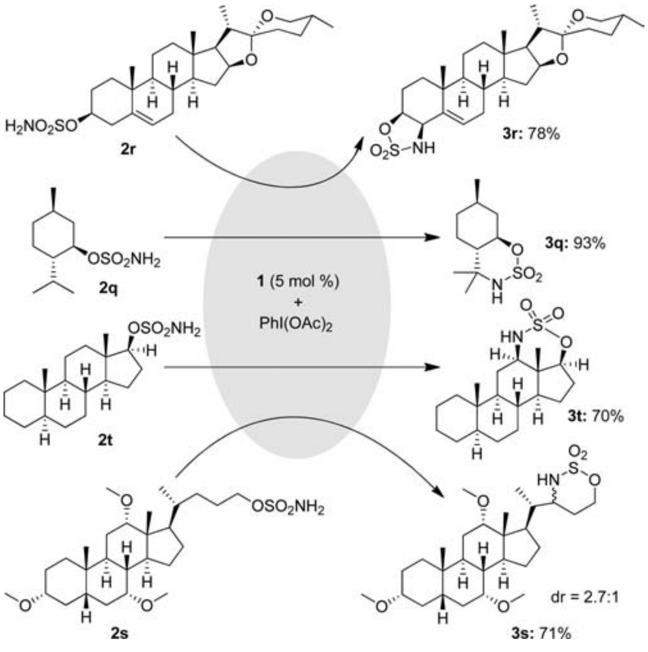
entry	substrate	product yield (%)^b	
1^c	 **2i**	 **3i**: 59 (9:1)^d	 **3i′**: 21 (2.5:1)^d
2^c	 **2j**	 **3j**: 89 (3:1)^d	
3	 **2k**	 **3k**: 68^e	 **3k′**: 21
4	 **2l**	 **3l**: 82^e	 **3l′**: 8
5	 **2m**	 **3m**: 85 (7:1)^d	
6	 **2n**	 **3n**: 81	 **3n′**: 6
7	 **2o**	 **3o**: 86	
8^c	 **2p**	 **3p**: 79 (1:1)^d	

^{a}Reaction conditions: substrate/**1**/PhI(OAc)$_2$/MgO = 1:0.05:1.4:2.3, MeCN, 80 °C, 12 h; substrate conversion: 100%. ^{b}Isolated yield. ^{c}Substrate/**1**/PhI(OAc)$_2$/MgO = 1:0.05:1.8:2.5. ^{d}*cis*/*trans* ratio. ^{e}*cis* only.

In view of the **1**-catalyzed amination of **2o** and **2p** selectively at acyclic 3° and cyclohexyl 2° C−H bonds, respectively, we prepared menthyl sulfamate ester **2q** which bears both types of C−H bonds. Under similar reaction conditions (**2q**/**1**/PhI(OAc)$_2$/MgO = 1:0.05:1.4:2.3), the cyclohexyl 2° C−H amination product of **2q** was not detected, whereas the 3° C−H amination product **3q** was obtained in 93% isolated yield (Scheme 1, substrate conversion: 100%).

We also examined the applicability of the "**1** + PhI(OAc)$_2$" protocol to selective amination of organic compounds with complexity, such as steroids bearing multiple cycloalkane

Scheme 1



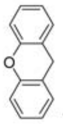
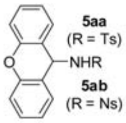
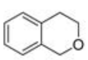
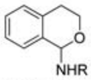
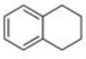
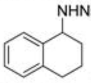
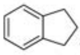
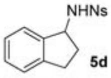
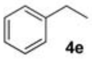
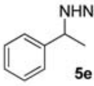
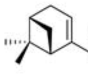
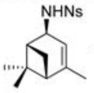
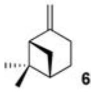
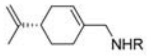
moieties. The substrates synthesized for this purpose included a spirost-5-ene derivative **2r**, a cholane derivative **2s**, and an androstane derivative **2t** (Scheme 1). When the reactions with substrate/**1**/PhI(OAc)$_2$/MgO ratio of 1:0.05:1.8:2.5 were performed at 80 °C for 12 h, the substrate conversion reached 100%. For **2r**, the amination occurred at allylic C−H bond to give **3r** in 78% isolated yield. Substrate **2s** underwent amination at a 2° C−H bond of the linear alkane chain moiety, with product **3s** isolated in 71% yield. Amination of **2t** afforded **3t**, a product resulting from amination of the 2° C−H bond of a cyclohexane moiety, in 70% isolated yield (Scheme 1).

Iron-catalyzed amination of steroids is rarely documented in literature. We are aware of one example,[31] in which case the catalyst was iron phthalocyanine complex [Fe(Pc)]$^+$ (a heme-like catalyst) with cholesteryl sulfamate ester as substrate, affording intramolecular allylic C−H amination product in 58% yield.

Intermolecular Amination of C(sp^3)−H Bonds of Benzylic and Allylic Hydrocarbons and Cyclic Alkanes. We employed cyclohexane, cyclopentane, cyclooctane, and adamantane as substrates in the study on the intermolecular amination catalyzed by **1**. Benzylic and allylic substrates were also used. Complex **1** exhibited a high catalytic activity in amination of alkanes as well as benzylic and allylic substrates, so that these substrates (except cyclopentane, see below) could be used as the limiting reagents in the reactions (like the **1**-catalyzed intramolecular reactions described above) without the need to be used in excess amounts (see Discussion section). The results obtained are depicted in Tables 3 and 4.

In the presence of catalyst **1** (5 mol %), reaction of the benzylic substrate xanthene (**4a**) with various nitrogen sources, including bromamine-T (NaBrNTs), PhI=NTs, PhI=NNs (Ns = SO$_2$-*p*-NO$_2$C$_6$H$_4$), and "PhI(OAc)$_2$ + H$_2$NTs", at 80 °C for 12 h gave benzylic 2° C−H amination products **5aa** or **5ab** (Table 3) in moderate-to-high yields. For the reactions with substrate/**1**/(nitrogen source) ratio of 1:0.05:1.5, the substrate conversions were 75%, 78%, 82%, and 81% for the four types of nitrogen sources, respectively; **5aa** was isolated in 54% and 55% yields (based on starting amount of substrate) using NaBrNTs and "PhI(OAc)$_2$ + H$_2$NTs", respectively, as nitrogen source. These isolated yields were lower than those of 58% (**5aa**) and 64% (**5ab**) obtained using nitrogen sources PhI=NTs and PhI=NNs.

Table 3. Intermolecular Amination of Benzylic and Allylic C(sp^3)−H Bonds Catalyzed by 1[a]

entry	substrate	nitrogen source	product	yield (%)[b]
1	 4a	PhI=NTs	 5aa (R = Ts) 5ab (R = Ns)	75 (**5aa**)
2		PhI=NNs		81 (**5ab**)
3	 4b	PhI=NTs	 R = Ts **5ba**, Ns **5bb**	80 (**5ba**)
4		PhI=NNs		86 (**5bb**)
5	 4c	PhI=NNs	 5c	76
6	 4d	PhI=NNs	 5d	79
7[c]	 4e	PhI=NNs	 5e	67
8	 6a	PhI=NNs	 7a	53
9	 6b	PhI=NTs	 R = Ts **7ba**, Ns **7bb**	63 (**7ba**)
10		PhI=NNs		57 (**7bb**)

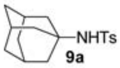
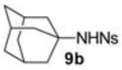
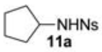
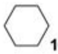
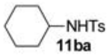
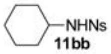
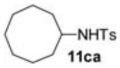
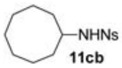
[a] Reaction conditions: substrate/**1**/(nitrogen source) = 1:0.05:2.0, 80 °C, 12 h; substrate conversion: 100%. [b] Isolated yield. [c] Substrate/**1**/nitrogen source = 1:0.05:2.2.

Complete substrate conversion was achieved for the reactions of **4a** with PhI=NR (R = Ts, Ns) at substrate/**1**/(PhI=NR) ratio of 1:0.05:2.0, leading to the isolated yields of 75% for **5aa** and 81% for **5ab** (entries 1 and 2, Table 3). Under the same or similar reaction conditions, isochroman (**4b**), 1,2,3,4-tetrahydronaphthalene (**4c**), indan (**4d**), and ethylbenzene (**4e**) were aminated at their benzylic 2° C−H bonds to give **5b**−**e** in 67−86% isolated yields (entries 3−7, Table 3; substrate conversion: 100%).

Allylic amination catalyzed by **1** was performed using natural products *α*-pinene (**6a**) and *β*-pinene (**6b**) under the same conditions as those for the amination of **4a**. With PhI=NNs as nitrogen source, *α*-pinene was converted to the allylic C−H bond amination product **7a** in 53% isolated yield (entry 8, Table 3). For the reaction of *β*-pinene with PhI=NNs and PhI=NTs, the rearranged amination products **7bb** and **7ba** were obtained in 57% and 63% yields, respectively (entries 10 and 9, Table 3).

It is striking that **1** is active to catalyze intermolecular amination of cyclohexane, cyclopentane, cyclooctane, and adamantane with PhI=NTs, PhI=NNs, or "PhI(OAc)$_2$ + H$_2$NR (R = Ts or Ns)". These alkanes, compared with the more reactive benzylic substrates **4a**−**e** and allylic substrates

Table 4. Intermolecular Amination of C(sp^3)−H Bonds of Cycloalkanes Catalyzed by **1**[a]

entry	substrate	nitrogen source	conv (%)[b]	product	yield (%)[c]
1	 **8**	PhI=NTs	73	 **9a**	63 (86^d)
2	 **8**	PhI=NNs	75	 **9b**	51 (68^d)
3[e]	 **10a**	PhI=NNs	-	 **11a**	52^f
4	 **10b**	PhI=NTs	49	 **11ba**	33 (68^d)
5	 **10b**	PhI=NNs	56	 **11bb**	41 (73^d)
6	 **10c**	PhI=NTs	52	 **11ca**	38 (74^d)
7		$PhI(OAc)_2$ + H_2NTs	42		27 (64^d)
8	 **10c**	PhI=NNs	60	 **11cb**	49 (82^d)
9		$PhI(OAc)_2$ + H_2NNs	49		37 (76^d)

[a]Reaction conditions. [g]Substrate/**1**/nitrogen source = 1:0.1:1.5, 80 °C, 24 h. [b]Determined by GC or ^{1}H NMR. [c]Isolated yield based on starting amount of substrate. [d]Yield based on conversion. [e]Substrate/**1**/(PhI=NNs) = 100:0.1:1 (due to the low boiling point of **10a**). [f]Isolated yield based on PhI=NNs.

6a,**b**, were aminated using a higher catalyst loading of 10 mol % and a longer reaction time of 24 h. For adamantane (**8**), the amination with PhI=NTs and PhI=NNs gave 3° C−H bond amination products **9a**,**b**, respectively, in up to 63% isolated yield (86% based on substrate conversion) (entries 1 and 2 in Table 4). Cyclopentane (**10a**) has a relatively low boiling point; this alkane was used in excess amount in its reaction with PhI=NNs giving **11a** in 52% yield (entry 3, Table 4). The amination of limiting reagents cyclohexane (**10b**) and cyclooctane (**10c**) by PhI=NTs and PhI=NNs afforded **11ba**/**11bb** and **11ca**/**11cb** in 33−49% isolated yields (68−82% based on substrate conversion) (entries 4−6 and 8, Table 4).

Notably, in the **1**-catalyzed amination of each of the cyclic alkanes (**8**, **10a**−**c**), only a single amination product was detected in the reaction mixture. For comparison, a mixture of amination products was detected in the amination of adamantane by excess amounts of "$FeCl_2$ + chloroamine-T" unless trapping reagents, such as SO_2Cl_2 or H_2S, were added after the reaction.[14]

Kinetic isotope effect (KIE) was investigated for the amination of cyclohexane with PhI=NTs using catalyst **1**. The k_H/k_D values determined at different temperatures were 3.4 (80 °C), 3.7 (50 °C), and 4.0 (25 °C).

For the amination of *para*-substituted ethylbenzenes p-YC_6H_4Et (Y = OMe, Me, H, Cl, Br, NO_2) with PhI=NTs catalyzed by **1**, the plot of log k_R vs σ_P^+ (k_R: relative amination rate) exhibited a linearity with $R = 0.98$ ($\rho = -0.55$) (Figure S1). A linear relationship between log k_R and σ_P^+ was also found for the **1**-catalyzed amination of ethylbenzene with $PhI{=}NSO_2$-p-YC_6H_4 (Y = OMe, Me, H, Cl, NO_2; $R = 0.98$, $\rho = 1.14$; Figure S2). The **1**-catalyzed amination of 9,10-dihydroanthracene, fluorene, cumene, ethylbenzene, cyclooctane, and cyclohexane with PhI=NTs well correlates with the C−H bond dissociation energy (BDE) of these hydrocarbons, as shown by the plot of log k' vs BDE (Figure S3).

In addition, we examined the catalytic behavior of $[Fe(Cl_3terpy)_2](ClO_4)_2$ and $[Fe(N4Py)(MeCN)](ClO_4)_2$ (N4Py = *N*,*N*-bis(2-pyridylmethyl)bis(2-pyridyl)methylamine)[42] toward amination of benzylic and alkane substrates. For the amination of ethylbenzene (**4e**) with PhI=NTs at a substrate/catalyst/(PhI=NTs) ratio of 1:0.05:1.5 at 80 °C, examination of the time course of the reaction (Figure 2) revealed that $[Fe(N4Py)(MeCN)](ClO_4)_2$ led to no detectable substrate conversion after 12 h, in contrast to a 47% substrate conversion obtained using catalyst **1** (the benzylic amination product was obtained in 37% yield (79% based on conversion, TON = 7.4) under the same reaction conditions. No amination of cyclic alkanes (such as cyclohexane) was found for catalysts $[Fe(Cl_3terpy)_2](ClO_4)_2$ and $[Fe(N4Py)(MeCN)](ClO_4)_2$ for a reaction time of 24 h (under similar conditions to those indicated in Table 4).

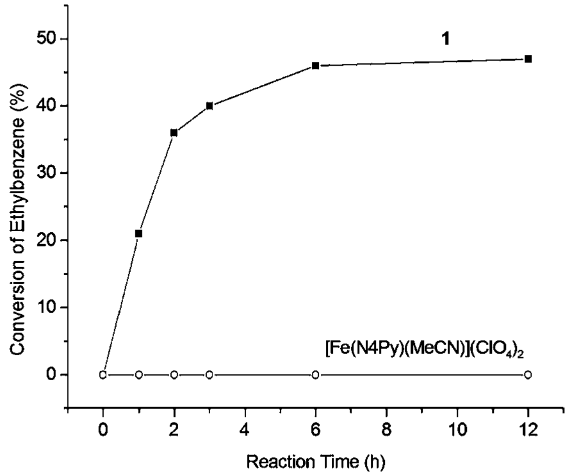


Figure 2. Time course plots for amination of ethylbenzene with PhI=NTs in MeCN catalyzed by **1** (■) and $[Fe(N4Py)(MeCN)](ClO_4)_2$ (○) under the same reaction conditions (substrate/catalyst/(PhI=NTs) = 1:0.05:1.5, 80 °C).

High-Resolution ESI-MS Studies. We monitored the reaction of **1** with PhI=NTs (4 equiv) in MeCN by ESI-MS. The spectrum of the reaction mixture showed a prominent cluster peak at m/z 306.05 assignable to $[Fe(qpy)(NTs)]^{2+}$ (calcd m/z 306.05) based on m/z value, isotope pattern, and collision-induced dissociation (Figure S4).

Remarkably, a minor cluster peak at m/z 390.56 assignable to $[Fe(qpy)(NTs)_2]^{2+}$ (calcd m/z 390.56) was also observed. The formulation of $[Fe(qpy)(NTs)_2]^{2+}$ is consistent with collision-induced dissociation experiment and high-resolution mass spectral data. As depicted in Figure 3, at a collision energy of 25 eV, the $[Fe(qpy)(NTs)_2]^{2+}$ species dissociates into fragments $[Fe(qpy)(NTs)]^{2+}$ and $[Fe(qpy)]^{2+}$ by loss of one and two NTs moieties, respectively. The observed m/z value of 390.5479 in the high-resolution ESI-MS closely matches that of 390.5615 calculated for $[Fe(qpy)(NTs)_2]^{2+}$, with a good agreement between the observed and simulated isotope patterns (see the inset of Figure 3). Similarly, analysis of the reaction mixture containing **1** and PhI=NNs by ESI-MS revealed a minor cluster peak at m/z 421.5368 assignable to $[Fe(qpy)(NNs)_2]^{2+}$ (calcd m/z 421.5332, Figure S5).

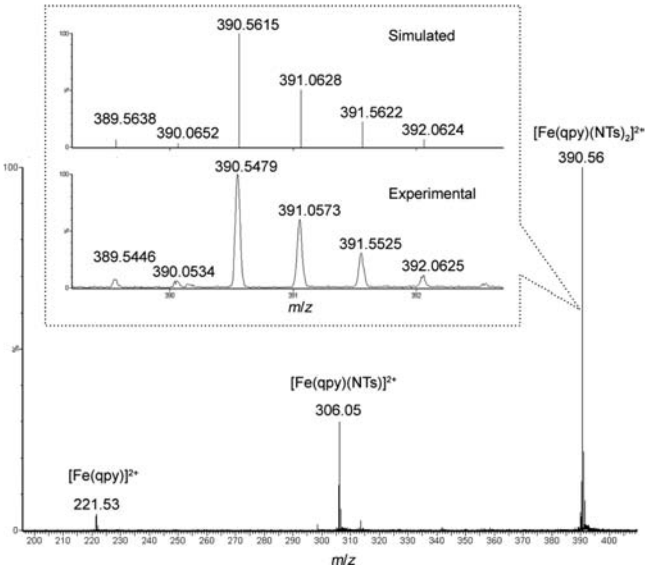


Figure 3. Collision-induced dissociation for the ion (m/z 390.56) assigned to $[Fe(qpy)(NTs)_2]^{2+}$ (collision energy: 25 eV).

When **1** was mixed with PhI═NTs in a 1:1 (instead of 1:4) ratio, analysis of the reaction mixture by ESI-MS revealed a prominent cluster peak at m/z 711.06 which can be assigned to $[Fe(qpy)(NTs)(ClO_4)]^+$ (calcd m/z 711.05, Figure S6). From the mass spectra of the 1:1 mixture of **1** with PhI═NTs, we did not find cluster peak assignable to $[Fe(qpy)(NTs)_2]^{2+}$.

As imide/nitrene intermediates might be prone to dimerization,[12] a doubly charged iron diazene complex, such as $[Fe(qpy)(RN{=}NR)]^{2+}$ which would give the same m/z value and isotope pattern as those of $[Fe(qpy)(NR)_2]^{2+}$, should be considered. We made efforts but were not successful to obtain TsN═NTs following a procedure included in the Supporting Information of a recent report.[43] We then turned to examine the feasibility of generating $[Fe(qpy)(RN{=}NR)]^{2+}$ (R = p-$MeOC_6H_4$) by mixing **1** with (p-$MeOC_6H_4$)N═N(C_6H_4-p-MeO)[44] (10 equiv) in MeCN (under the conditions similar to those for ESI-MS analysis of the mixture of **1** with PhI═NTs (4 equiv)). Analysis of such a reaction mixture by high-resolution ESI-MS did not reveal the cluster peak attributed to $[Fe(qpy)(RN{=}NR)]^{2+}$ (R = p-$MeOC_6H_4$) nor to its dimerized form $[Fe_2(qpy)_2(RN{=}NR)_2]^{4+}$. Monitoring the time course of the intensity of the above-mentioned cluster peaks at m/z 306.05 (assignable to $[Fe(qpy)(NTs)]^{2+}$) and m/z 390.56 (assignable to $[Fe(qpy)(NTs)_2]^{2+}$) revealed that the latter species was considerably less stable than the former and rapidly lost intensity after ~3 min, with concomitant increase in the intensity of the former (Figure S7). The dimerized form of $[Fe(qpy)(TsN{=}NTs)]^{2+}$, i.e. $[Fe_2(qpy)_2(TsN{=}NTs)_2]^{4+}$ (calcd m/z 390.56) has not been detected; this quadruply charged ion should have a markedly different isotope pattern from that of the observed species at m/z 390.56. These findings, together with the collision-induced dissociation (Figure 3) and the absence of the cluster peak at m/z 390.56 (assignable to $[Fe(qpy)(NTs)_2]^{2+}$) in the mass spectrum of the 1:1 mixture of **1** with PhI═NTs, do not lend support for assignment of the cluster peak at m/z 390.56 to $[Fe(qpy)(TsN{=}NTs)]^{2+}$ but are consistent with the assignment to $[Fe(qpy)(NTs)_2]^{2+}$.

UV–vis measurements revealed that treatment of **1** (1 mM) with PhI═NTs (1 equiv) in MeCN at −20 °C led to immediate disappearance of the broad absorption band of **1** at λ_{max} 534 nm (ε = 630 cm^{-1} mol^{-1} dm^3), accompanied by immediate formation of a new broad absorption band at λ_{max} 490 nm (Figure S8). This new band disappeared upon addition of PPh_3 (8 equiv), with formation of a broad absorption band at λ_{max} ~530 nm resembling that of **1** (SFigure S9). A similar UV–vis spectral change was observed when styrene (0.5 mL), instead of PPh_3, was added, and in the reaction mixture, the styrene aziridination product was detected by ^1H NMR spectroscopy. These observations could be attributed to the formation of reactive iron–imide/nitrene species in the reaction of **1** with PhI═NTs.

Our numerous attempts to isolate qpy-supported iron–imide/nitrene complexes, such as $[Fe(qpy)(NR)_2]^{2+}$ and $[Fe(qpy)(NR)]^{2+}$ (R = Ts, Ns), have not been successful. Detection of these species by other spectral methods, such as ^1H NMR, proved difficult, probably due to their paramagnetism, high reactivity, or short lifetime. When **1** was treated with PhI═NTs (1 or 2 equiv) in MeCN-d_3 at −20 °C, the ^1H NMR spectrum of the reaction mixture was featureless, revealing the formation of paramagnetic species. In the course of isolation of the product by diffusion of diethyl ether, a μ-oxo dimer, $\{[Fe(qpy)(H_2O)]_2O\}(ClO_4)_4$,[45] was obtained. To shed insight into the reactive iron–imide/nitrene intermediate(s), we performed X-band EPR experiments with the reaction mixture obtained by rapidly mixing **1** with PhI═NTs (8 equiv) in MeCN at around −40 °C (this took 1–2 min) followed by immediately freezing the as-formed reaction mixture to 4 K. No signal attributable to Fe^V species[46] was observed. Paramagnetic species (or a mixture of paramagnetic species) that could be attributed to Fe^{III} species was observed (Figure S10). It should be noted that Fe^{IV} species is conceived to be EPR-silent in the X-band EPR experiments,[47] and Fe^{VI}-nitride species is reported to be diamagnetic.[48]

Density Functional Theory (DFT) Calculations. The electronic structures of $[Fe(qpy)(NTs)_2]^{2+}$ ($\mathbf{C_{NTs}}$) and $[Fe(qpy)(NTs)]^{2+}$ (**C**) and their amination reactions with cyclohexane (including KIEs), have been examined by DFT calculations with Gaussian 09 package[49] using OLYP hybrid functional (see Supporting Information, including Figures S11–S14 depicted therein, for details). The computed Fe–NTs distances in the ground states of $\mathbf{C_{NTs}}$ (1.819, 1.884 Å) and **C** (1.822 Å) are markedly longer than that computed for the octahedral complex $[Fe(N4Py)(NTs)]^{2+}$ (1.75 Å).[24] The imide ligands in both the $\mathbf{C_{NTs}}$ and **C** species have radical nitrene character and can be considered as $[^{\bullet}NTs]^-$. In the amination of cyclohexane by these $\mathbf{C_{NTs}}$ and **C** species, the calculated free energy barriers (with single point correction in MeCN solvent) for the rate-determining H-atom abstraction are 15.3 kcal/mol for $\mathbf{C_{NTs}}$ and 14.2 kcal/mol for **C**. Upon binding ClO_4^- or $NHTs^-$ to the *trans* site of **C** to form $[Fe(qpy)(NTs)(ClO_4)]^+$ ($\mathbf{C_{ClO4}}$) and $[Fe(qpy)(NTs)(NHTs)]^+$ ($\mathbf{C_{NHTs}}$),[50] the amination reaction has considerably higher barriers of 17.6 and 24.3 kcal/mol, respectively. It is noted that the ion $[Fe(qpy)(NTs)(ClO_4)]^+$ has actually been detected by ESI-MS of the reaction mixture as described in previous section.

DISCUSSION

Amination of $C(sp^3)$–H bonds of alkanes via nonheme iron-catalyzed nitrogen group insertion reactions requires a system that can generate highly reactive nonheme iron imide (or nitrene) intermediates. Previously reported related catalytic systems[6] using nonheme iron complexes or simple iron salts resulted in the amination of relatively weak C(sp^3)−H bonds,[27,51] including the following reactions: (i) intramolecular amination of benzylic 3° C−H bond of $\text{PhI}{=}\text{NSO}_2(2,5\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ catalyzed by $[\text{Fe(cyclam)Cl}_2]\text{Cl}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) and FeCl_3;[6a] (ii) intramolecular amination of benzylic 2° C−H bonds of sulfamate esters **2c,f,h** with PhI(OAc)_2 catalyzed by $[\text{Fe(Cl}_3\text{terpy)}_2](\text{ClO}_4)_2$;[6c] (iii) intermolecular amination of benzylic 2° C−H bonds of ethylbenzenes with "NBS + $\text{H}_2\text{NXO}_n\text{Ar}$" (NBS = *N*-bromosuccinimide; X = C, *n* = 1; X = S, *n* = 2) catalyzed by FeCl_2;[6b] and (iv) intermolecular amination of benzylic 1° C−H bond of toluene with N_3Ad (1-azidoadamantane) catalyzed by $[\text{Fe}(^{\text{Ad}}\text{L})\text{Cl(OEt}_2)]$ ($^{\text{Ad}}\text{L}$ = 1,9-bis(1-adamatanyl)-5-mesityl-dipyrromethene).[6d] In all the reported intermolecular reactions,[6b,d] the substrates were used in excess; particularly, the amination of benzylic 1° C−H bond of toluene[6d] (these bonds are usually difficult to be functionalized)[52] was performed in neat toluene.

The iron quinquepyridine complex **1** is an active catalyst for intra- and intermolecular amination of benzylic C−H bonds (see Tables 1−3), allylic C−H bonds (Scheme 1; entry 8, Table 3), and, remarkably, the C−H bonds of cycloalkanes or cycloalkane/linear alkane moieties in sulfamate esters including those of steroids (entries 7 and 8 in Table 2, Scheme 1, and Table 4) with the substrates as limiting agents. For all of these reactions catalyzed by **1**, the amination products have been isolated in up to 93% yield.

For the amination of steroids by metal-catalyzed nitrogen group insertion into C−H bonds, we are not aware of previous examples that involve nonheme iron catalysts, besides the above-mentioned intramolecular allylic C−H bond amination of cholesteryl sulfamate ester, an unsaturated steroid, catalyzed by the heme-like $[\text{Fe(Pc)}]^+$.[31] There are a few reports on intermolecular amination of unsaturated steroids with PhI=NTs or "$\text{PhI(OAc)}_2 + \text{NH}_2\text{R}$ (R = Ts, Ns)" as nitrogen source and using manganese[53] or ruthenium[53c] porphyrins, dirhodium complexes,[54] and ruthenium−salen complexes[55] as catalysts, examples of which include amination of benzylic C−H bond of equilenin acetate[53a] and amination of allylic C−H bonds of cholesteryl acetates.[53b,c,54,55] All of these intermolecular reactions afforded the aminated steroids in up to 47% yields. Intramolecular amination via aziridination of an unsaturated steroid with PhI=O catalyzed by $[\text{Cu(MeCN)}_4]\text{PF}_6$ (68% aziridine yield) followed by nucleophilic aziridine opening has also been reported.[56] The substrates **2r−t** (Scheme 1) used in this work were not employed in previous amination reactions catalyzed by metal complexes. The **1**-catalyzed amination of **2s** and **2t** with PhI(OAc)_2 are unique examples of metal-catalyzed amination of C(sp^3)−H bonds of saturated steroids.

Intermolecular amination of pinene by reactive metal-imide/nitrene intermediates has been documented in previous reports[57] involving the amination of *α*-pinene (**6a**) with "$\text{PhI(OCO}^t\text{Bu)}_2 + \text{H}_2\text{NS(NTs)(O)}$-*p*-$\text{MeC}_6\text{H}_4$" catalyzed by a dirhodium complex, affording the allylic C−H amination product in 71−91% yields. This reaction and the iron-catalyzed conversion of **6a** to **7a** reported herein (Table 3) are in contrast with the formation of aziridines in 59−71% yields found for the reaction of **6a** with free nitrenes.[58] In the case of **1**-catalyzed amination of *β*-pinene (**6b**) with PhI=NR (R = Ts, Ns), the formation of rearranged products **7ba** and **7bb** is also different from the amination of **6b** by free nitrenes (which afforded ene-type amination products in 42−58% yields without ring-opening)[58] but is reminiscent of some other types of transformation of **6b** reported in literature,[59] such as the reactions of **6b** with radicals derived from NaN_3[59a] or alkoxyamines,[59b,c] to give rearranged products analogous to **7ba** and **7bb**.

Using catalyst **1** and with cyclohexane and cyclooctane substrates as limiting reagents, the 2° C(sp^3)−H bonds of these alkanes were effectively aminated, resulting in high product selectivity (yield based on substrate conversion) of up to 82%, with TON of up to 4.9 comparable to that obtained for the hydroxylation of cyclohexane (10 equiv) with H_2O_2 catalyzed by $[\text{Fe(TPA)(MeCN)}_2]^{2+}$ (TON = 3.0, TPA = tris(2-pyridylmethyl)amine).[32h] Recent report revealed that **1** is an active catalyst for various organic oxidation reactions.[45] The interesting catalytic activity of **1** is possibly associated with the lack of reactive C−H bonds (or other reactive groups) in the qpy coligand (which disfavors degradation of the key intermediates via intramolecular reactions such as previously reported formation of nonheme iron amido complexes)[21c,25,38] and the high coordination number supported by qpy (such as 7-coodinate iron in **1**; this high-coordination number generates reactive iron−imide/nitrene intermediates, as suggested by DFT calculations and discussed below).

In heme iron systems reported in literature, excess amounts of cyclohexane and cyclooctane were used for the intermolecular amination of these two cyclic alkanes. The cyclohexane amination with PhI=NTs mediated by [Fe(TPP)Cl] (H_2TPP = 5,10,15,20-tetraphenylporphyrin) was performed in CH_2Cl_2−cyclohexane (1:1 v/v) mixed solvent.[28] A 25-fold excess of cyclooctane was employed in its amination with N_3Ar (Ar = 4-nitrophenyl) catalyzed by $[\text{Fe(F}_{20}\text{TPP)Cl}]$ [$\text{H}_2\text{F}_{20}\text{TPP}$ = 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin].[30b]

Several catalytic systems employing other metal catalysts also use excess cyclic alkane substrates in the amination reaction.[60] These include the use of neat cyclohexane in its amination reaction with PhI=NTs[60a] or "$^t\text{BuOOBu}^t + \text{H}_2\text{NR}$" (R = Ad, Cy, $\text{CH}_2\text{CH}_2\text{Ph}$)[60e] catalyzed by copper complexes, the use of 10 equiv of cyclohexane, cyclopentane, and cyclooctane in their amination reactions with PhI=NNs catalyzed by a silver complex[60b] and the use of 2−10 equiv of cyclohexane and cyclooctane in their amination reactions with $\text{Cl}_3\text{CCH}_2\text{OC(O)NHOTs}$ catalyzed by dirhodium complexes.[60c,d]

Amination of cyclic alkanes present in limiting amounts has previously been reported using the following catalytic systems:[61] dirhodium-catalyzed amination of cyclooctane with "$\text{PhI(OAc)}_2 + \text{H}_2\text{NSO}_3\text{CH}_2\text{CCl}_3$" (31% yield, TON = 16.5),[61a,b] copper-catalyzed amination of cyclohexane with N_3Ad (32% yield, TON = 12.8),[61c] and dirhodium-catalyzed amination of cyclopentane, cyclohexane, cycloheptane, cyclooctane with "$\text{PhI(OCOBu}^t)_2 + \text{H}_2\text{NS(NTs)(O)}$-*p*-$\text{MeC}_6\text{H}_4$" (48−66% yields, TON = 16−22).[61d]

Complex **1** effectively catalyzed amination of cyclic alkanes in limiting amounts with PhI=NR and "$\text{PhI(OAc)}_2 + \text{H}_2\text{NR}$" (R = Ts, Ns) as nitrogen sources. The **1**-catalyzed amination of cyclohexane and cyclooctane gave **11a,b** and **13a,b** (Table 3) in 27−49% isolated yields (based on starting substrate). These yield values are comparable to those indicated above for dirhodium[61a,b] and copper[61c] catalysts using nitrogen sources "$\text{PhI(OAc)}_2 + \text{H}_2\text{NSO}_3\text{CH}_2\text{CCl}_3$" and N_3Ad, respectively. So far the highest product yields in metal-catalyzed amination of limiting reagents cyclohexane (50% yield, TON = 16.7) and cyclooctane (61% yield, TON = 20.3) were obtained using dirhodium catalyst $[\text{Rh}_2\{(S)\text{-nta}\}_4]$ (nta is a carboxylate ligand) with the "$PhI(OCOBu^t)_2$ + $H_2NS(NTs)(O)$-*p*-MeC_6H_4" nitrogen source.[61d]

Given the detection of species assignable to $[Fe(qpy)(NTs)]^{2+}$ (**C**) and $[Fe(qpy)(NTs)_2]^{2+}$ ($\mathbf{C_{NTs}}$) by ESI-MS from the reaction mixture of **1** and PhI═NTs (4 equiv), the **1**-catalyzed amination of $C(sp^3)$−H bonds with PhI═NTs possibly involves mono(imide/nitrene) and bis(imide/nitrene) iron species. We propose the likely involvement of $[Fe(qpy)(NR)(X)]^{n+}$ ($\mathbf{C_X}$) with X = NR, solvent, or anion in the **1**-catalyzed amination of $C(sp^3)$−H bonds with PhI═NR. Another species to be considered is $[Fe(qpy)(NR)\{PhI(NR)\}]^{2+}$, which is analogous to previously proposed $[Mn(tpfc)(NR)\{ArI(NR)\}]$ (tpfc =5,10,15-tris(pentafluorophenyl)corrole),[62] a nitrogen analogue of the proposed M(ArIO) intermediates in metal-catalyzed oxygen atom transfer using ArI═O.[63] According to crossover experiments analogous to that performed for $[Mn(tpfc)(NR)\{ArI(NR)\}]$,[62] the involvement of $[Fe(qpy)(NR)\{PhI(NR)\}]^{2+}$ in the **1**-catalyzed reactions is less favored. The crossover experiments were performed using two PhI═NSO_2-*p*-YC_6H_4 nitrogen sources: PhI═NTs (Y = Me) and PhI═NBs (Y = H). Complex **1** was first treated with PhI═NTs (1 equiv); after complete reaction, PhI═NBs (1 equiv) was added with subsequent addition of isochroman (**4b**). The reaction gave a ~1:1 ratio of the $C(sp^3)$−H bond amination products corresponding to NTs and NBs transfer. A similar ratio of ~1:1 was obtained for the aziridination products of styrene by **1** and PhI═NTs (1 equiv) and subsequently PhI═NBs (1 equiv). In the previous report on imide complexes of manganese corrole,[62] the ratio of styrene aziridination products corresponding to NR (R = SO_2-*p*-$^tBuC_6H_4$) and NR′ (R′ = SO_2-*p*-MeC_6H_4) transfer from $[Mn(tpfc)(NR)\{ArI(NR')\}]$ was reported to be 1:100, whereas that from the bis(imide) intermediate $[Mn(tpfc)(NR)(NR')]$ was expected to be 1:1.[62] In this work, we have not been able to observe $[Fe(qpy)(NTs)\{PhI(NTs)\}]^{2+}$ by ESI-MS analysis of the reaction mixture of **1** with PhI═NTs. The crossover experiments do not lend support to the assignment of the major active species to the $[Fe(qpy)(NR)\{PhI(NR)\}]^{2+}$ (if formed) that behaves like $[Mn(tpfc)(NR)\{ArI(NR)\}]$ (i.e., only the coordinated ArI(NR) undergoes nitrogen group transfer). However, it is noted that the findings from the crossover experiments could not distinguish the possible oxidizing agents, such as other Fe-PhI(NR) adducts and iron mono- and bis(imide/nitrene) species.

Generation of iron−imide/nitrene intermediates in the reaction of **1** with PhI═NTs is suggested by other type of nitrogen group transfer reactions mediated by **1**, including **1**-catalyzed aziridination of alkenes with PhI═NTs (Table S1). The Hammett plots (Figures S1 and S2) and the correlation between relative amination rates and C−H BDEs (Figure S3) are also consistent with the involvement of electrophilic metal−imide/nitrene intermediates via H-atom abstraction. The amination reactions of $C(sp^3)$−H bonds catalyzed by **1** took place under moderate conditions (at 80 °C), and these reaction conditions are compatible with the computed activation barriers of 14.2−15.3 kcal/mol for the amination of cyclohexane by $[Fe(qpy)(NTs)]^{2+}$ ($^5\mathbf{C}$) and $[Fe(qpy)(NTs)_2]^{2+}$ ($^3\mathbf{C_{NTs}}$).

KIE values obtained from DFT calculations lend support to the reaction mechanisms.[64] The computed KIE values (with Wigner correction)[65] for the amination of cyclohexane at 80 °C by $\mathbf{C_{NTs}}$ (k_H/k_D = 3.3) is similar to the corresponding experimental value (k_H/k_D = 3.4). Further calculations on the cyclohexane amination by $\mathbf{C_{NTs}}$ at the other temperatures of 50 and 25 °C gave k_H/k_D of 3.7 and 4.2, respectively, also in good agreement with the experimental values (50 °C: k_H/k_D = 3.7; 25 °C: k_H/k_D = 4.0). On the other hand, the computed k_H/k_D values at 80 °C for **C**, $\mathbf{C_{ClO4}}$, and $\mathbf{C_{NHTs}}$ are 2.5, 5.1, and 5.6, respectively.

To provide more insight into the amination of $C(sp^3)$−H bonds of cyclic alkanes by $[Fe(qpy)(NR)(X)]^{n+}$ ($\mathbf{C_X}$), we performed the following experiments: (i) Complex **1** was treated with 1.1 equiv of PhI═NTs in MeCN, followed by addition of cyclohexane (1 equiv). From this reaction, we did not observe formation of significant amount of the cyclohexane amination product (**11a**) after the reaction mixture had been stirred at 80 °C for 12 h. As described above, ESI-MS analysis of 1:1 mixture of **1** and PhI═NTs showed cluster peaks assigned to $[Fe(qpy)(NTs)(ClO_4)]^+$ ($\mathbf{C_{ClO4}}$) but not $[Fe(qpy)(NTs)_2]^{2+}$ ($\mathbf{C_{NTs}}$). We also examined the effect of (PhI═NTs)/**1** ratio on the amination of cyclohexane. Upon treatment of excess cyclohexane with **1** and PhI═NTs at (PhI═NTs)/**1** molar ratios of 0.5, 1, 2, and 3, the ratio of the corresponding amination product **11ba** formed was ~0:1:100:400. (ii) When bromamine-T, instead of PhI═NTs, was used as nitrogen source, **1** did not catalyze the amination of cyclohexane under the conditions indicated in Table 4. Through ESI-MS analysis of the reaction mixture of **1** with bromamine-T, we found the cluster peak assigned to $[Fe(qpy)(NTs)Br]^+$ ($\mathbf{C_{Br}}$), without observation of the cluster peak attributed to $\mathbf{C_{NTs}}$. (iii) In the presence of pyridine additive (2 equiv), **1** was found not to catalyze the amination of cyclohexane with PhI═NTs under the conditions indicated in Table 4 but could catalyze aziridination of styrene though the substrate conversion decreased to 22% (from 100% obtained for the same aziridination without pyridine additive). ESI-MS analysis of a reaction mixture of **1** with PhI═NTs (4 equiv) in MeCN containing pyridine (2 equiv) revealed a cluster peak at *m*/*z* 345.7 attributable to $[Fe(qpy)(NTs)(py)]^{2+}$ ($\mathbf{C_{py}}$, calcd *m*/*z* 345.6, Figure S15); no cluster peak attributed to $\mathbf{C_{NTs}}$ was found.

It has been reported that the reactions of $[Fe(Cl_3terpy)_2]^{2+}$ and $[Fe(N4Py)(MeCN)]^{2+}$ with ArI=NTs (Ar = phenyl or mesityl) generated mono(imide) species $[Fe(Cl_3terpy)_2(NTs)]^{2+}$ (detected by ESI-MS)[6c] and $[Fe(N4Py)(NTs)]^{2+}$ (characterized by ESI-MS, UV−vis, ^1H NMR, EXAFS, Mössbauer spectroscopy,[24] and DFT calculations),[24,66] respectively. These iron imide species might be insufficiently reactive toward the $C(sp^3)$−H bond of cyclohexane, since very little if not nil amination of cyclohexane with PhI═NTs was observed using catalysts $[Fe(Cl_3terpy)_2]^{2+}$ and $[Fe(N4Py)(MeCN)]^{2+}$ under the reaction conditions employed in this study.

Based on the aforementioned experiments described in (i)−(iii) and the findings of related catalytic experiments with $[Fe(Cl_3terpy)_2]^{2+}$ and $[Fe(N4Py)(MeCN)]^{2+}$ as catalysts, we conceive that the intermediate $[Fe(qpy)(NR)_2]^{2+}$ ($\mathbf{C_{NR}}$) would not play a minor role in the amination of C−H bonds of cyclohexane, although the importance of other reactive intermediates, such as $[Fe(qpy)(NR)]^{2+}$ (**C**) and Fe-PhI(NR) adduct, could not be excluded with the present findings. According to DFT calculations, the ground states of $\mathbf{C_{NTs}}$ and **C** feature radical nitrene character of the imide ligand. Radical nitrene character of coordinated imide ligands has been established previously, for example, in recently reported mono(imide) complexes [Fe(L)(NR)Cl][6d] and [Co(Por)-

(NR)][67] and may contribute to the reactivity of **C_{NTs}** and **C** toward amination of saturated C−H bonds. [Fe(L)(NR)Cl] (L = a monoanionic dipyrromethene ligand) is documented to be an Fe^{III} complex.[6d] **C_{NTs}** and **C** could be considered as Fe^{IV} and Fe^{III} species, respectively, on the basis of the $[^{\bullet}NTs]^-$ form of their imide ligand(s) revealed by DFT calculations. However, formulation of the oxidation states based on DFT calculations is highly speculative. To clearly determine the iron oxidation state(s) in the proposed intermediates $[Fe(qpy)(NR)(X)]^{n+}$ (**C_X**), further studies are needed including characterization by, for example, Mössbauer measurements.

In literature, iron bis(imide) intermediates have not been proposed for the nitrogen group transfer reactions catalyzed by iron complexes.[6,8−13,28,30,31] Metal bis(imide) complexes that are reactive toward nitrogen group transfer to form C−N bonds are sparse.[33] Several uranium bis(imide) complexes feature 7-coordinate uranium adopting pentagonal bipyramidal geometry.[68] To the best of our knowledge, investigations on the reactivity of bis(imide) complexes of the first-row transition metals toward amination of C−H bonds have not been reported previously, regardless of experimental studies or theoretical calculations.

■ CONCLUSIONS

We have demonstrated that the nonheme iron complex $[Fe(qpy)(MeCN)_2](ClO_4)_2$ (**1**) is an active catalyst for the intra- and intermolecular amination of various $C(sp^3)$−H bonds, including amination of cyclic alkanes and of cycloalkane/linear alkane moieties in saturated steroids. The substrate scope spans cycloalkanes, benzylic/allylic hydrocarbons, natural products α-pinene and β-pinene, and a wide variety of sulfamate esters including those bearing methylcyclohexane, isononane, menthane, spirost-5-ene, cholane, and androstane backbones. The amination reactions can be performed by employing the cyclic alkane substrates as limiting reagents with PhI═NR or "$PhI(OAc)_2 + H_2NR$" (R = Ts, Ns) as nitrogen source. The interesting catalytic activity of the "**1** + PhI═NR" system is likely to arise from the generation of reactive cationic 7-coordinate iron−imide/nitrene intermediate(s) $[Fe(qpy)(NR)(X)]^{n+}$ (**C_X**, X = NR, solvent, or anion) as proposed on the basis of experimental studies (including ESI-MS analysis) and DFT calculations. The DFT optimized ground states of these proposed reactive iron−imide/nitrene species, such as **C_{NTs}**, feature imide ligand(s) with radical nitrene characters. The present work provides unique examples of nonheme iron-catalyzed amination of cyclic alkanes and steroid compounds and lends credence to the possible use of nonheme iron complexes as practical catalysts for $C(sp^3)$−H amination reactions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental section including detailed procedures, characterization data and NMR spectra of compounds, computational details, Tables S1 and S2, and Figures S1−S15. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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