The Yang Research Group
Precise Synthesis Lab at Tongji University

Summary

几类Fe-N物种的形成与性质

Reporter: Junchun Zhang

2024.3.8

Contents

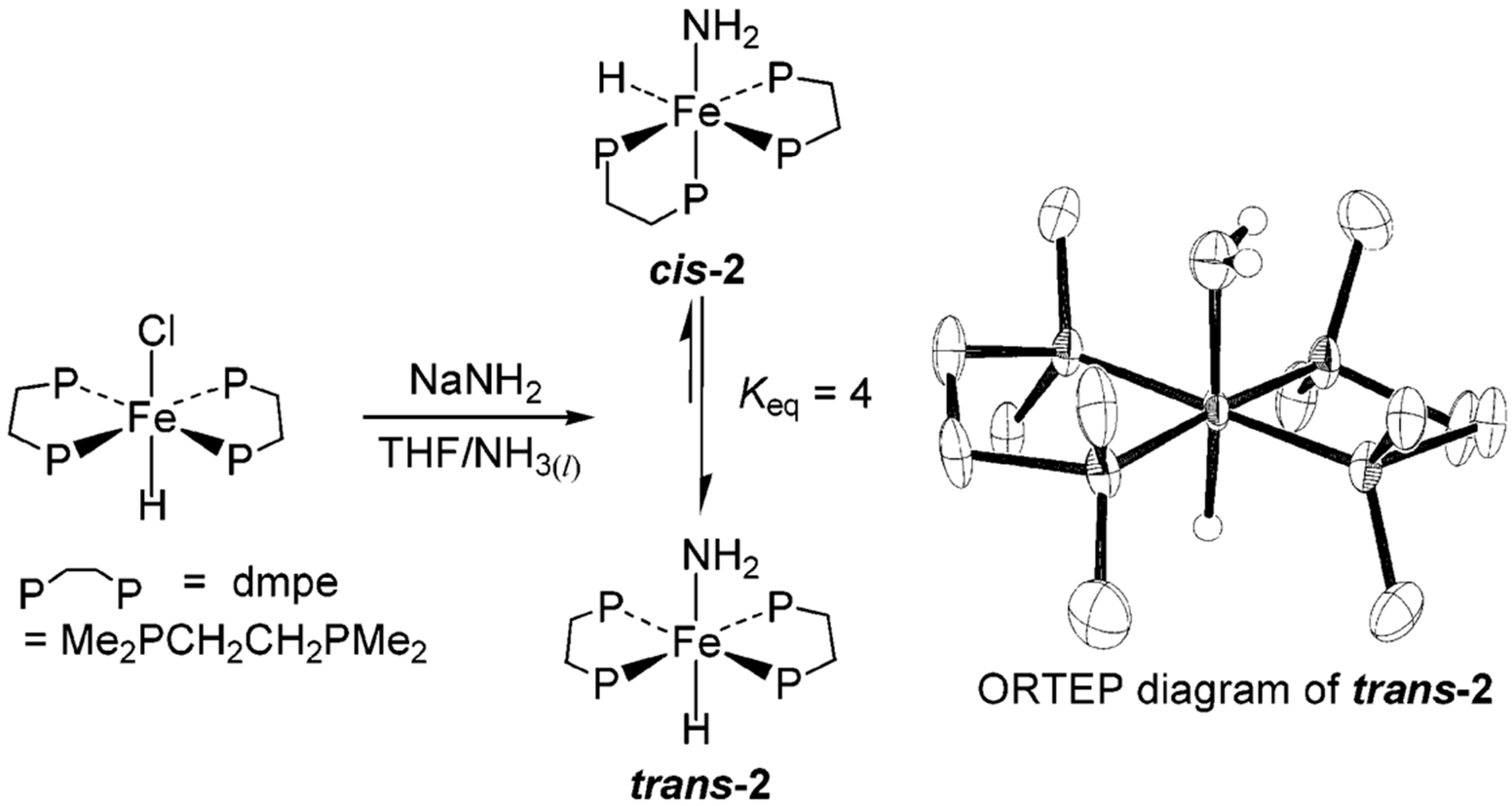
1 Fe-$NH_{2/3}$

2 Fe-NHR

3 Fe=N

4 Proposal

Scheme 1

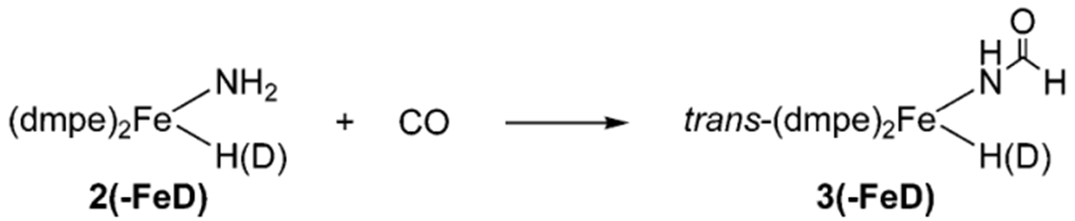


ORTEP diagram of ***trans*-2**

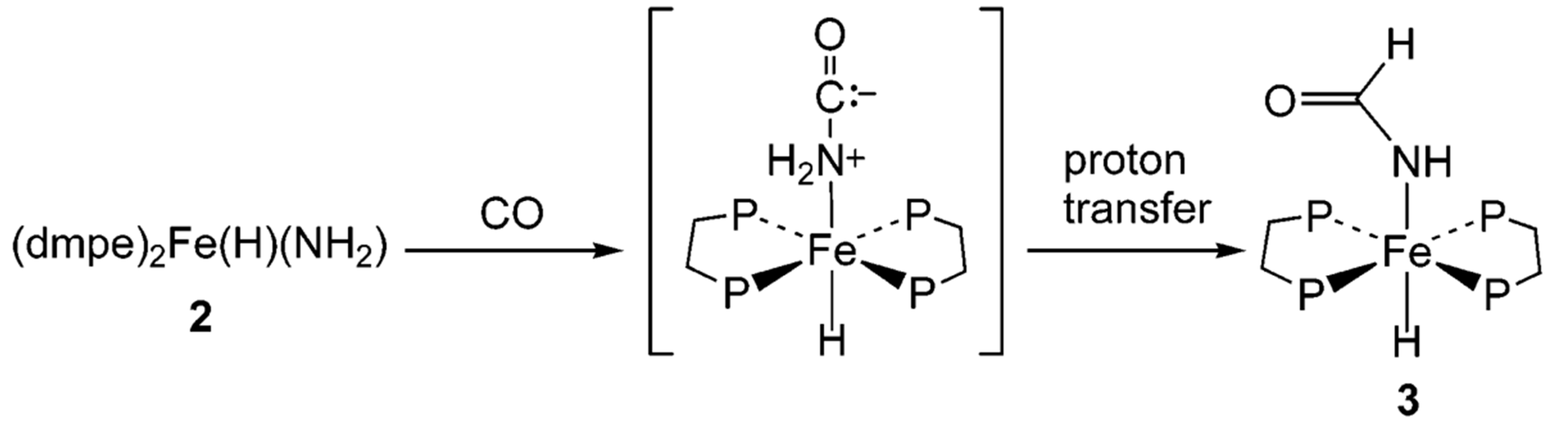
2003年，Bergman报道了一例氨基铁(II)配合物的合成。
这也是目前最常用的铁氨配合物的合成方法之一：N^-配体与Cl^-配体的配体交换

Daniel J. Fox and Robert G. Bergman*. Synthesis of a First-Row Transition Metal Parent Amido Complex and Carbon Monoxide Insertion into the Amide N-H Bond. J. Am. Chem. Soc. 2003, 125, 8984-8985

Fe-$NH_{2/3}$



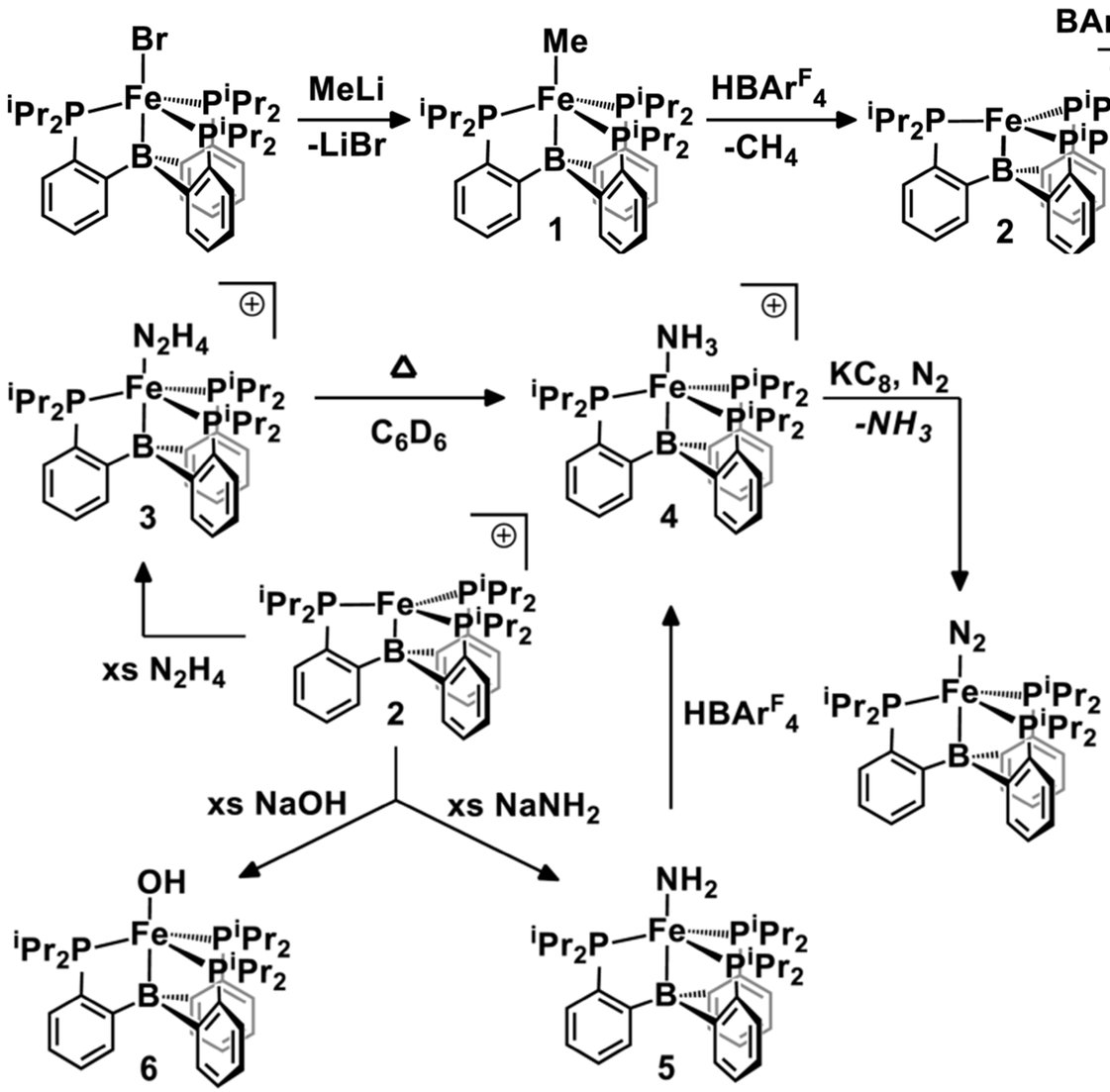
Bergman发现了这类Fe(II)-NH_2配合物的一个特殊性质：N-H接受了CO的插入。



根据实验结果，他们推测其反应机理可能是通过N对CO的亲核进攻实现。
这不仅提供了一种Fe-NH2合成思路，更提供了一种Fe-酰胺配合物的合成思路。

Daniel J. Fox and Robert G. Bergman*. Synthesis of a First-Row Transition Metal Parent Amido Complex and Carbon Monoxide Insertion into the Amide N-H Bond. J. Am. Chem. Soc. 2003, 125, 8984-8985

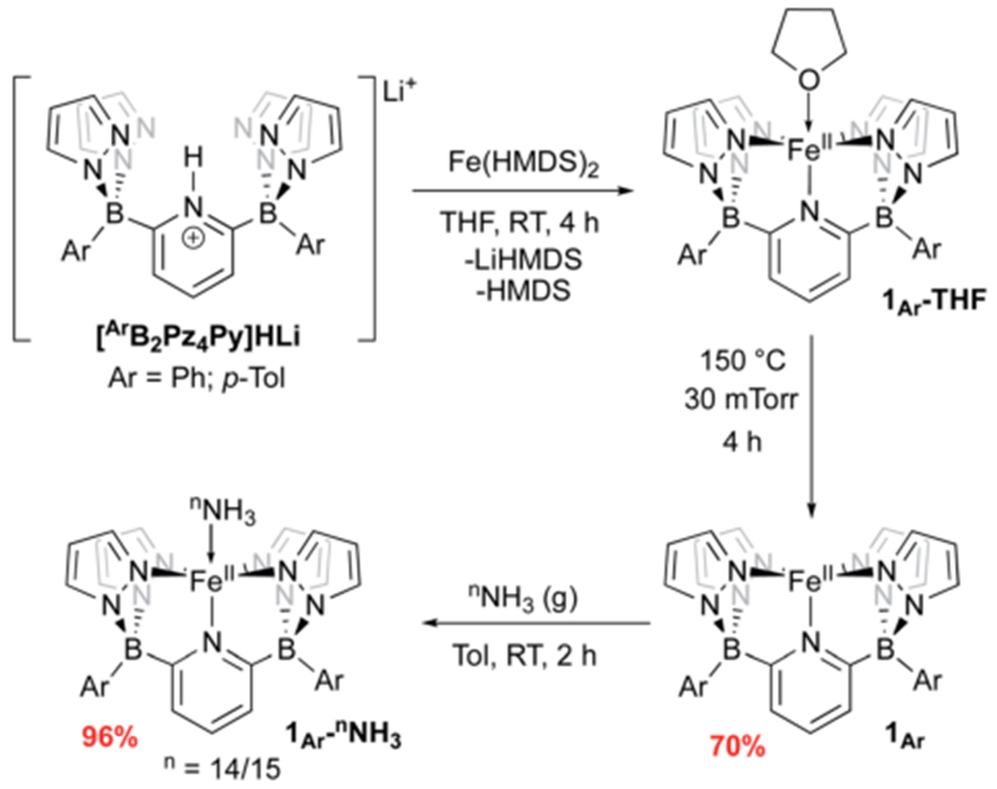
Fe-$NH_{2/3}$



2012年，Peters合成了一类有空配位的Fe(I)物种，通过这类物种接受N亲核试剂的配位从而形成简单的Fe-氨/肼/羟基配合物。

John S. Anderson, Marc-Etienne Moret, and Jonas C. Peters*. Conversion of Fe−NH2 to Fe−N2 with release of NH3. J. Am. Chem. Soc. 2013, 135, 534−537.

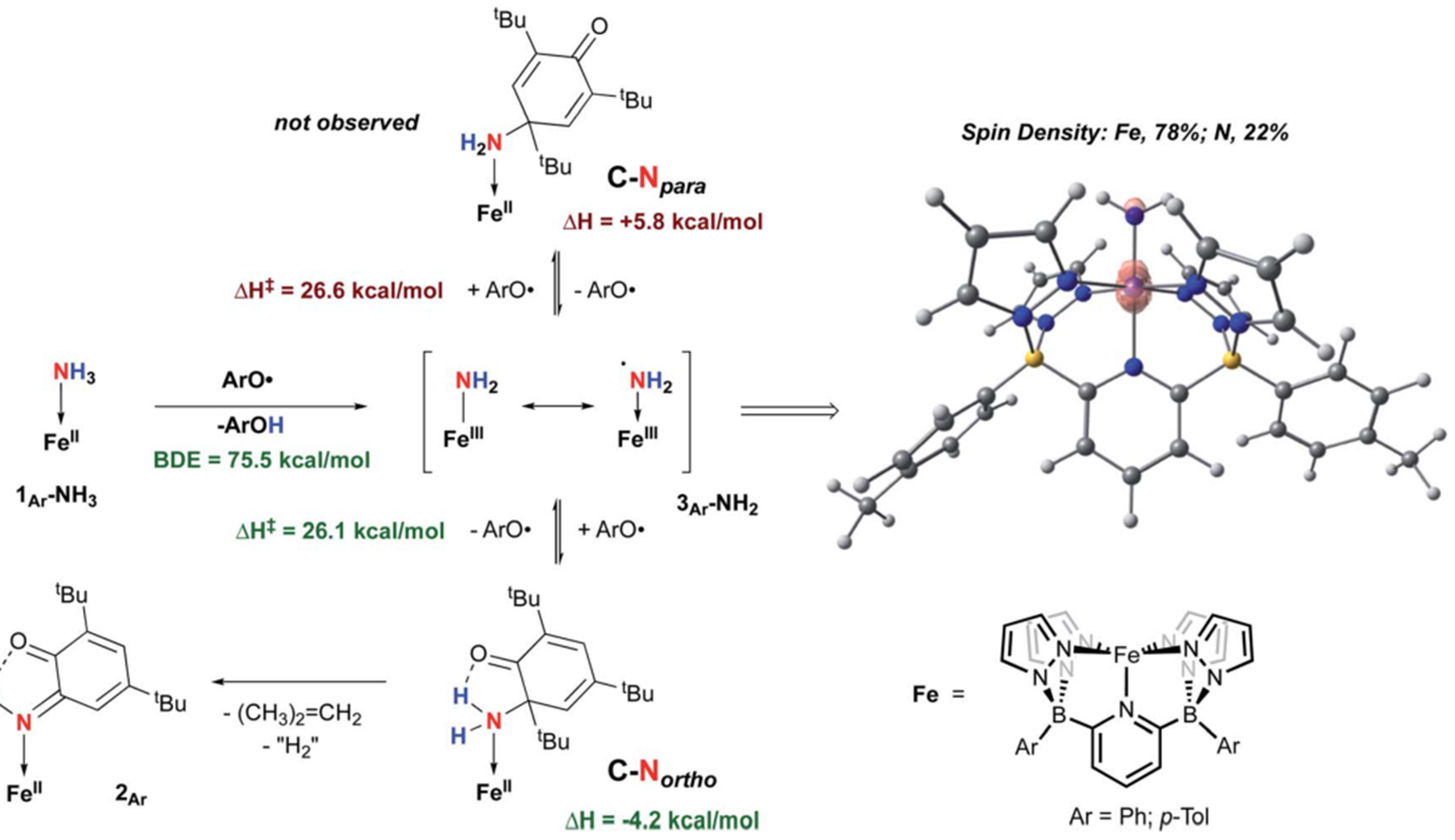
Fe-$NH_{2/3}$



2021年，Piers报道了一例空配位Fe(II)配合物的合成。
这种配合物同样能通过接受N亲核试剂的进攻实现Fe-N配合物的形成。

Lucie Nurdin, Yan Yang, Peter G. N. Neate, Warren E. Piers, *Laurent Maron, * Michael L. Neidig,* Jian-Bin Lina and Benjamin S. Gelfand. Activation of ammonia and hydrazine by electron rich Fe(II) complexes supported by a dianionic pentadentate ligand platform through a common terminal Fe(III) amido intermediate. Chem. Sci., 2021 , 12, 2231–2241

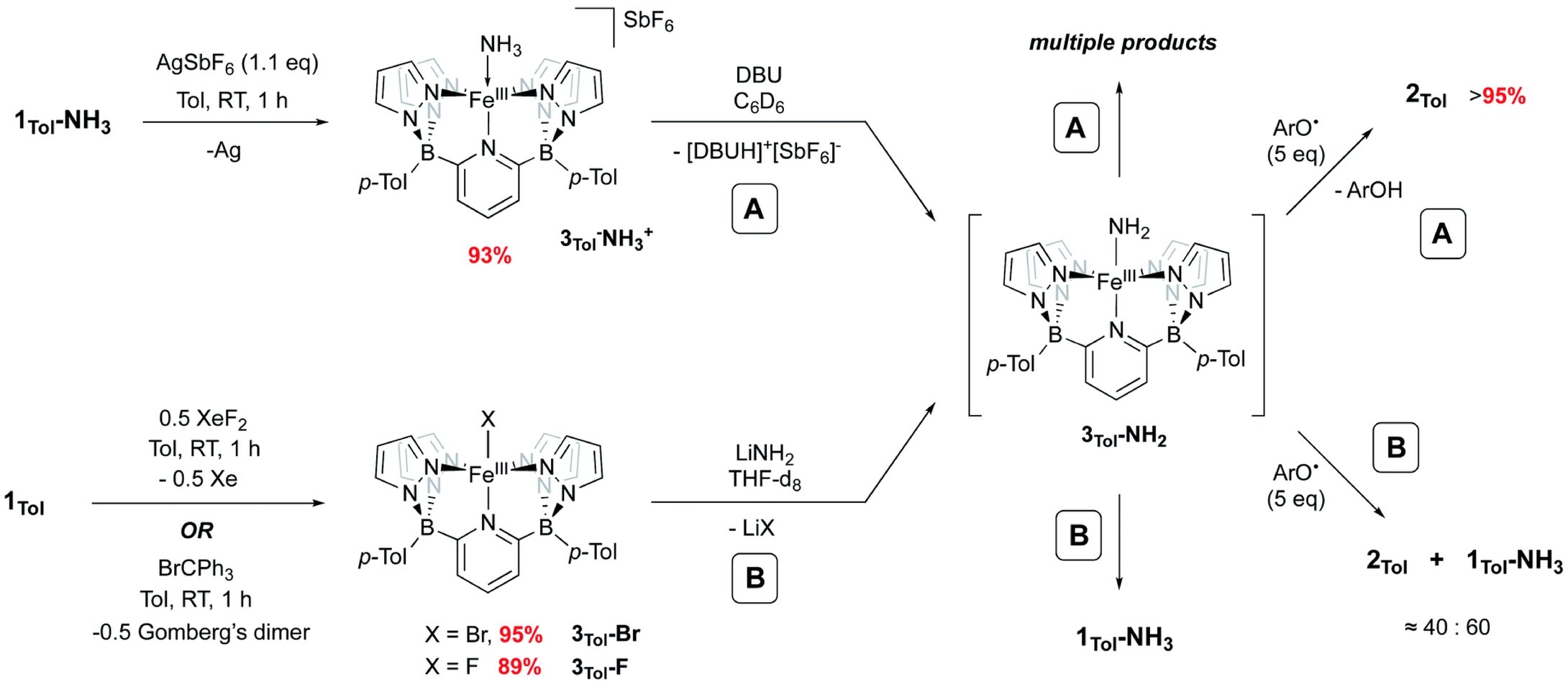
Fe-$NH_{2/3}$



Piers通过自由基实验证据推测：Fe(II)-NH_3在与一个自由基发生HAT后，产生的Fe(III)-NH_2的N原子具有一定的自由基性质，能够对芳环发起进攻

Lucie Nurdin, Yan Yang, Peter G. N. Neate, Warren E. Piers, *Laurent Maron, * Michael L. Neidig,* Jian-Bin Lina and Benjamin S. Gelfand. Activation of ammonia and hydrazine by electron rich Fe(II) complexes supported by a dianionic pentadentate ligand platform through a common terminal Fe(III) amido intermediate. Chem. Sci., 2021 , 12, 2231–2241

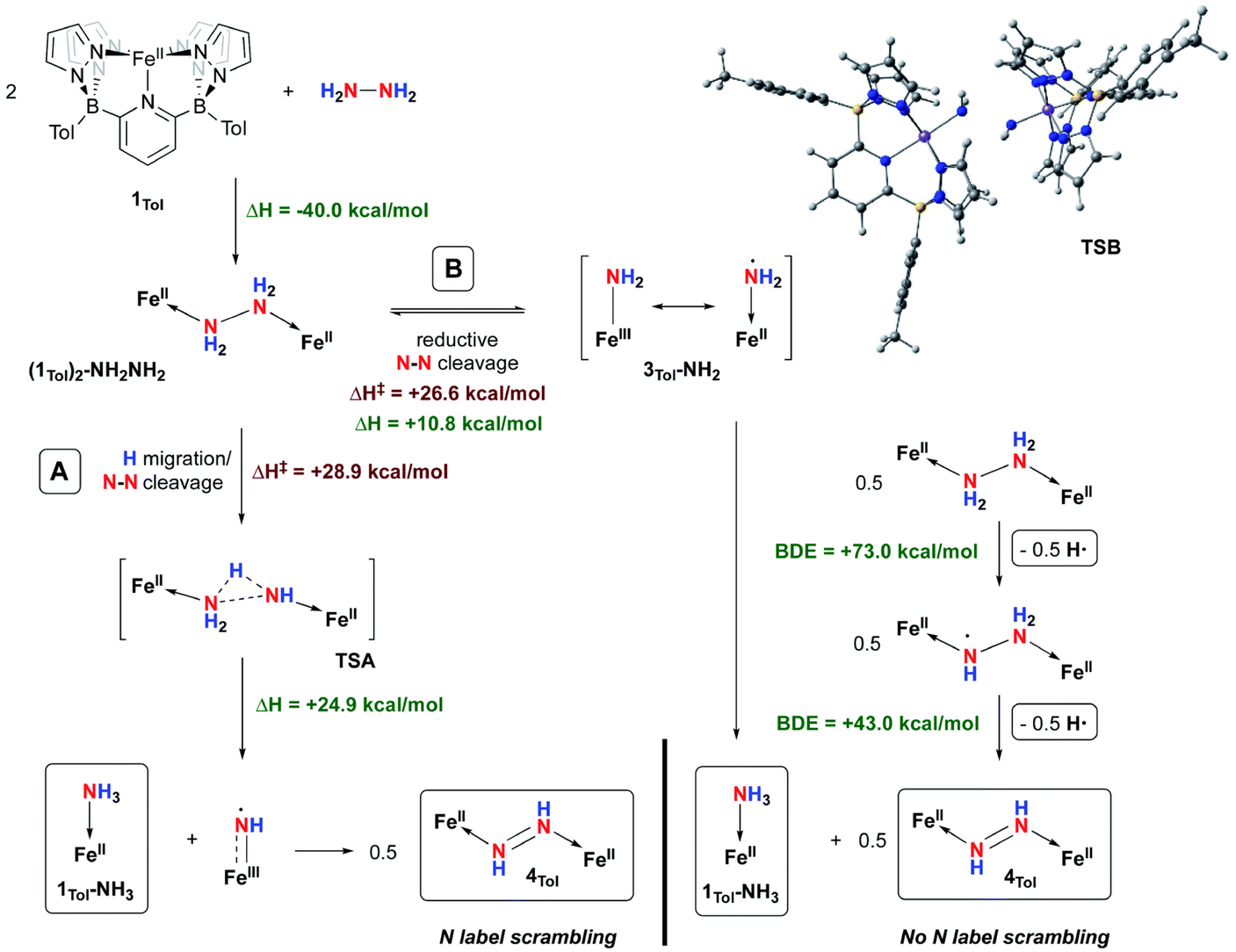
Fe-$NH_{2/3}$



Piers提出了两种合成这类Fe(III)-NH_2的方法：先配位再氧化或是先氧化再配位。

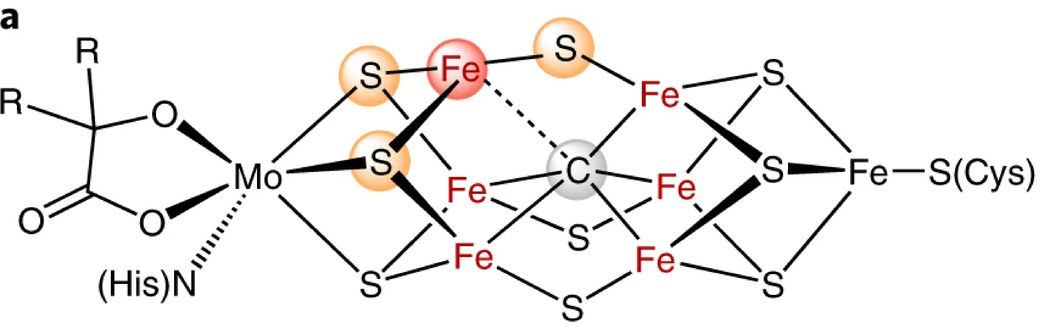
Lucie Nurdin, Yan Yang, Peter G. N. Neate, Warren E. Piers, *Laurent Maron, * Michael L. Neidig,* Jian-Bin Lina and Benjamin S. Gelfand. Activation of ammonia and hydrazine by electron rich Fe(II) complexes supported by a dianionic pentadentate ligand platform through a common terminal Fe(III) amido intermediate. Chem. Sci., 2021 , 12, 2231–2241

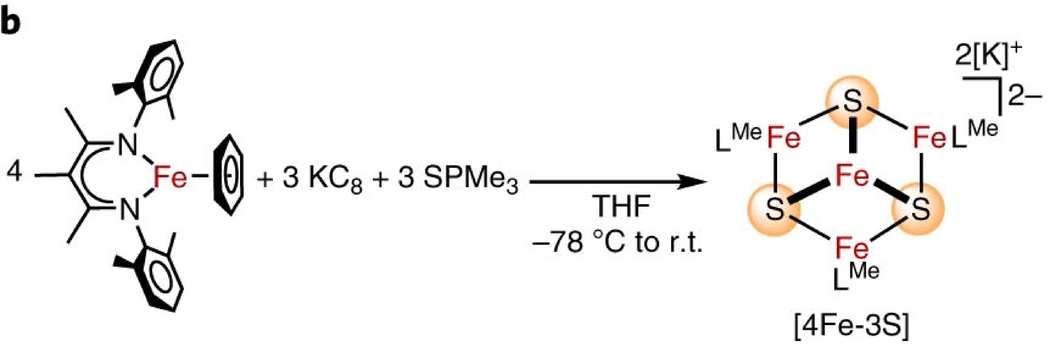
Fe-$NH_{2/3}$

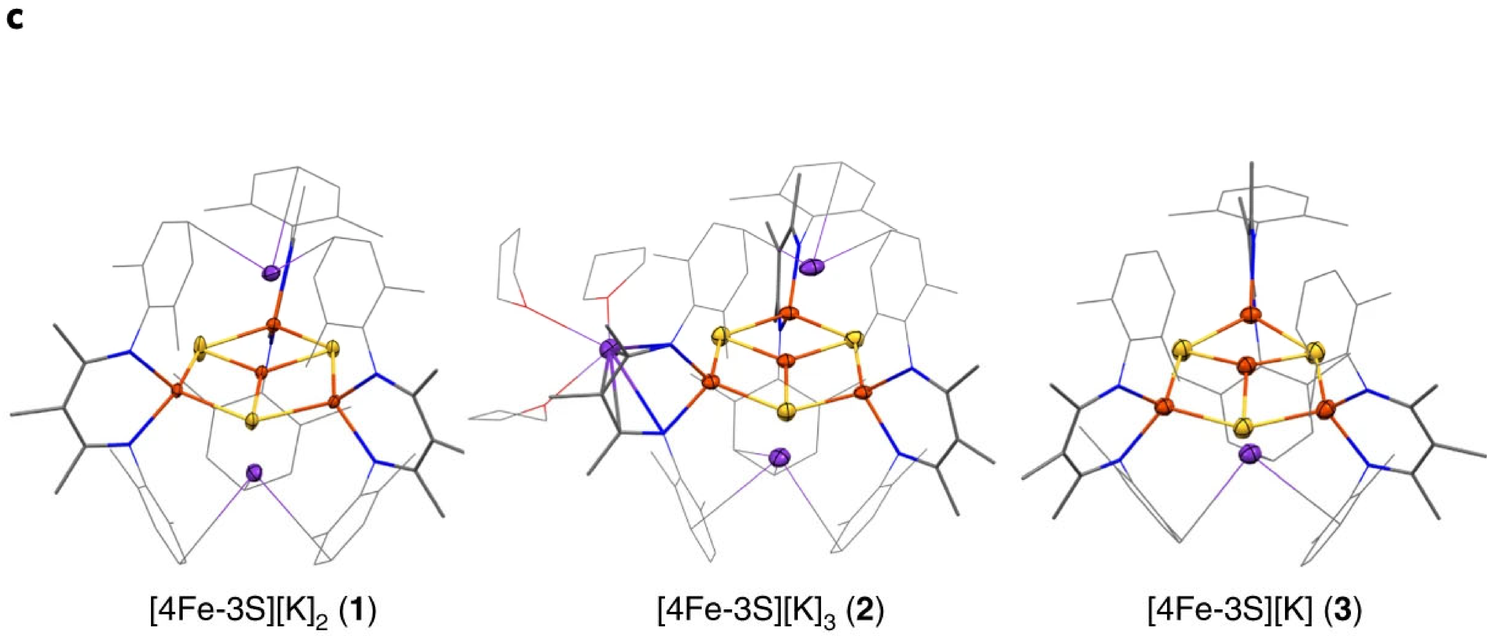


另外，通过与肼的配位及催化肼的裂解，Piers发现了肼同样能形成这类Fe(III)-NH_2。

Lucie Nurdin, Yan Yang, Peter G. N. Neate, Warren E. Piers, *Laurent Maron, * Michael L. Neidig,* Jian-Bin Lina and Benjamin S. Gelfand. Activation of ammonia and hydrazine by electron rich Fe(II) complexes supported by a dianionic pentadentate ligand platform through a common terminal Fe(III) amido intermediate. Chem. Sci., 2021 , 12, 2231–2241



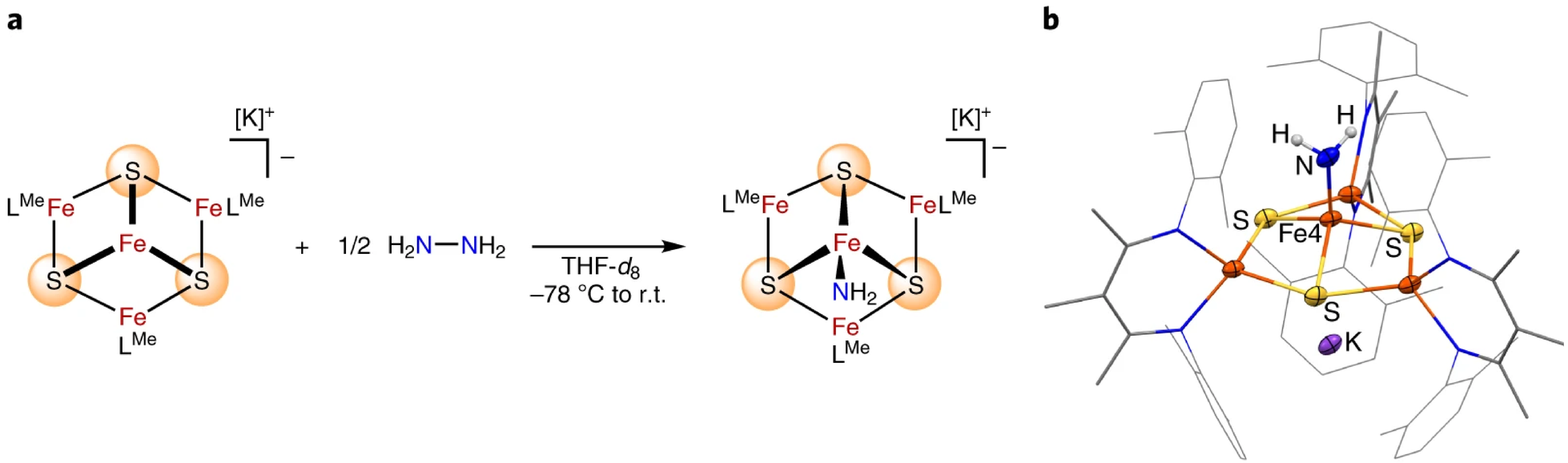




2019年，Holland报道了一例Fe(II)-S团簇化合物的合成。

Daniel E. DeRosha, Vijay G. Chilkuri, Casey Van Stappen, Eckhard Bill, Brandon Q. Mercado, Serena DeBeer, Frank Neese and Patrick L. Holland*. Planar three-coordinate iron sulfide in a synthetic [4Fe-3S] cluster with biomimetic reactivity. Nat. Chem. 11, 1019–1025 (2019).

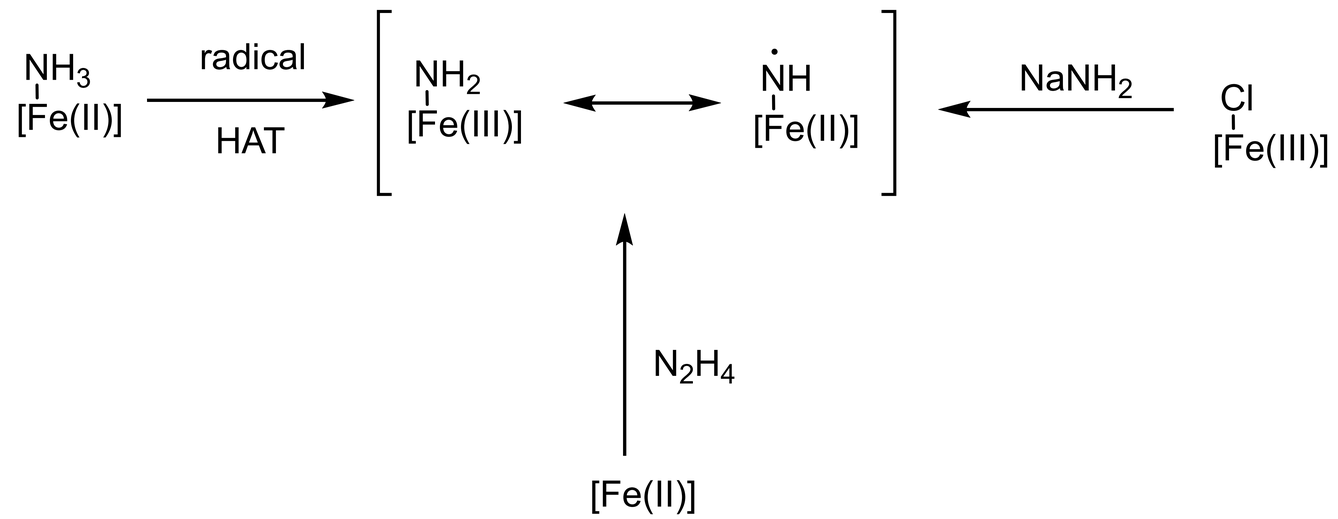
Fe-$NH_{2/3}$



这种Fe(II)-S团簇物种能够裂解肼，在低温下产生Fe(III)-NH2物种。

Daniel E. DeRosha, Vijay G. Chilkuri, Casey Van Stappen, Eckhard Bill, Brandon Q. Mercado, Serena DeBeer, Frank Neese and Patrick L. Holland*. Planar three-coordinate iron sulfide in a synthetic [4Fe-3S] cluster with biomimetic reactivity. Nat. Chem. 11, 1019–1025 (2019).

Fe-$NH_{2/3}$ Conclusin

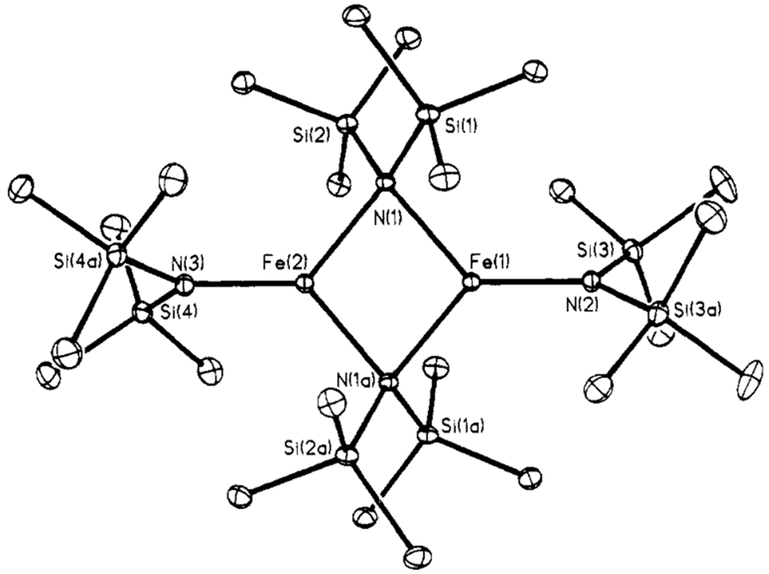


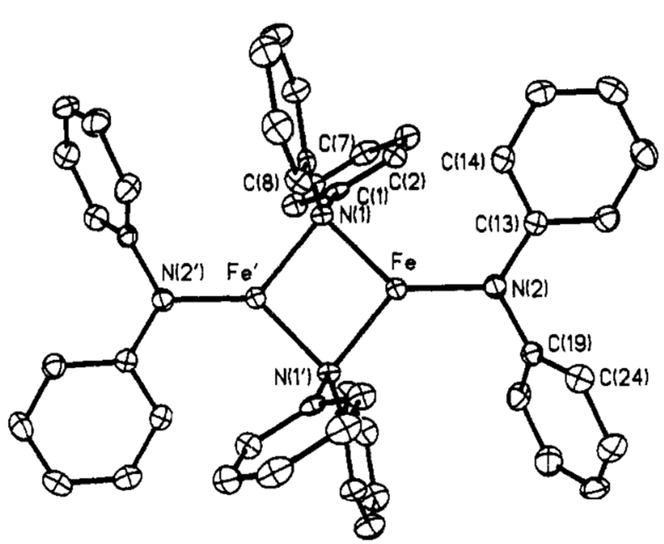
$$FeBr_2 + 2LiN(SiMe_3)_2 \xrightarrow{Et_2O} \underset{\mathbf{1}}{[Fe\{N(SiMe_3)_2\}_2]_2} + 2LiBr \quad (1)$$

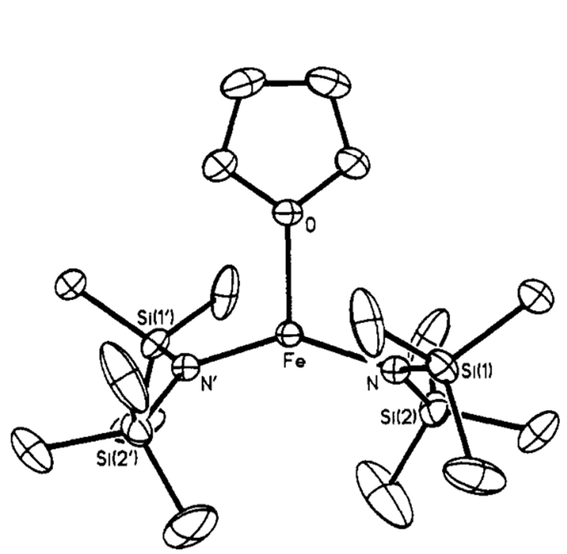
$$FeBr_2 + 2LiNPh_2 \xrightarrow{THF} \underset{\mathbf{2}}{[Fe(NPh_2)_2]_2} + 2LiBr \quad (2)$$

$$FeBr_2 + 2LiN(SiMe_3)_2 \xrightarrow{THF} \underset{\mathbf{3}}{Fe[N(SiMe_3)_2]_2(THF)} + 2LiBr \quad (3)$$

1990年，Power报道了两例铁(II)仲胺N-配合物的合成与表征。

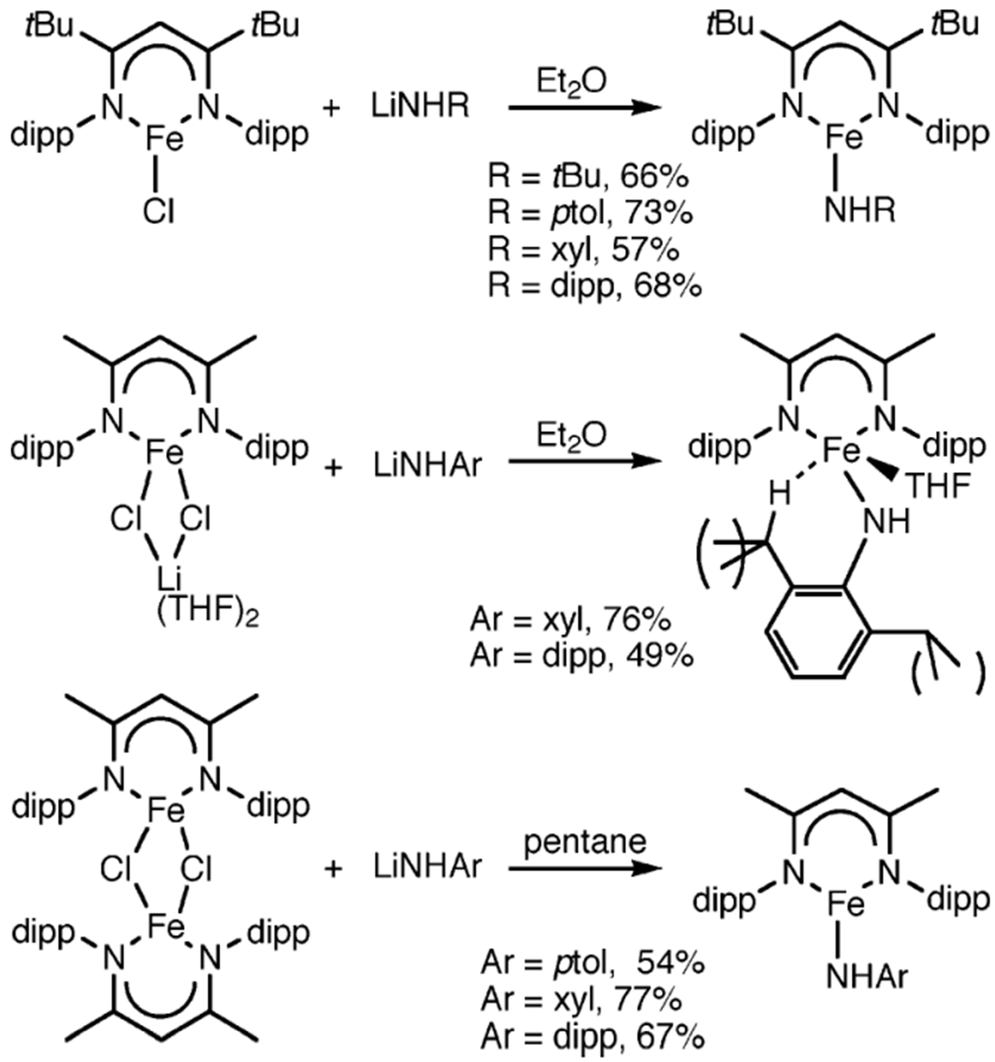






Marilyn M. Olmstead, Philip P. Power,* and Steven C. Shoner. Three-Coordinate Iron Complexes: X-ray Structural Characterization of the Amide-Bridged Dimers [Fe(NR2)2]2 (R = SiMe3, C6H5) and the Adduct Fe[N(SiMe3)2]2(THF) and Determination of the Association Energy of the Monomer Fe{N(SiMe3)2}2 in Solution. Inorg. Chem. 1991, 30, 2547-2551.

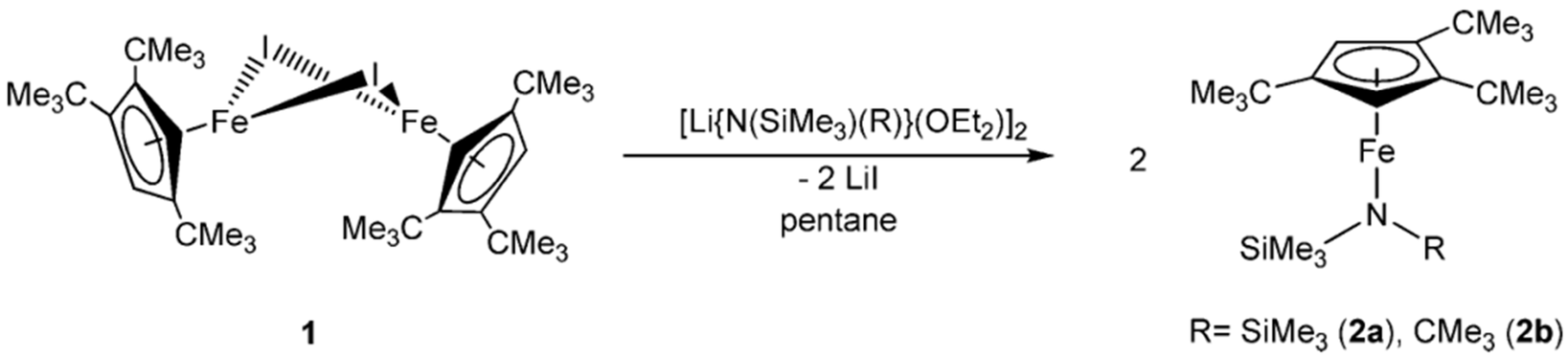
Fe-NHR



2004年，Holland报道了卟啉配体以外的新的Fe配体类型形成的Fe(II)-N配合物。

Nathan A. Eckert, Jeremy M. Smith, Rene J. Lachicotte, and Patrick L. Holland*. Low-Coordinate Iron(II) Amido Complexes of β-Diketiminates: Synthesis, Structure, and Reactivity. Inorg. Chem. 2004, 43, 3306−3321

Fe-NHR



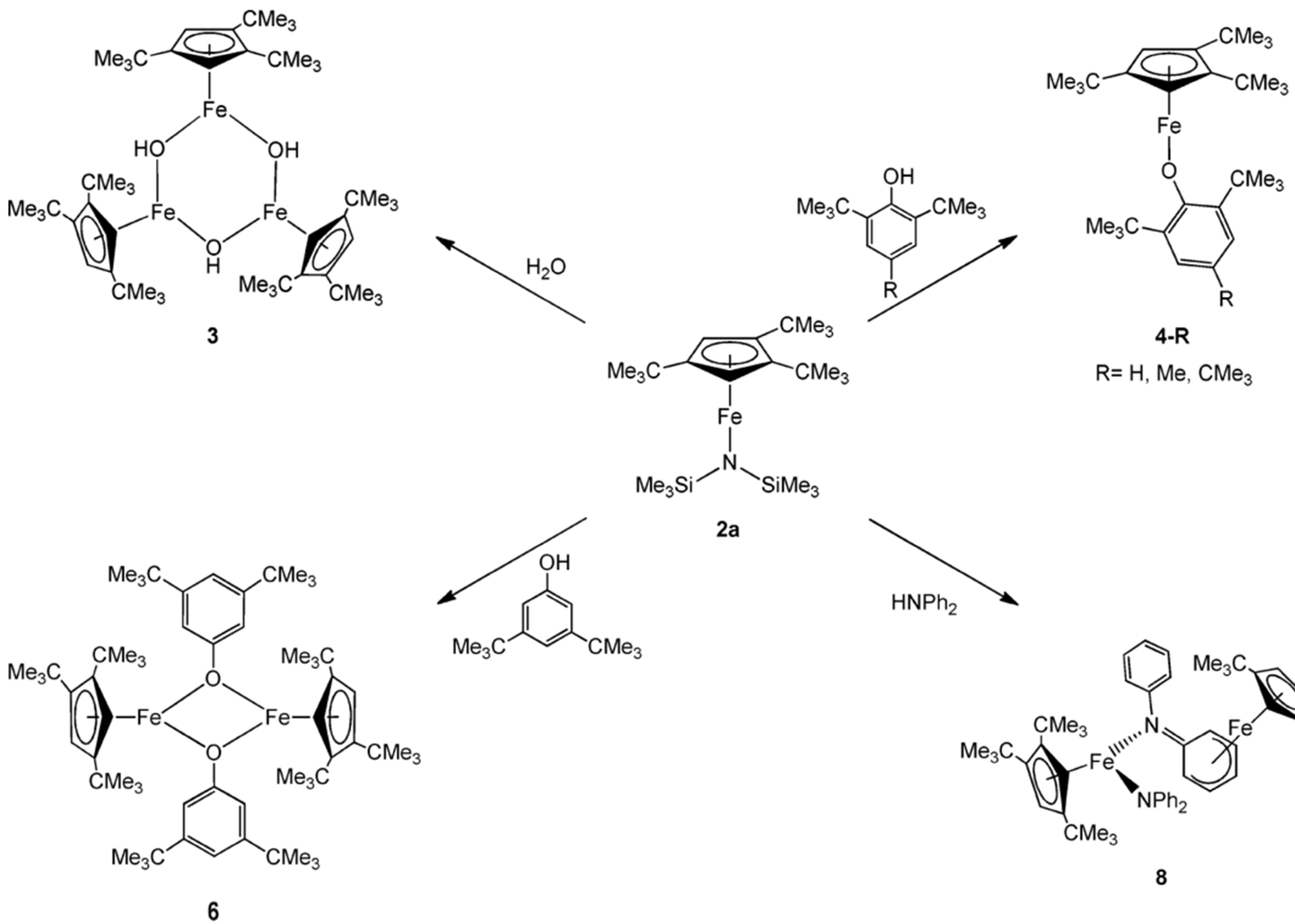
1

R= $SiMe_3$ (**2a**), CMe_3 (**2b**)

2012年，Walter报道了一种二茂铁衍生物的Fe(II)-N配合物。

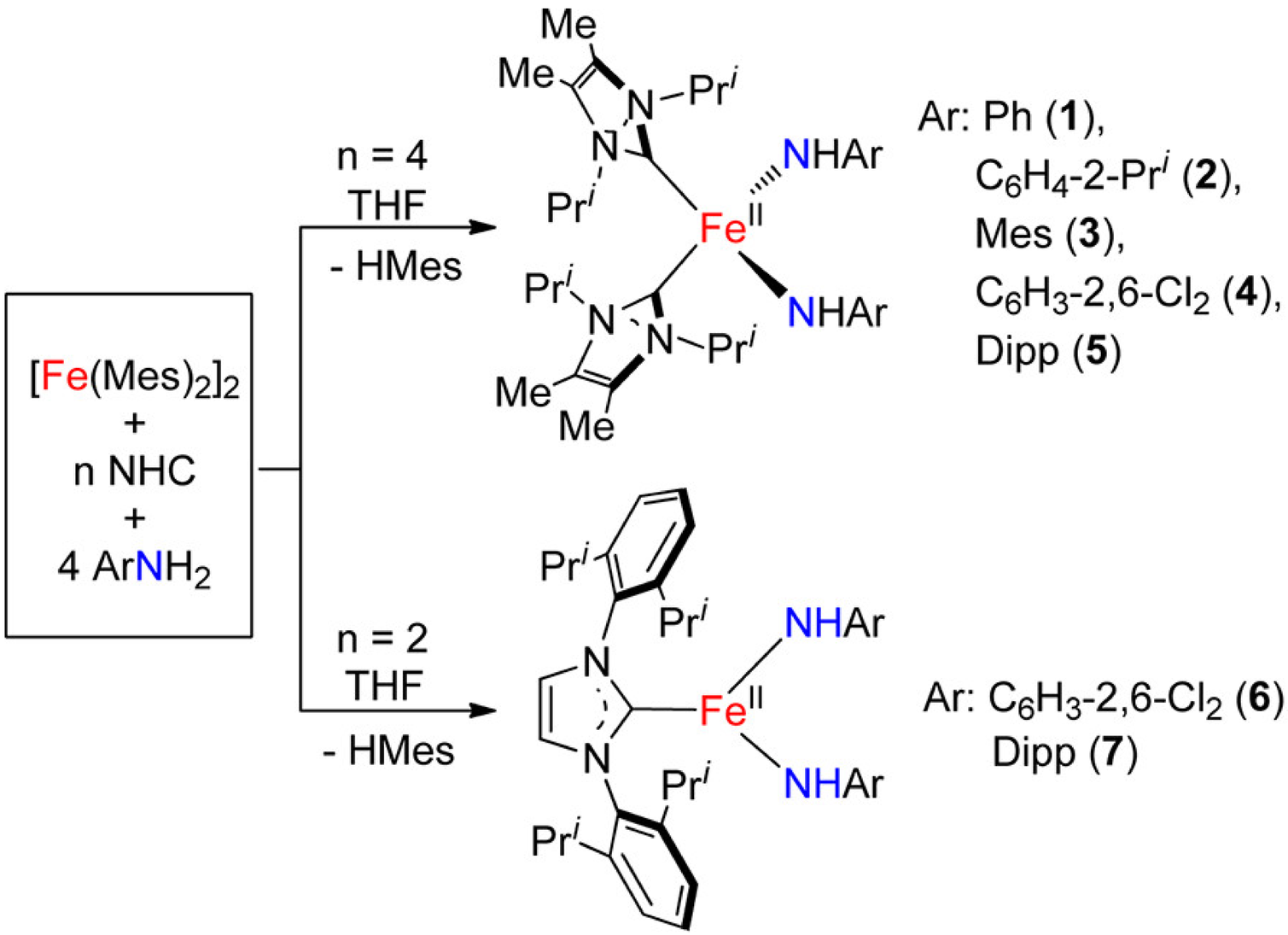
Marc D. Walter*, and Peter S. White. Lachicotte, and Patrick L. Holland*. Reactivity Studies on [Cp′FeI]2: Monomeric Amido, Phenoxo, and Alkyl Complexes. Inorg. Chem. 2012, 51, 11860−11872

Fe-NHR



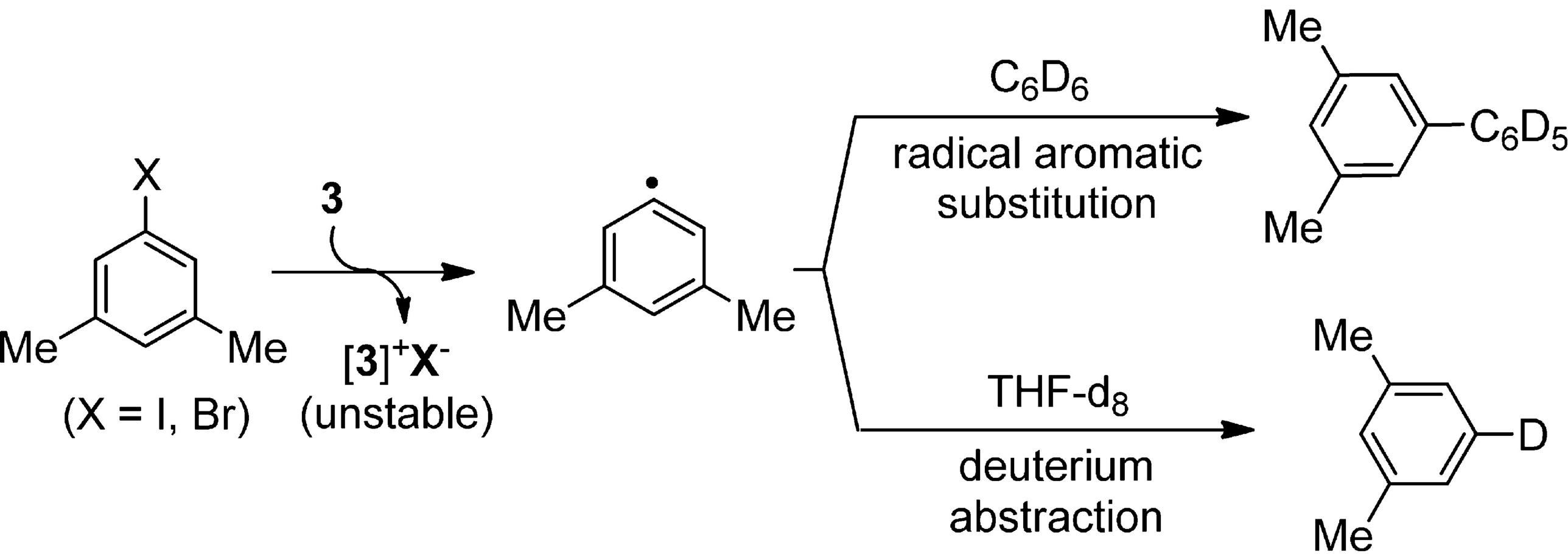
Walter描述了这类Fe(II)-N物种发生配体交换的性质以及倾向于二聚体形成的性质。

Marc D. Walter*, and Peter S. White. Lachicotte, and Patrick L. Holland*. Reactivity Studies on [Cp′FeI]2: Monomeric Amido, Phenoxo, and Alkyl Complexes. Inorg. Chem. 2012, 51, 11860−11872



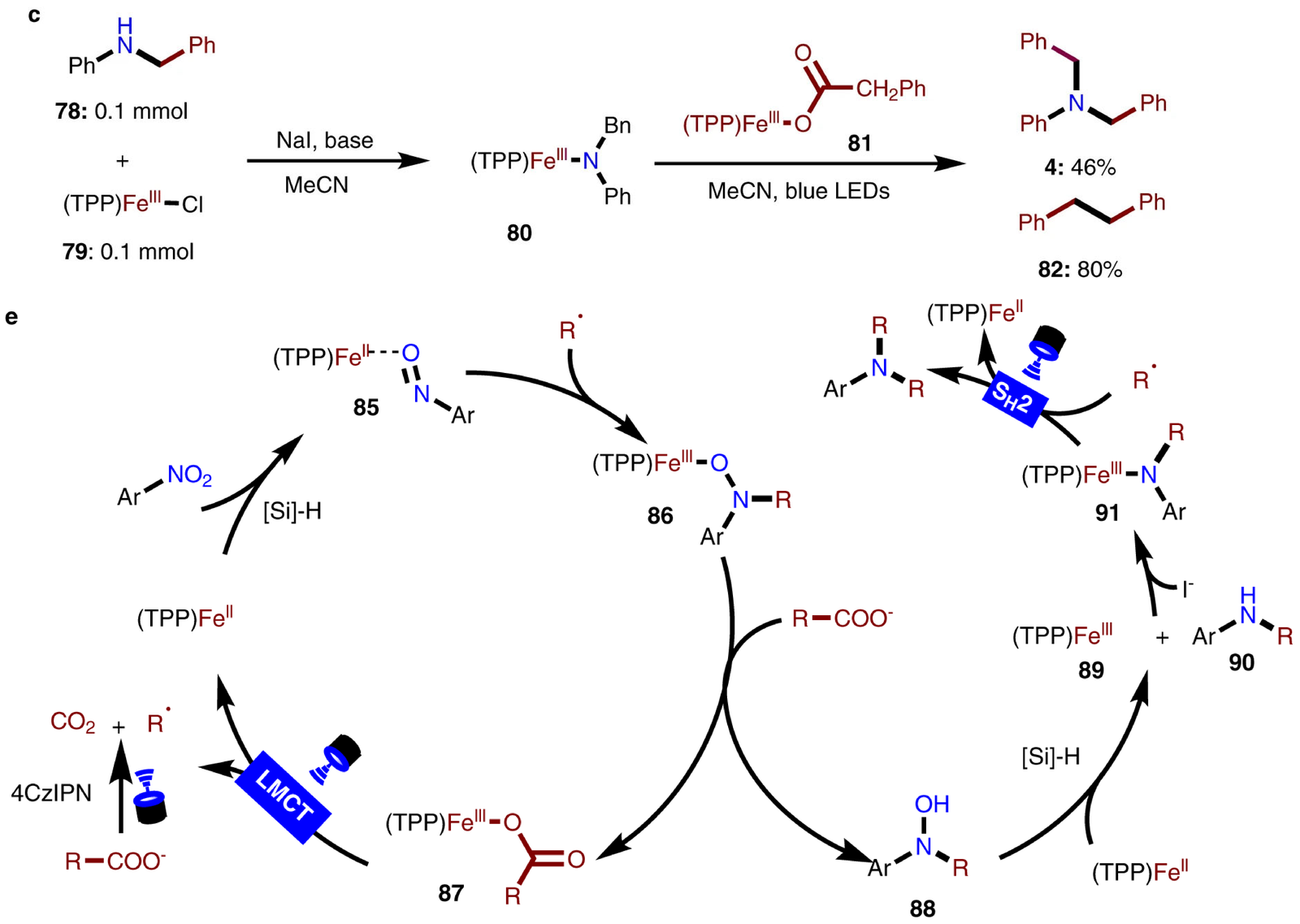
2013年，Deng通过二芳基铁和NHC、芳胺的配体交换合成了NHC配体的Fe(II)-二芳胺物种。

Xiaojie Wang, Zhenbo Mo, Jie Xiao, and Liang Deng*. Monomeric Bis(anilido)iron(II) Complexes with N-Heterocyclic Carbene Ligation: Synthesis, Characterization, and Redox Reactivity toward Aryl Halides. Inorg. Chem. 2013, 52, 59−65.



这种化合物具有一定还原性，能够还原卤代芳烃产生芳基自由基。

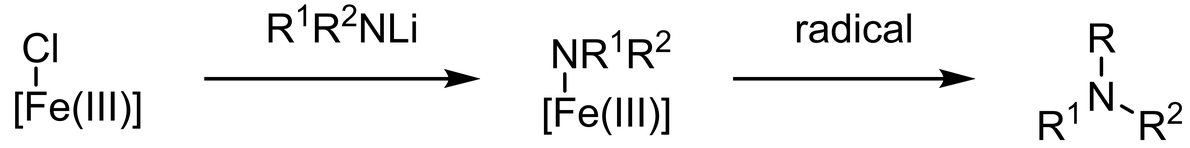
Xiaojie Wang, Zhenbo Mo, Jie Xiao, and Liang Deng*. Monomeric Bis(anilido)iron(II) Complexes with N-Heterocyclic Carbene Ligation: Synthesis, Characterization, and Redox Reactivity toward Aryl Halides. Inorg. Chem. 2013, 52, 59−65.



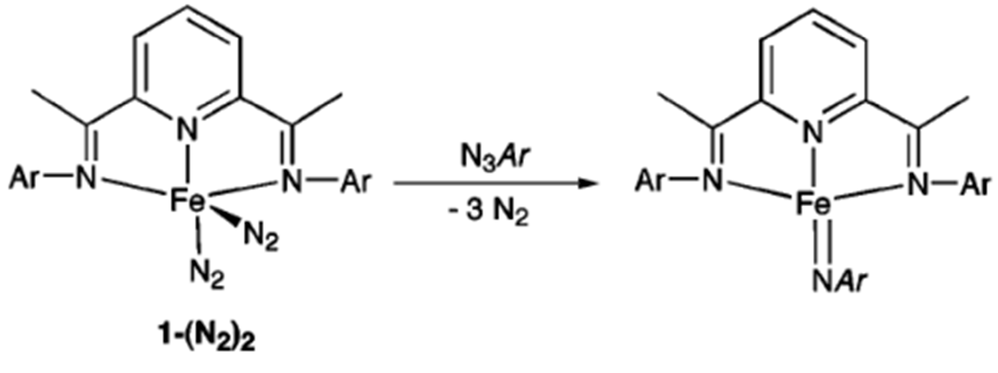
2022年，Xie报道了一例Fe(III)-胺配合物接受自由基进攻的案例。

Shuaishuai Wang, Tingrui Li, Chengyihan Gu, Jie Han, Chuan-Gang Zhao, Chengjian Zhu, Hairen Tan & Jin Xie*. Decarboxylative tandem C-N coupling with nitroarenes via S_H2 mechanism. Nat Commun 13, 2432 (2022).

Fe-NHR Conclusion

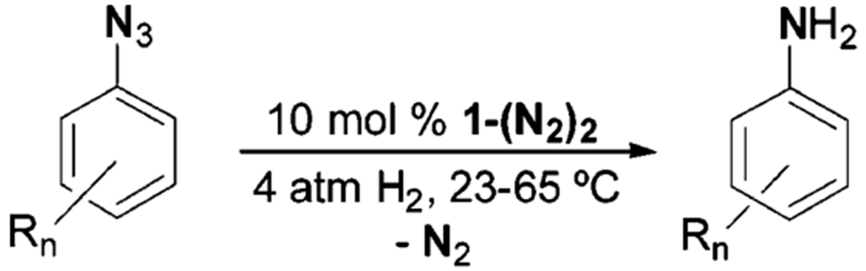


Fe=N



2a: *Ar* = 2,6-$^{i}Pr_2$-C_6H_3 (93 %)
2b: *Ar* = 2,6-Et_2-C_6H_3 (72 %)
2c: *Ar* = 2,5-$^{t}Bu_2$-C_6H_3 (95 %)
2d: *Ar* = 2,4,6-Me_3-C_6H_2 (91 %)

(1)



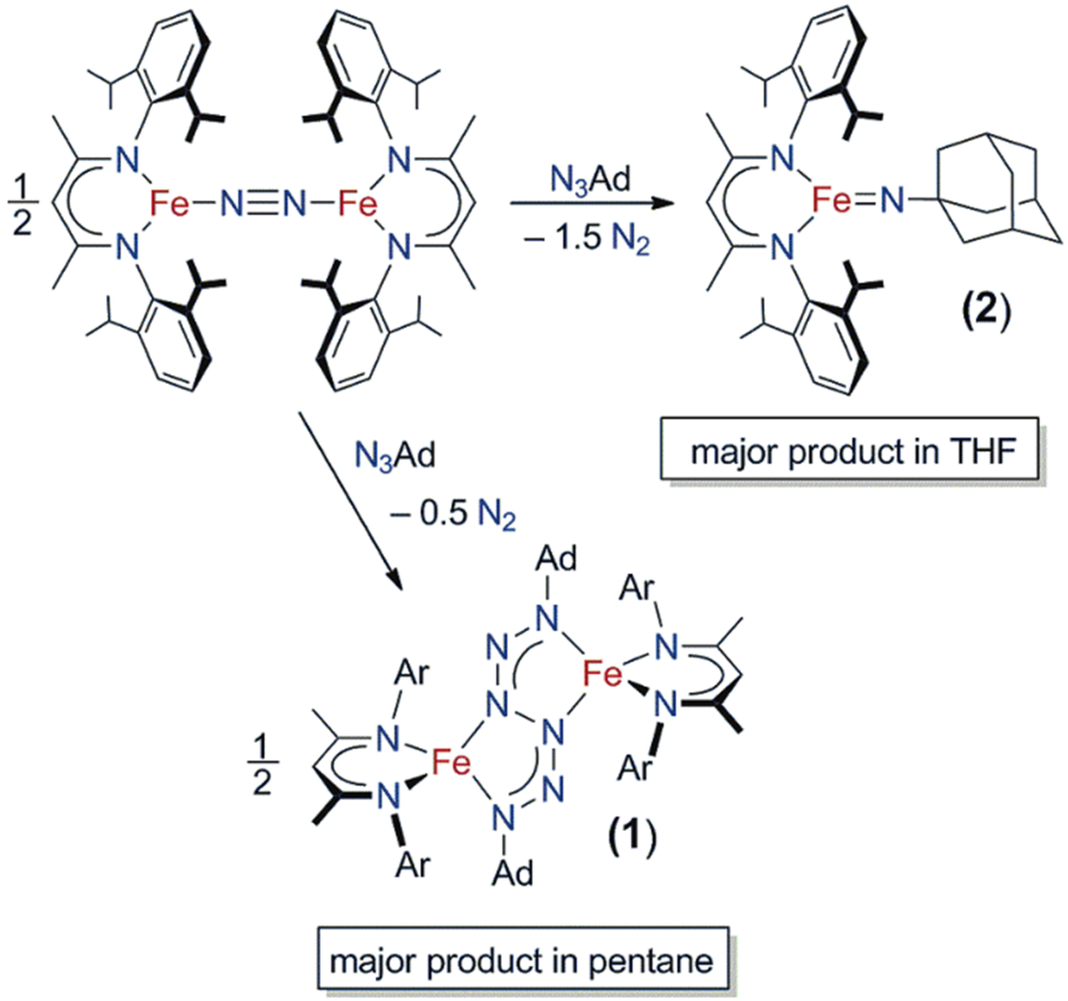
(3)

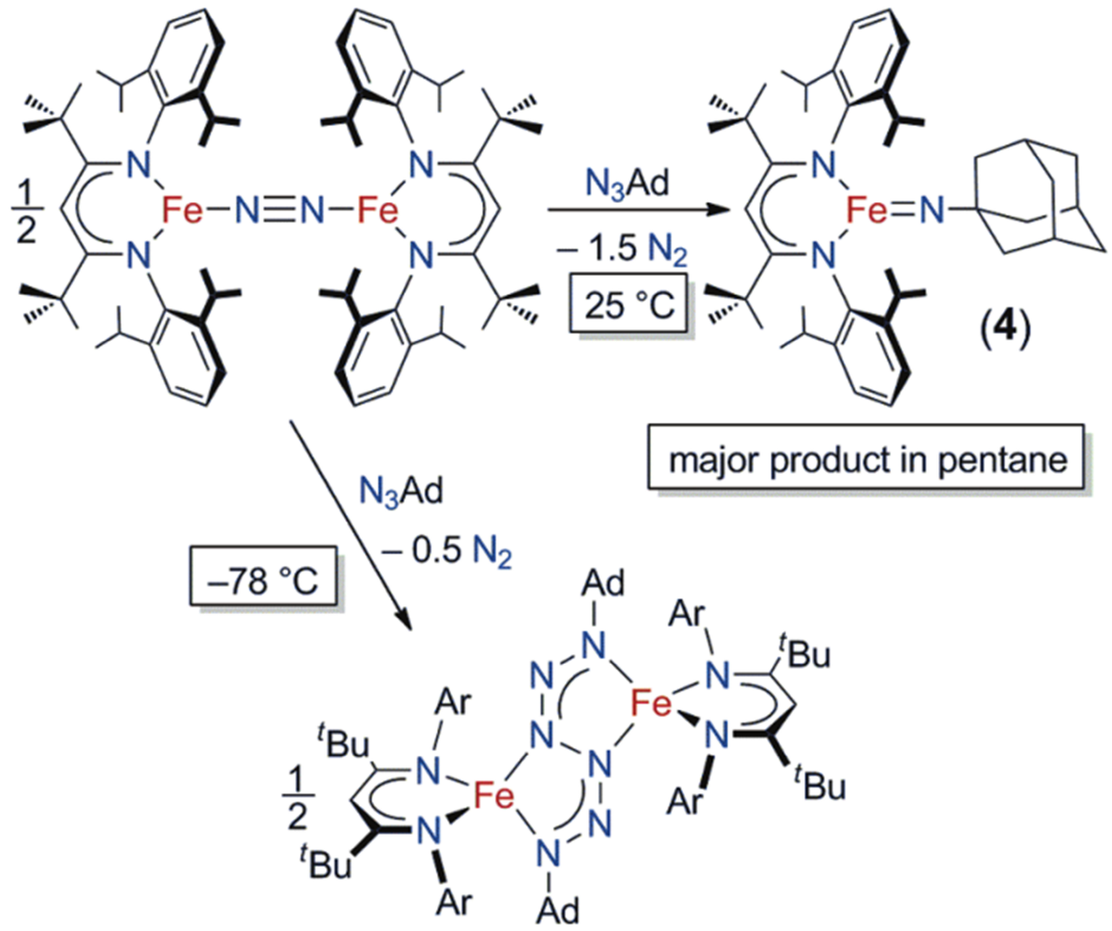
R_n: 2,6-$^{i}Pr_2$ > 2,5-$^{t}Bu_2$ > 2,6-Et_2 >>> 2,4,6-Me_3

2006年，Chirik报道了Fe(II)=N这类氮宾物种的形成。
在氢气的存在下，通过这种氮宾中间体的反应历程能够将叠氮化合物还原为胺。

Suzanne C. Bart, Emil Lobkovsky, Eckhard Bill, and Paul J. Chirik*. Synthesis and Hydrogenation of Bis(imino)pyridine Iron Imides. J. Am. Chem. Soc. 2006, 128, 5302-5303.

Fe=N

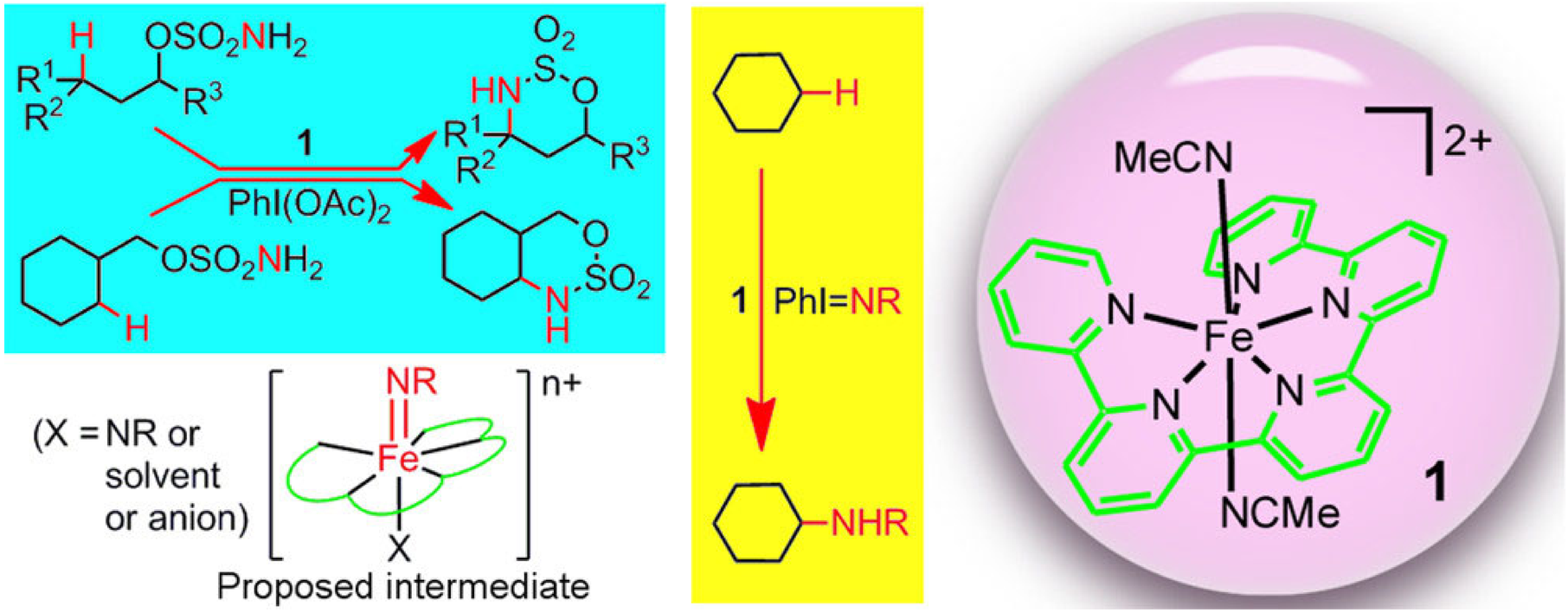




2010年，Holland报道了Fe(I)与叠氮化物形成Fe(III)=NAd的实例。
他们通过实验发现：Lewis碱和大位阻配体的存在能够促进这类氮宾中间体的形成，抑制二聚体和副产物的产生。

Ryan E. Cowley, Nathan J. DeYonker, Nathan A. Eckert, Thomas R. Cundari,* Serena DeBeer,* Eckhard Bill,* Xavier Ottenwaelder, Christine Flaschenriem, and Patrick L. Holland*. Three-Coordinate Terminal Imidoiron(III) Complexes: Structure, Spectroscopy, and Mechanism of Formation. Inorg. Chem. 2010, 49, 6172–6187.

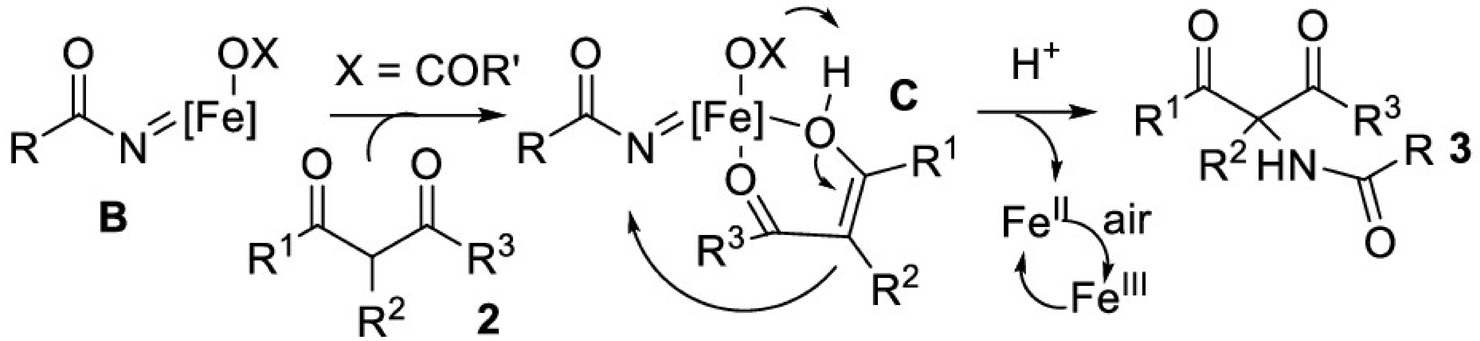
Fe=N



2013年，Che报道了PhI(I)化合物脱去PhI与Fe(II)形成氮宾的实例。

Yungen Liu, Xiangguo Guan, Ella Lai-Ming Wong, Peng Liu, Jie-Sheng Huang, and Chi-Ming Che*. Nonheme Iron-Mediated Amination of C(sp3)–H Bonds. Quinquepyridine-Supported Iron-Imide/Nitrene Intermediates by Experimental Studies and DFT Calculations. J. Am. Chem. Soc. 2013, 135, 19, 7194–7204.

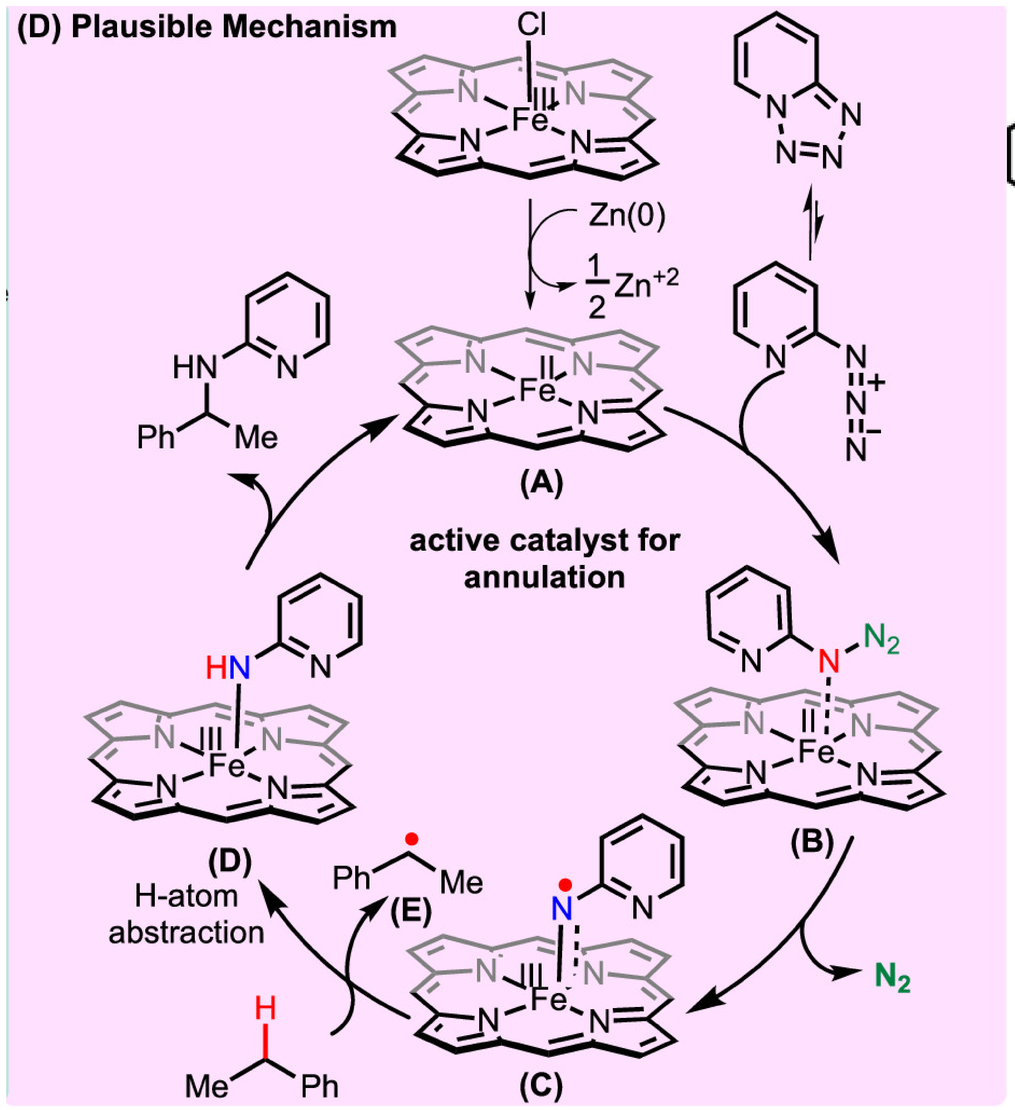
(2) Proposed Mechanism: photo/iron co-catalysis in C-H bond insertion

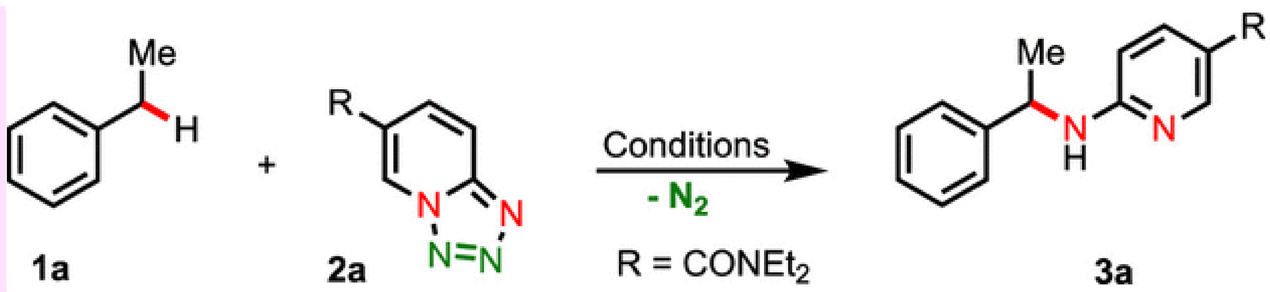


2022年，Qiu报道了N-羟基酰胺酯化合物与Fe(II)氧化加成形成氮宾的实例。

Ming Hou, Zhide Zhang, Xiaojing Lai, Qianshou Zong*, Xinpeng Jiang*, Meng Guan, Rui Qi, and Guanyinsheng Qiu*. Nonheme Iron-Mediated Amination of C(sp3)–H Bonds. Photoredox/Iron Dual-Catalyzed Insertion of Acyl Nitrenes into C–H Bonds. Org. Lett. 2022, 24, 23, 4114–4118.

Fe=N

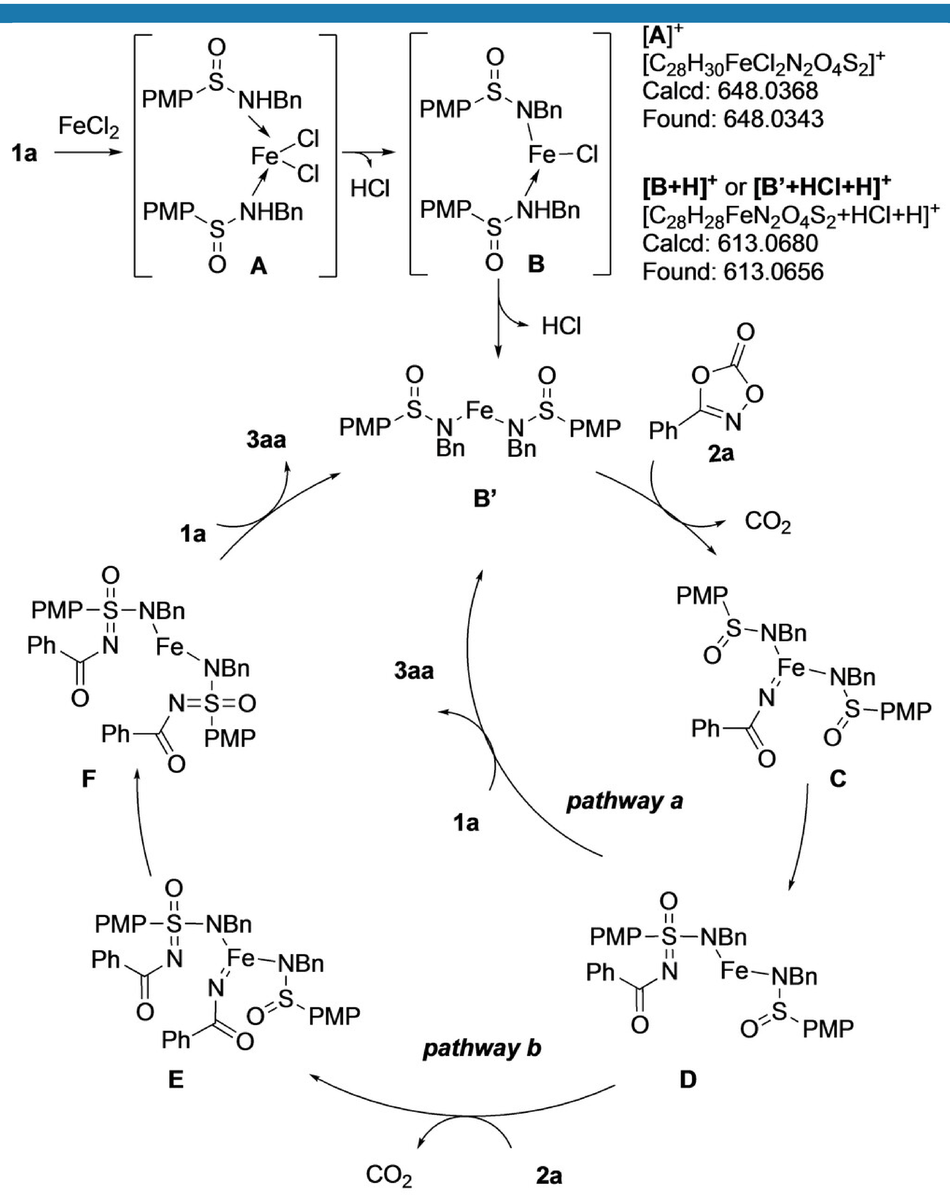


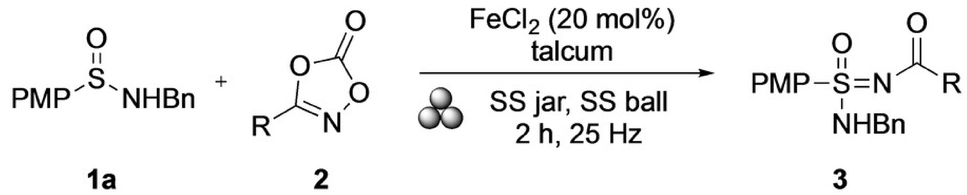


2022年，Chattopadhyay报道了叠氮类似物吡啶四氮唑脱去N_2与Fe(II)形成氮宾的实例。

Hillol Khatua, Subrata Das, Sima Patra, Sandip Kumar Das, Satyajit Roy, and Buddhadeb Chattopadhyay**. Iron-Catalyzed Intermolecular Amination of Benzylic C(sp3)−H Bonds. J. Am. Chem. Soc. 2022, 144, 21858−21866.

Fe=N

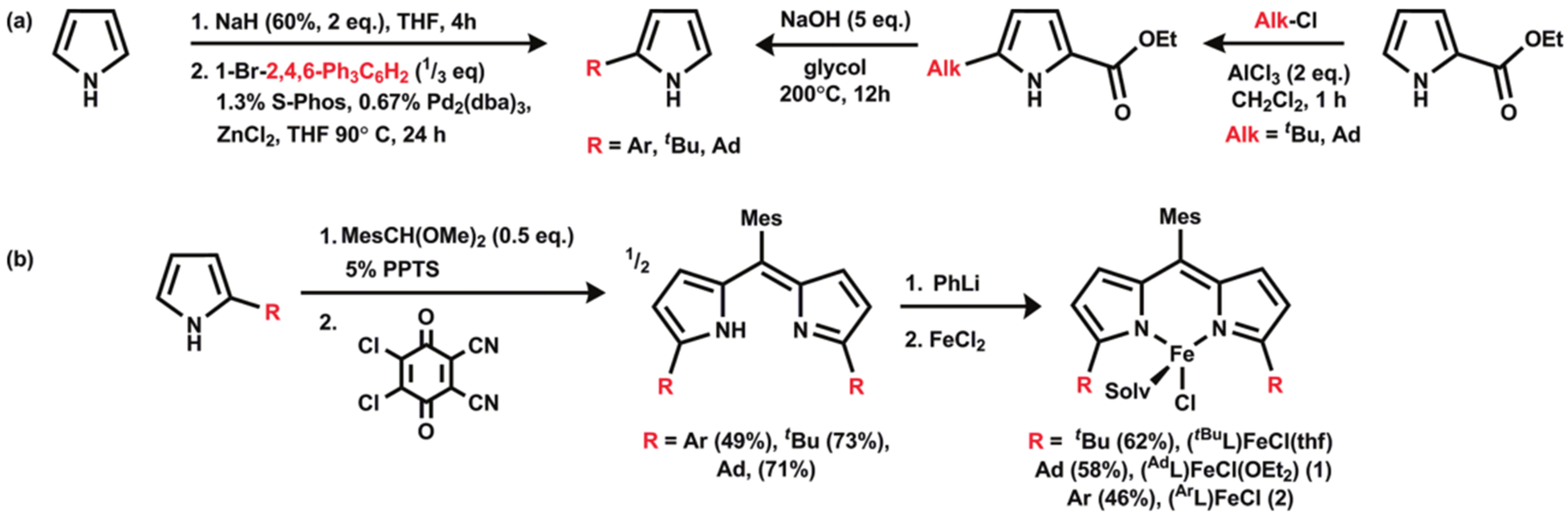




2024年，Bolm报道了二恶唑酮脱去CO_2与Fe(II)形成酰胺氮宾的实例。

Shulei Pan, Florian F. Mulks,* Peng Wu, Kari Rissanen, and Carsten Bolm*. Mechanochemical Iron-Catalyzed Nitrene Transfer Reactions: Direct Synthesis of N-Acyl Sulfonimidamides from Sulfinamides and Dioxazolones. Angew. Chem. Int. Ed. 2024, 63, e202316702.

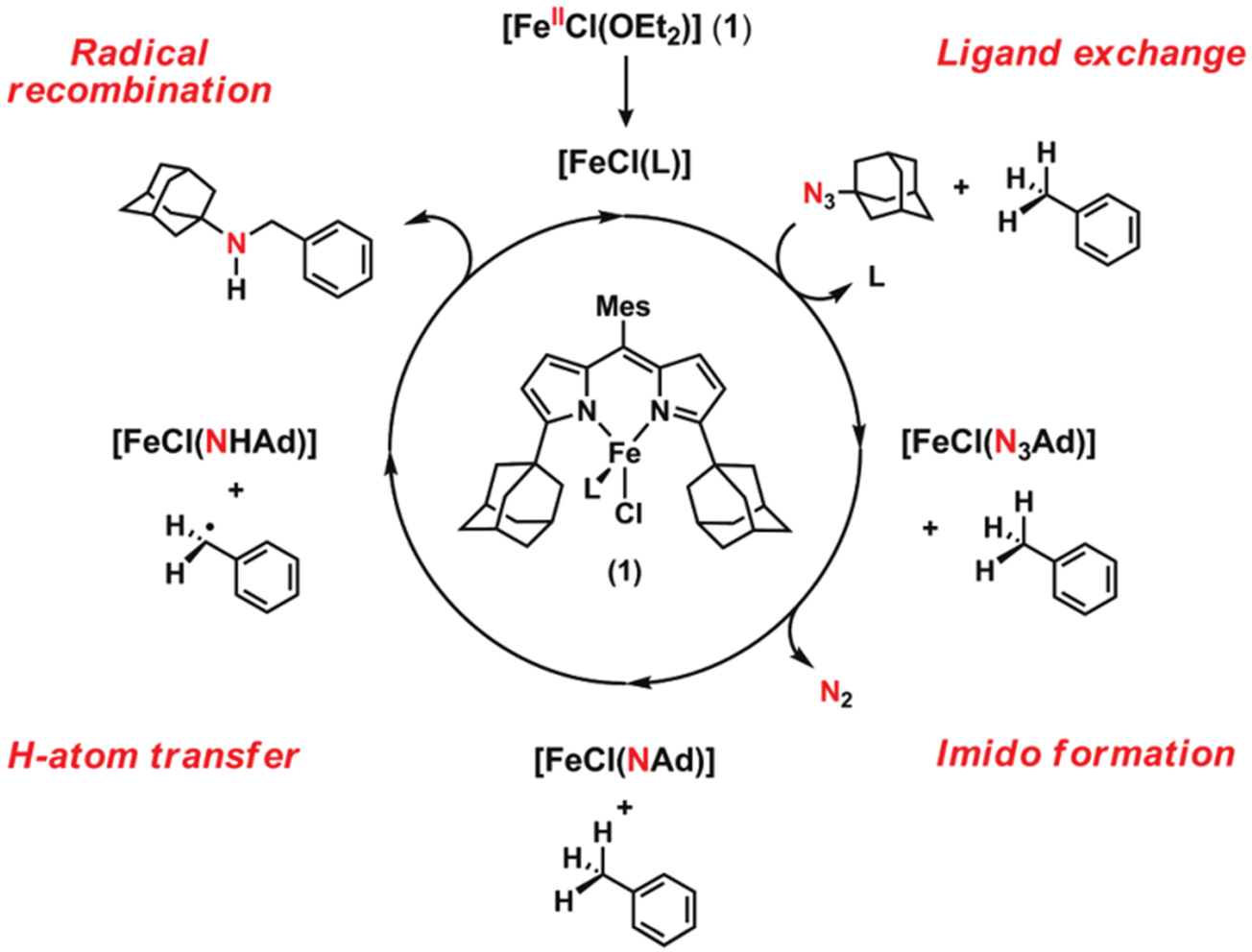
Fe=N



2011年，Betley报道了一类新的Fe(III)卟啉类似化合物。

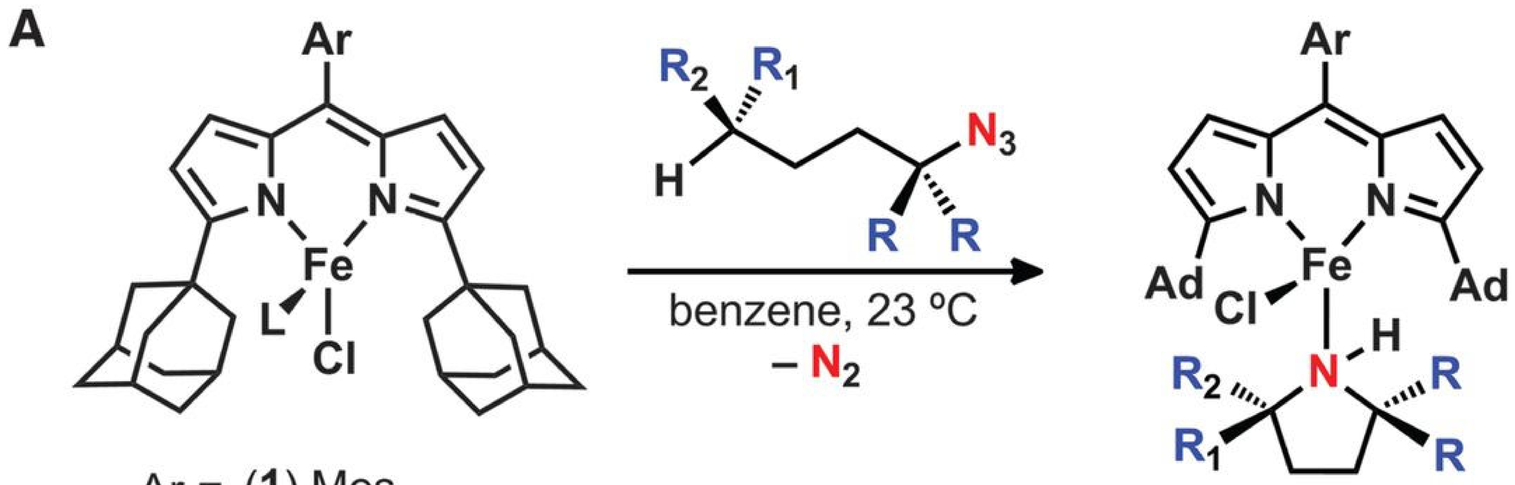
Evan R. King, Elisabeth T. Hennessy, and Theodore A. Betley*. Catalytic C-H Bond Amination from High-Spin Iron Imido Complexes. J. Am. Chem. Soc. 2011, 133, 4917–4923.

Fe=N



这类化合物同样能与叠氮化合物形成氮宾，通过HAT和外球的自由基进攻实现新的C-N构筑。

Evan R. King, Elisabeth T. Hennessy, and Theodore A. Betley*. Catalytic C-H Bond Amination from High-Spin Iron Imido Complexes. J. Am. Chem. Soc. 2011, 133, 4917–4923.



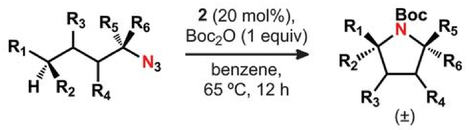
Ar = (**1**) Mes
(**2**) 2,6-$Cl_2C_6H_3$

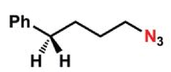
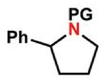
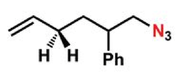
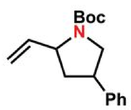
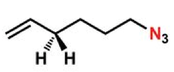
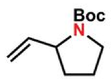
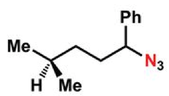
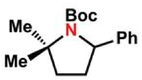
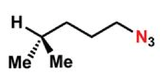
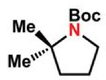
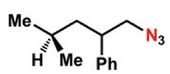
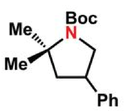
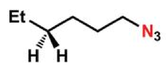
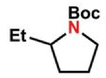
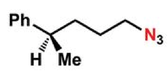
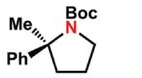
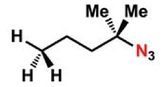
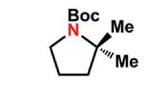
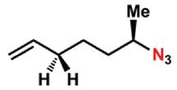
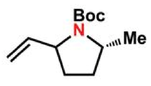
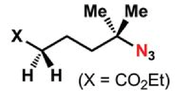
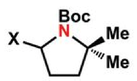
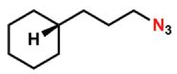
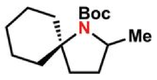
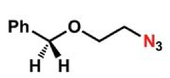
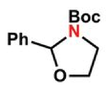
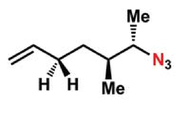
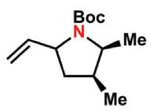
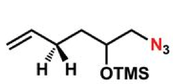
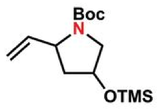
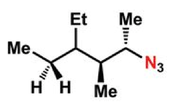
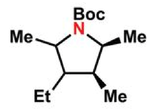
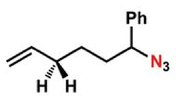
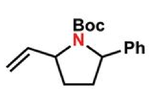
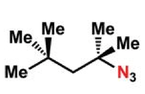
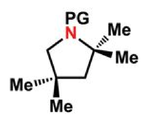
R_1, R_2, R = (**3**) Ph, H, H
(**4**) C_2H_3, H, H
(**5**) Me, Me, H
(**6**) Et, H, H
(**7**) H, H, Me

2013年，Betley在已有的研究的基础上，设计了一类碳链叠氮底物，通过分子内的1,5-HAT实现了C-N的构筑。

Elisabeth T. Hennessy and Theodore A. Betley*. Complex N-Heterocycle Synthesis via Iron-Catalyzed, Direct C–H Bond Amination. Science, 340, 591-595(2013).

Fe=N



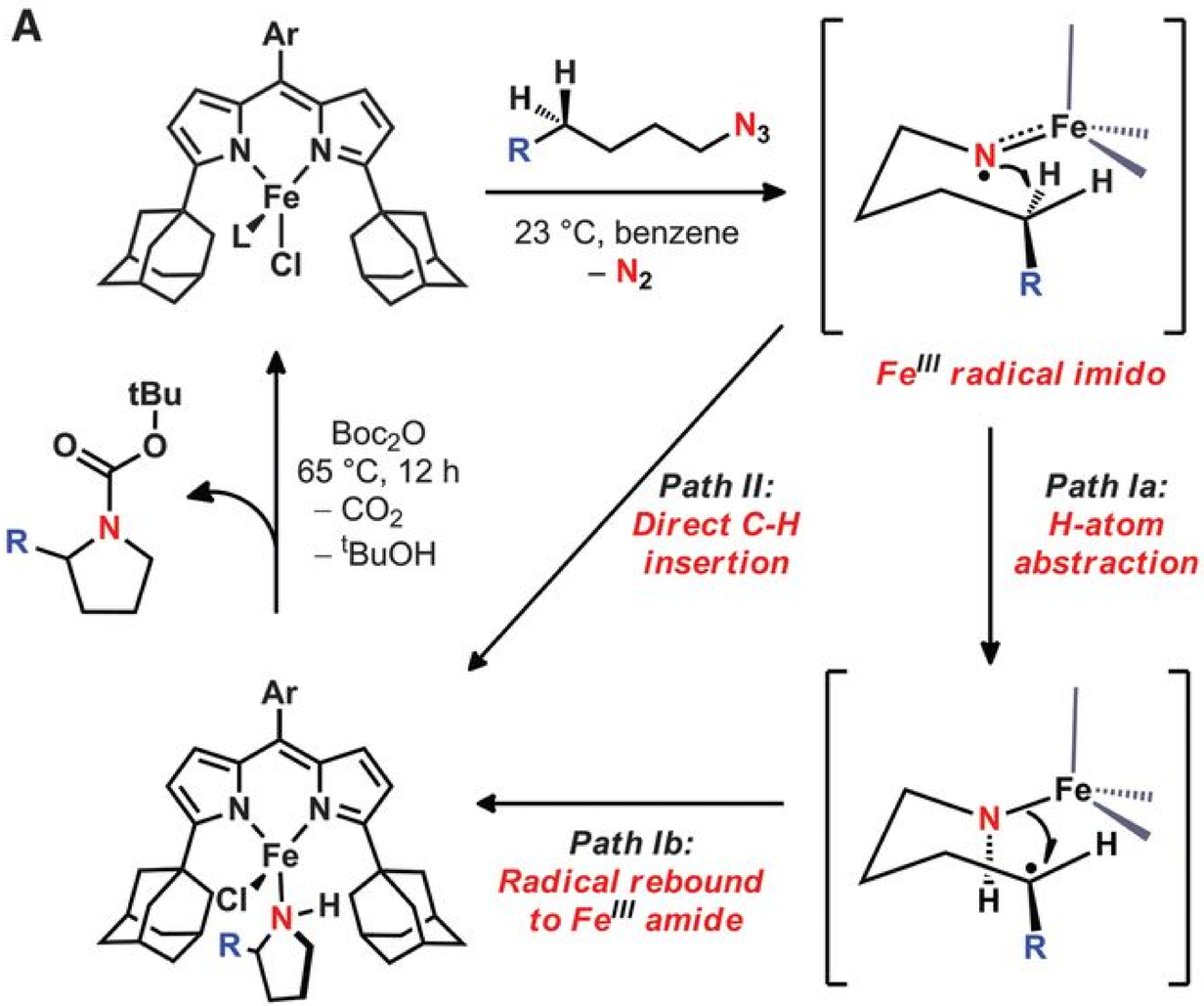
Entry	Azide	Pyrrolidine	Yield (%)*	Entry	Azide	Pyrrolidine	Yield (%)*
1			98†§ (PG = Fmoc) 93†§ 57‡§ (PG = Boc)	10			66 1:5:1.0 dr
2			72‡§	11			70
3			60§ 49‡§	12			98
4			19‡§	13			75‡ 93% ee
5			17‡§	14			84 1.1:1.0 dr
6	 (X = CO_2Et)		11	15			67
7			47	16			73 2.1:1.0 dr
8			68‡	17			58 5.5:1.5: 1.0:0.08 dr
9			60 3.9:1.0 dr	18			14 (PG = Boc) 78† (PG = Fmoc)

* ^{1}H NMR yield using ferrocene or trimethoxybenzene as an internal standard unless otherwise noted. † Stoichiometric reaction with one equivalent of catalyst **2**. ‡ Isolated yield. § 10 mol% catalyst **2**.

该反应具有良好的底物范围和选择性，对一些易离去基团同样有较优容忍性。

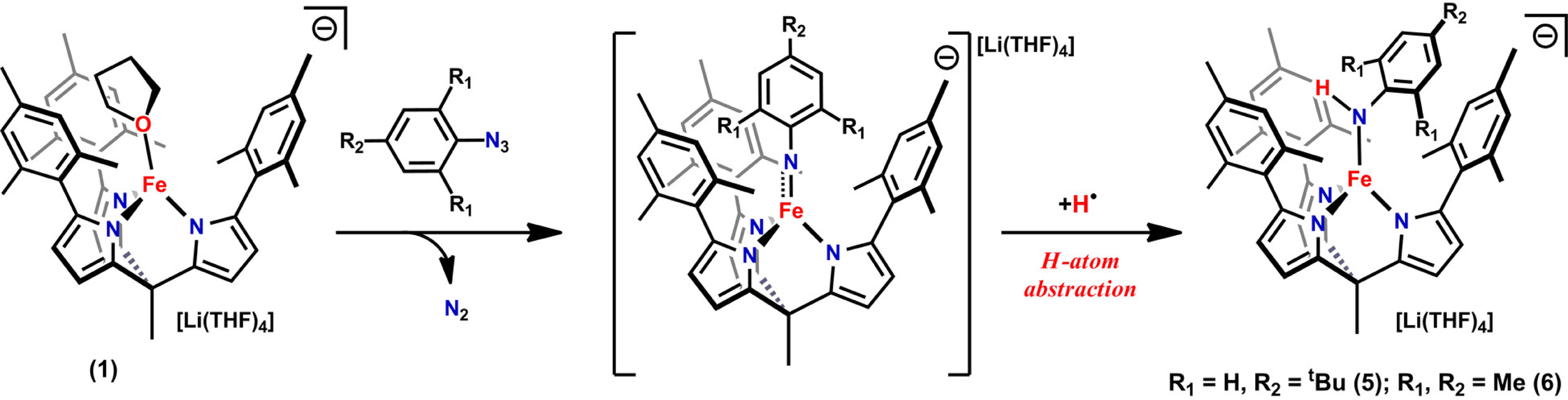
Elisabeth T. Hennessy and Theodore A. Betley*. Complex N-Heterocycle Synthesis via Iron-Catalyzed, Direct C–H Bond Amination. Science, 340, 591-595(2013).

Fe=N



Elisabeth T. Hennessy and Theodore A. Betley*. Complex N-Heterocycle Synthesis via Iron-Catalyzed, Direct C–H Bond Amination. Science, 340, 591-595(2013).

Fe=N

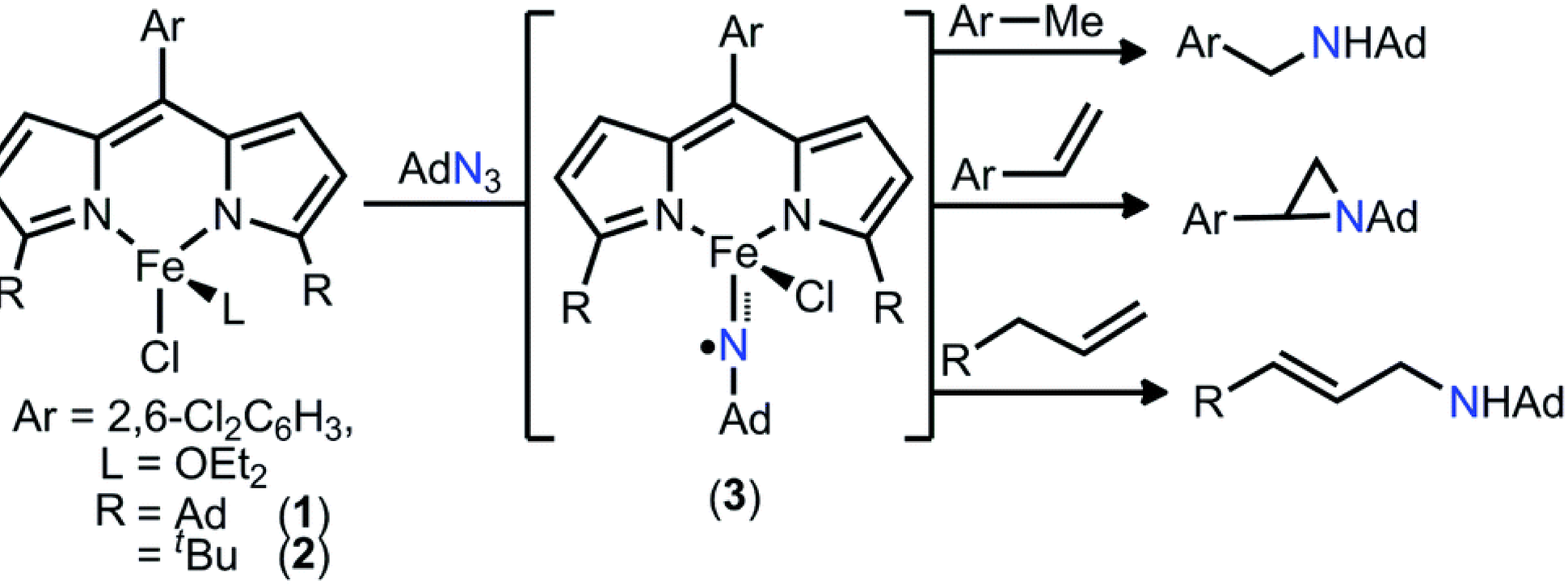


(1)

R_1 = H, R_2 = ^{t}Bu (5); R_1, R_2 = Me (6)

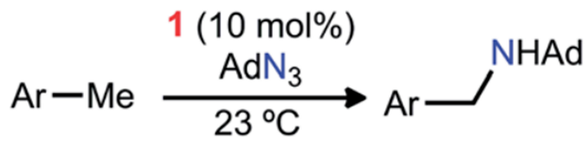
2014年，Betley通过DFT计算和中间体的合成表征，
提出氮宾中间体易于通过HAT向酰胺或者胺配体转化。

Graham T. Sazama and Theodore A. Betley*. Multiple, Disparate Redox Pathways Exhibited by a Tris(pyrrolido)ethane Iron Complex. Inorg. Chem. 2014, 53, 269−281.

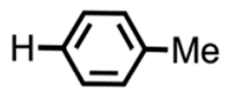
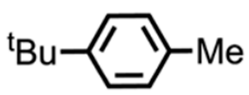
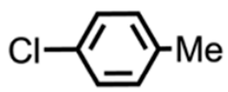
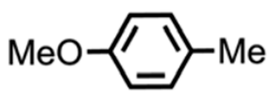
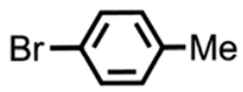


根据这一机理，他们在2014年发表了这类氮宾化合物与芐基底物、烯烃底物和烯丙基底物反应形成新的胺的方法。

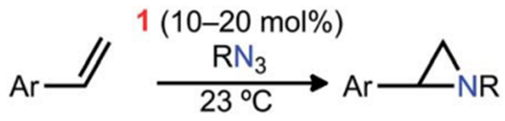
Elisabeth T. Hennessy, Richard Y. Liu, Diana A. Iovan, Ryan A. Duncan and Theodore A. Betley*. Iron-mediated intermolecular N-group transfer chemistry with olefinic substrates. Chem. Sci., 2014, 5, 1526.



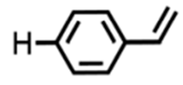
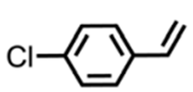
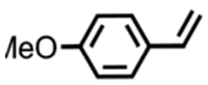
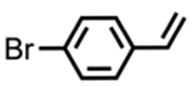
Benzylic amination

Entry	Substrate	Yield[b] (%)	k_x/k_H[c]
1		60[d]	1.00
2		46	1.10
3		52	1.14
4		47	1.08
5		47	1.18

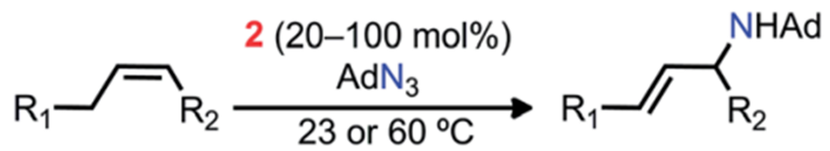
Elisabeth T. Hennessy, Richard Y. Liu, Diana A. Iovan, Ryan A. Duncan and Theodore A. Betley*. Iron-mediated intermolecular N-group transfer chemistry with olefinic substrates. Chem. Sci., 2014, 5, 1526.



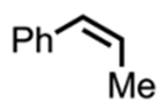
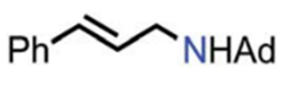
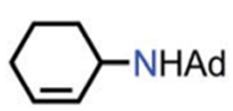
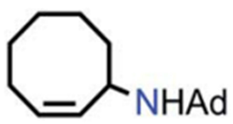
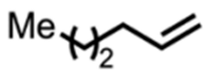
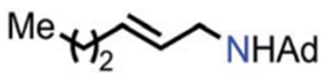
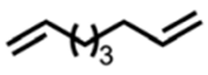
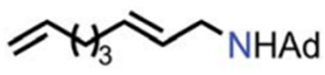
Aziridination

Substrate	Yield[b] (%)	k_x/k_H[c]	Entry	Azide	Yield[f] (%)
	85[e]	1.00	10	$^{t}BuN_3$	86
	80	1.11	11	$^{n}BuN_3$	53
	75	1.20	12	PhN_3	17
	80	1.09	13	p-$^{t}BuPhN_3$	64
			14	p-$NO_2PhSO_2N_3$	0
			15	$TMSN_3$	0

Elisabeth T. Hennessy, Richard Y. Liu, Diana A. Iovan, Ryan A. Duncan and Theodore A. Betley*. Iron-mediated intermolecular N-group transfer chemistry with olefinic substrates. Chem. Sci., 2014, 5, 1526.

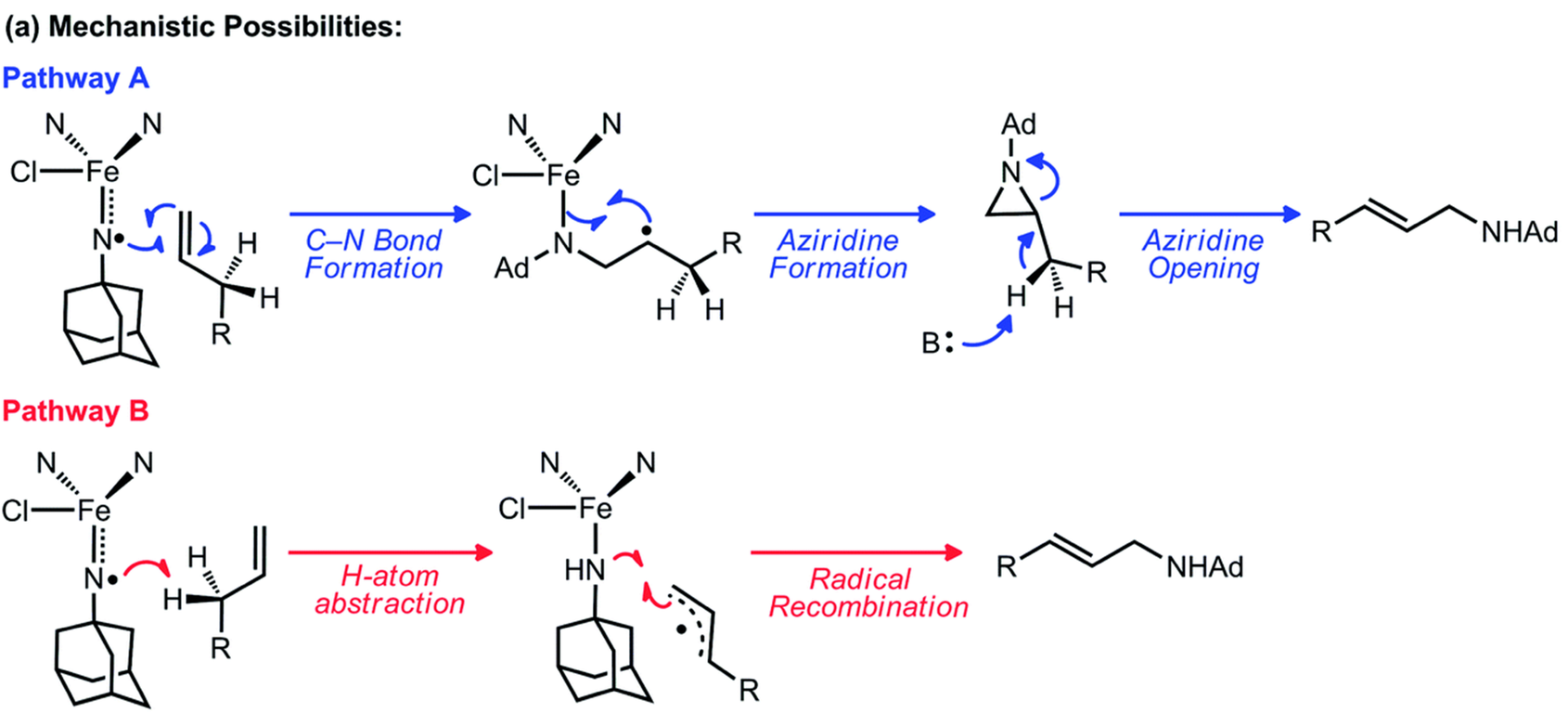


Allylic amination

Entry	Substrate	Product	Yield[g] (%)
16			38[j]
17			12[h], 7(9)[i], 17(19)[j]
18			18[j]
19			77[h], 29[i], 43[j]
20			52[h], 15(15)[i], (38)[j]

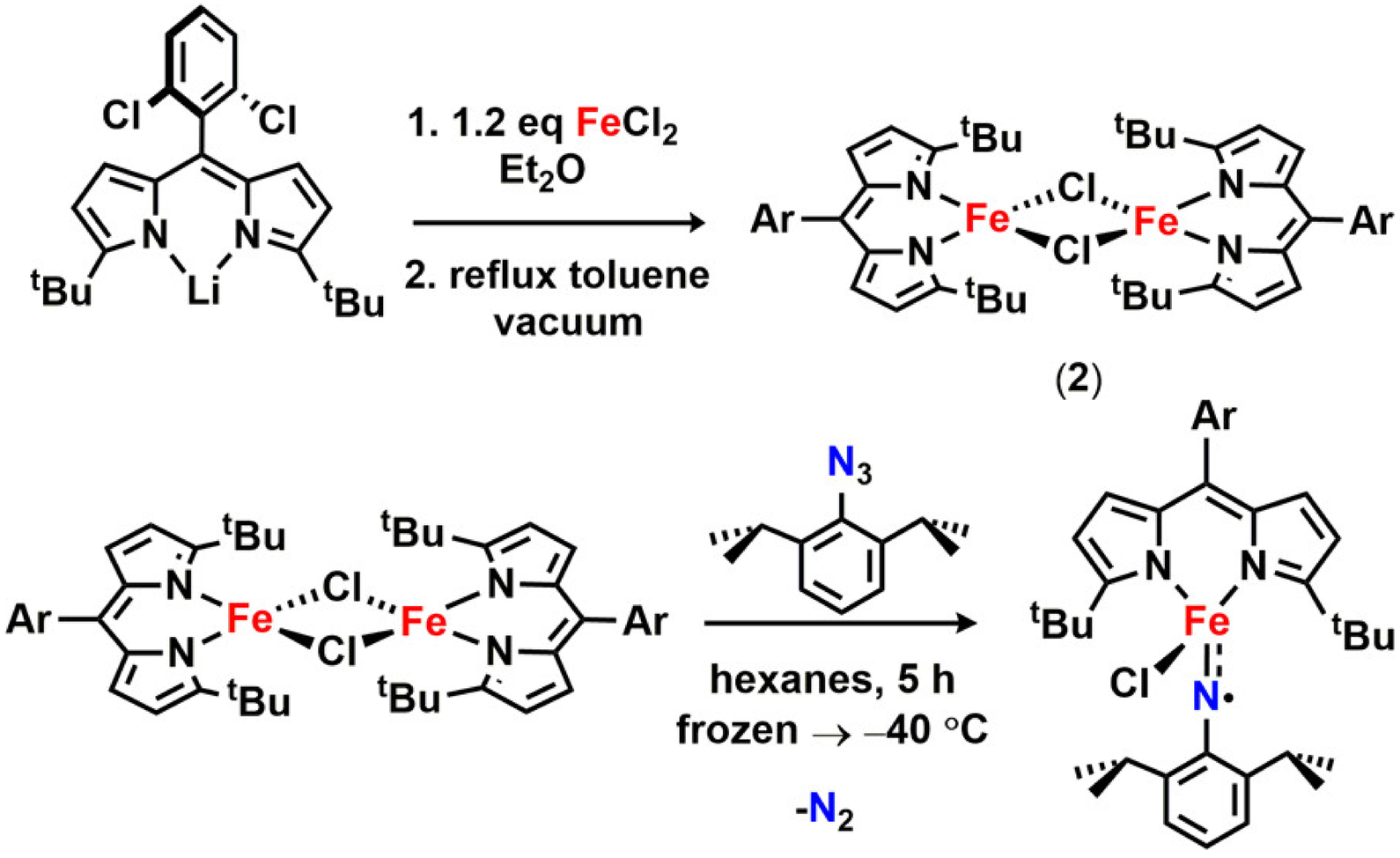
Elisabeth T. Hennessy, Richard Y. Liu, Diana A. Iovan, Ryan A. Duncan and Theodore A. Betley*. Iron-mediated intermolecular N-group transfer chemistry with olefinic substrates. Chem. Sci., 2014, 5, 1526.

Fe=N



Elisabeth T. Hennessy, Richard Y. Liu, Diana A. Iovan, Ryan A. Duncan and Theodore A. Betley*. Iron-mediated intermolecular N-group transfer chemistry with olefinic substrates. Chem. Sci., 2014, 5, 1526.

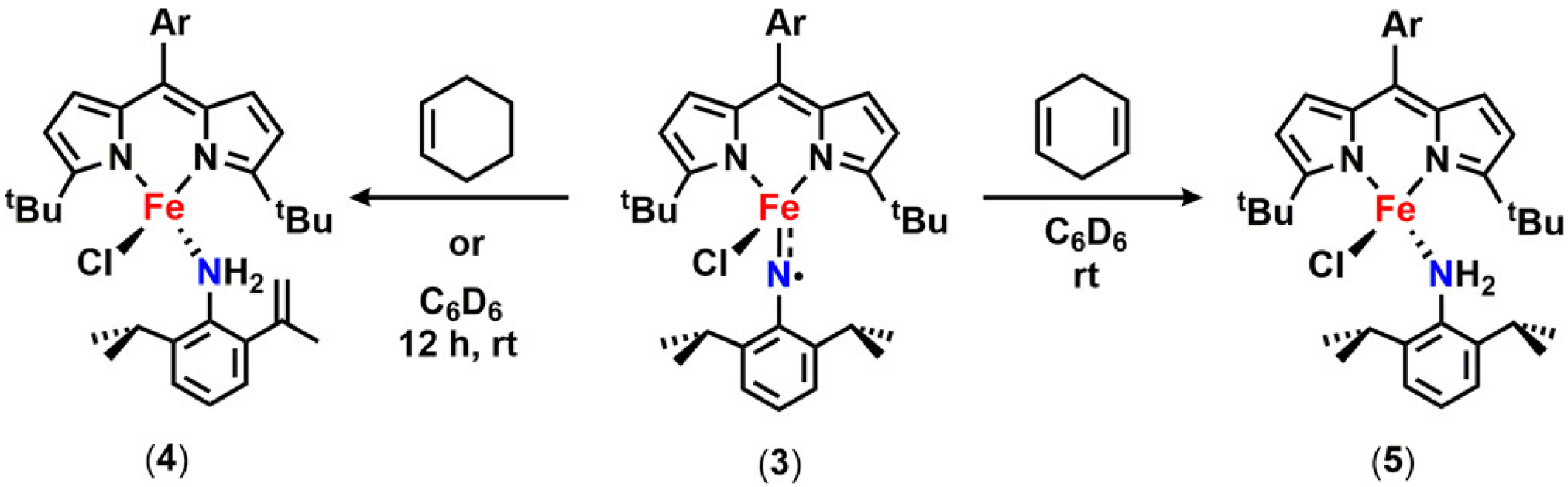
Fe=N



2016年,Betley对反应中可能存在的氮宾中间体做了更加细致的研究。
他们发现Fe(II)催化剂可能会以二聚体的形式存在，在加入叠氮化物后二聚体解离产生Fe(IV)=N中间体。

Diana A. Iovan and Theodore A. Betley*. Characterization of Iron-Imido Species Relevant for N-Group Transfer Chemistry. J. Am. Chem. Soc. 2016, 138, 1983−1993.

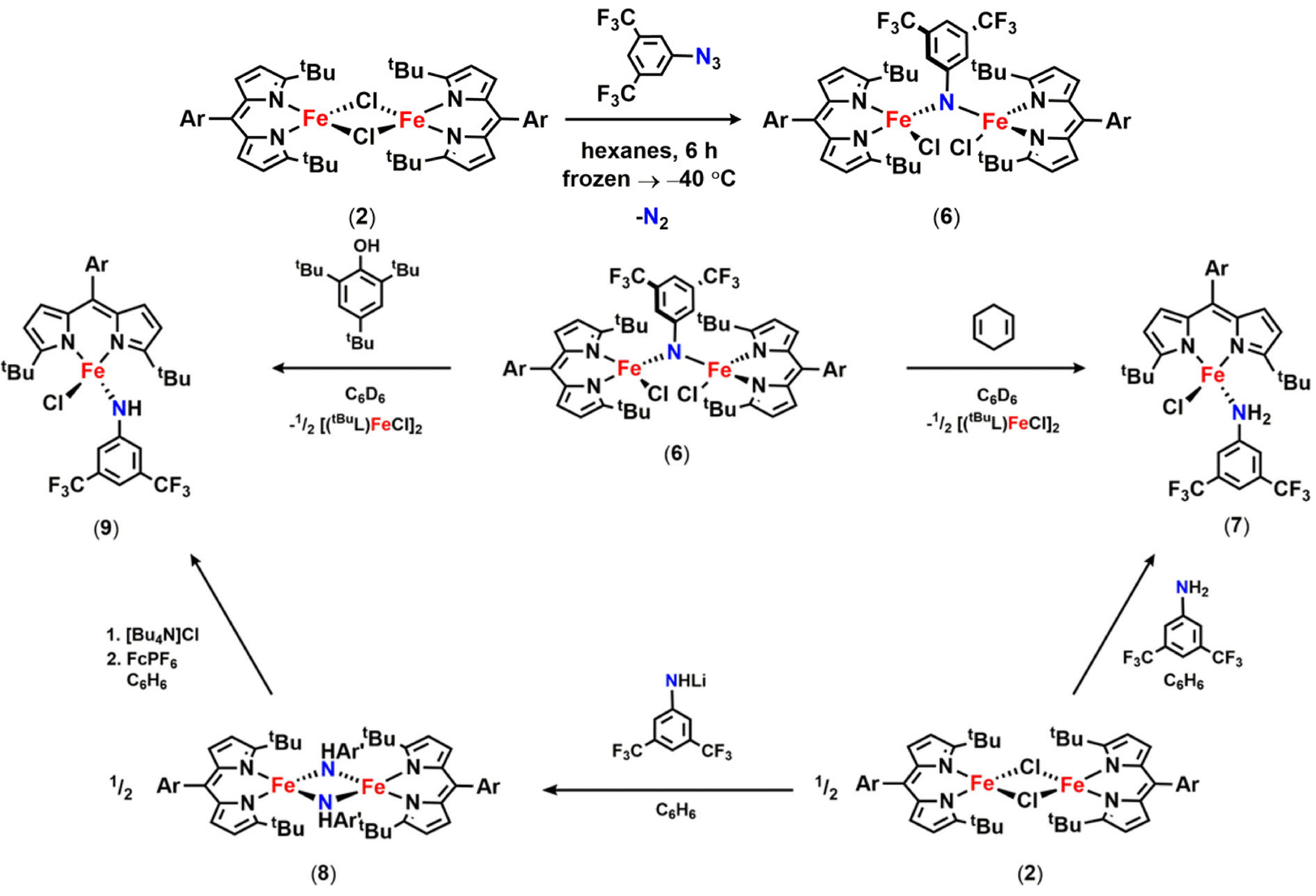
Fe=N



这种氮宾中间体不稳定，常温静置即会发生分子内氢原子提取(HAA)反应。
环己二烯会定量的将其转化为对应的芳胺，但C-H更强的环己烯存在时氮宾中间体更倾向于分子内HAA。

Diana A. Iovan and Theodore A. Betley*. Characterization of Iron-Imido Species Relevant for N-Group Transfer Chemistry. J. Am. Chem. Soc. 2016, 138, 1983−1993.

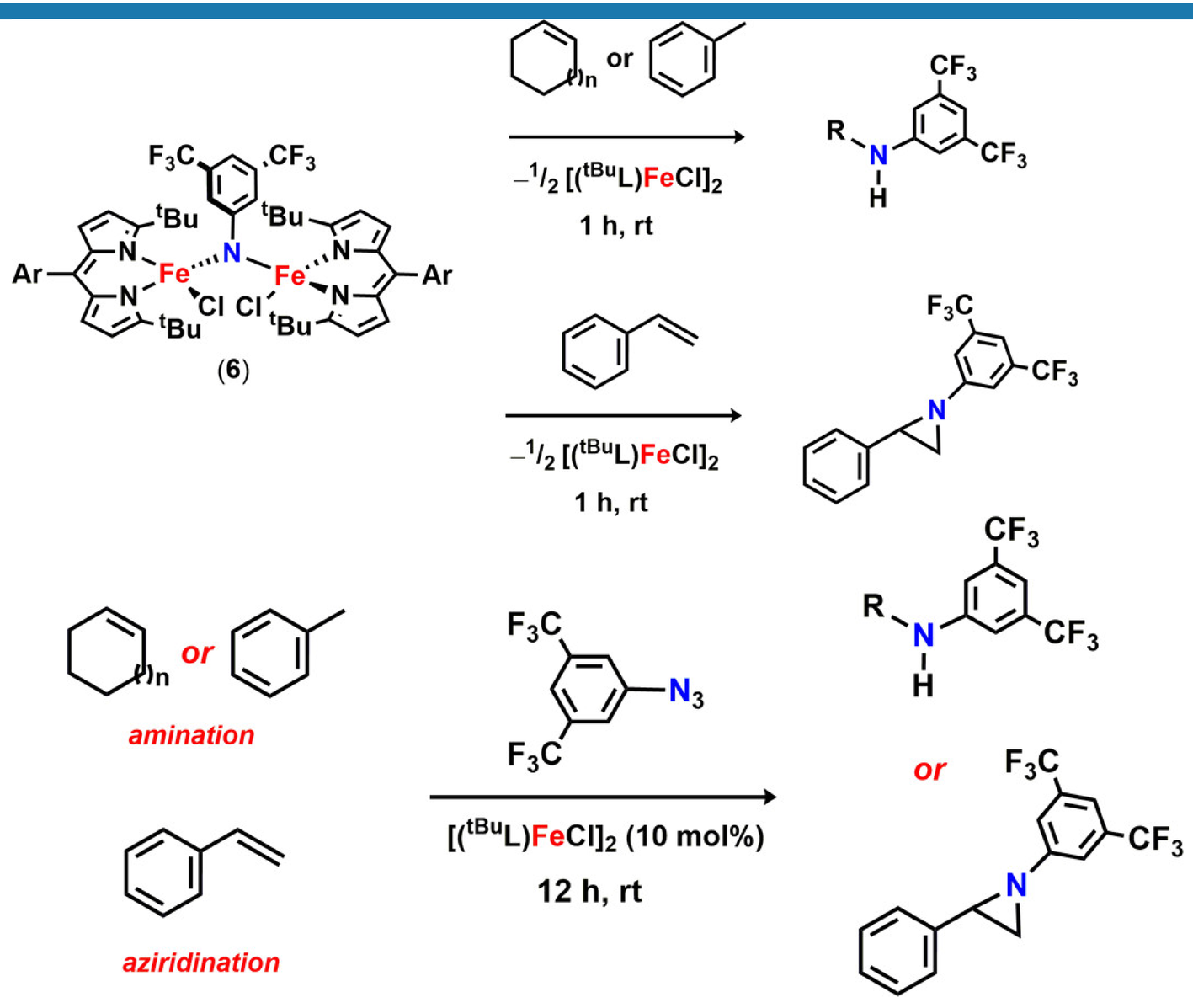
Fe=N



换用更缺电的芳基叠氮会产生桥接胺中间体。这类中间体有与氮宾中间体类似的反应性质。

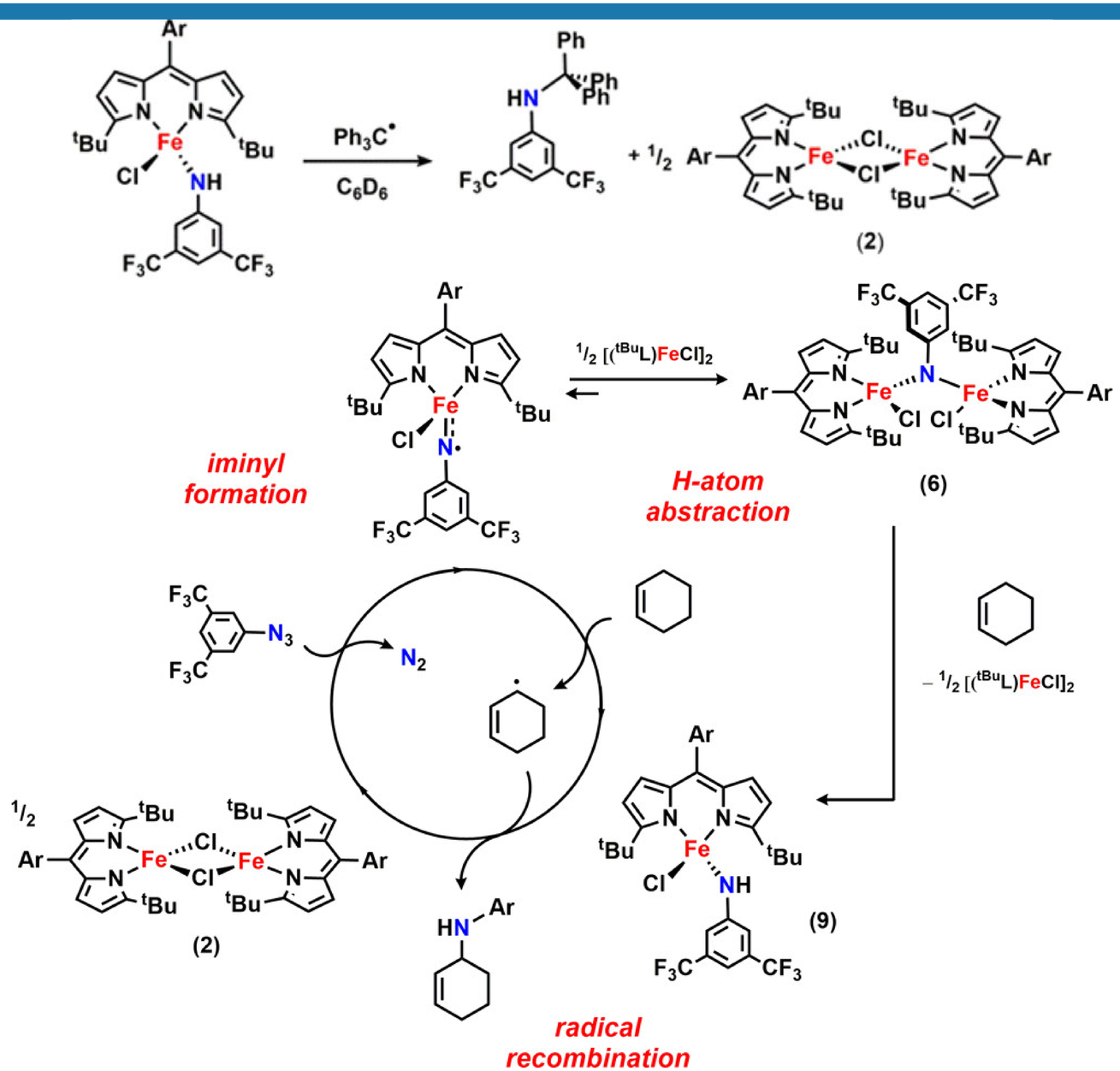
Diana A. Iovan and Theodore A. Betley*. Characterization of Iron-Imido Species Relevant for N-Group Transfer Chemistry. J. Am. Chem. Soc. 2016, 138, 1983−1993.

Fe=N



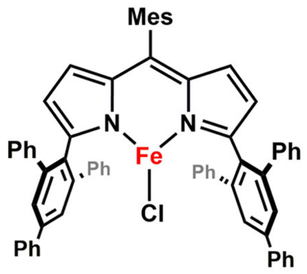
Diana A. Iovan and Theodore A. Betley*. Characterization of Iron-Imido Species Relevant for N-Group Transfer Chemistry. J. Am. Chem. Soc. 2016, 138, 1983−1993.

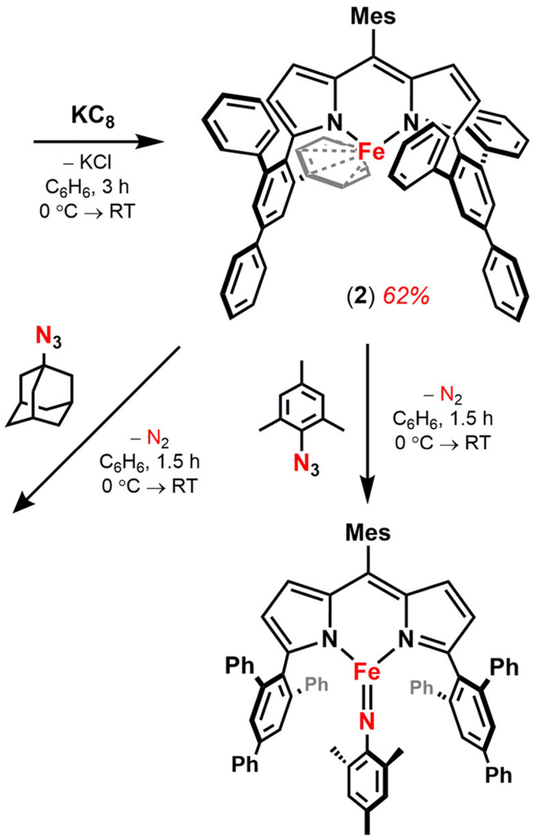
Fe=N

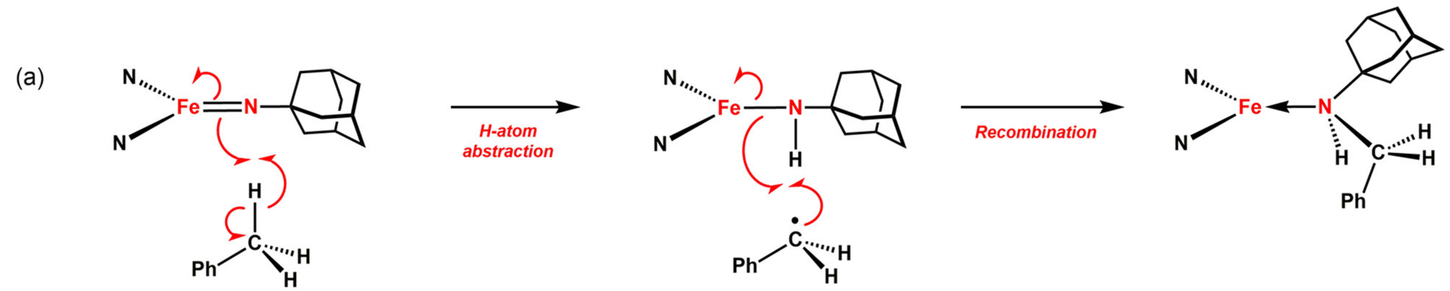


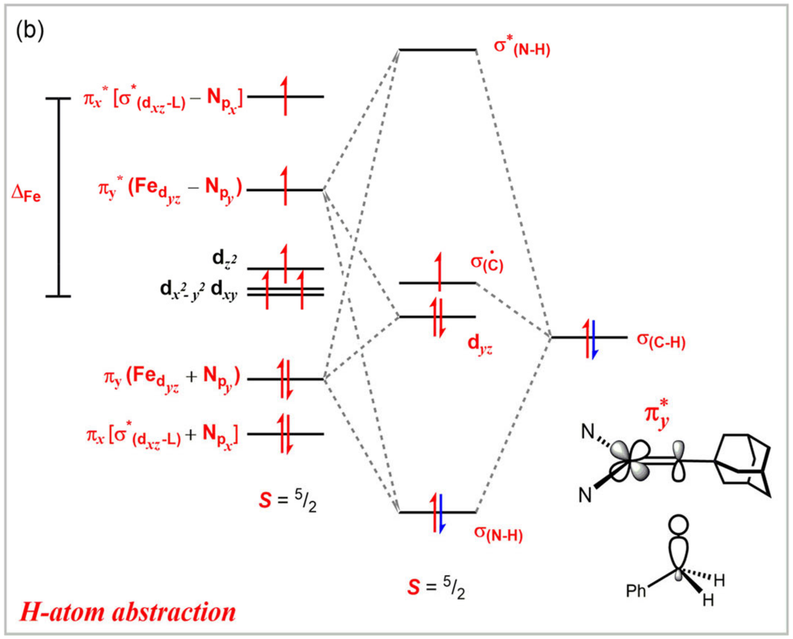
Diana A. Iovan and Theodore A. Betley*. Characterization of Iron-Imido Species Relevant for N-Group Transfer Chemistry. J. Am. Chem. Soc. 2016, 138, 1983−1993.

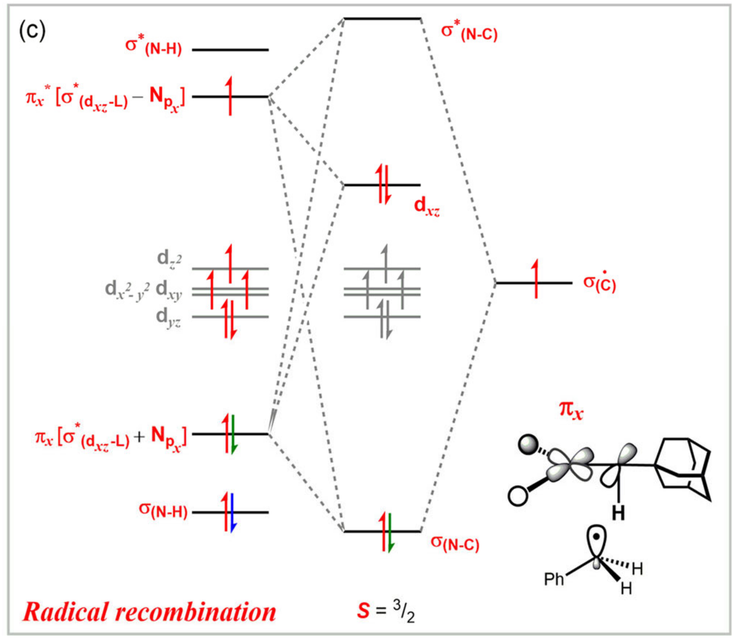
Fe=N







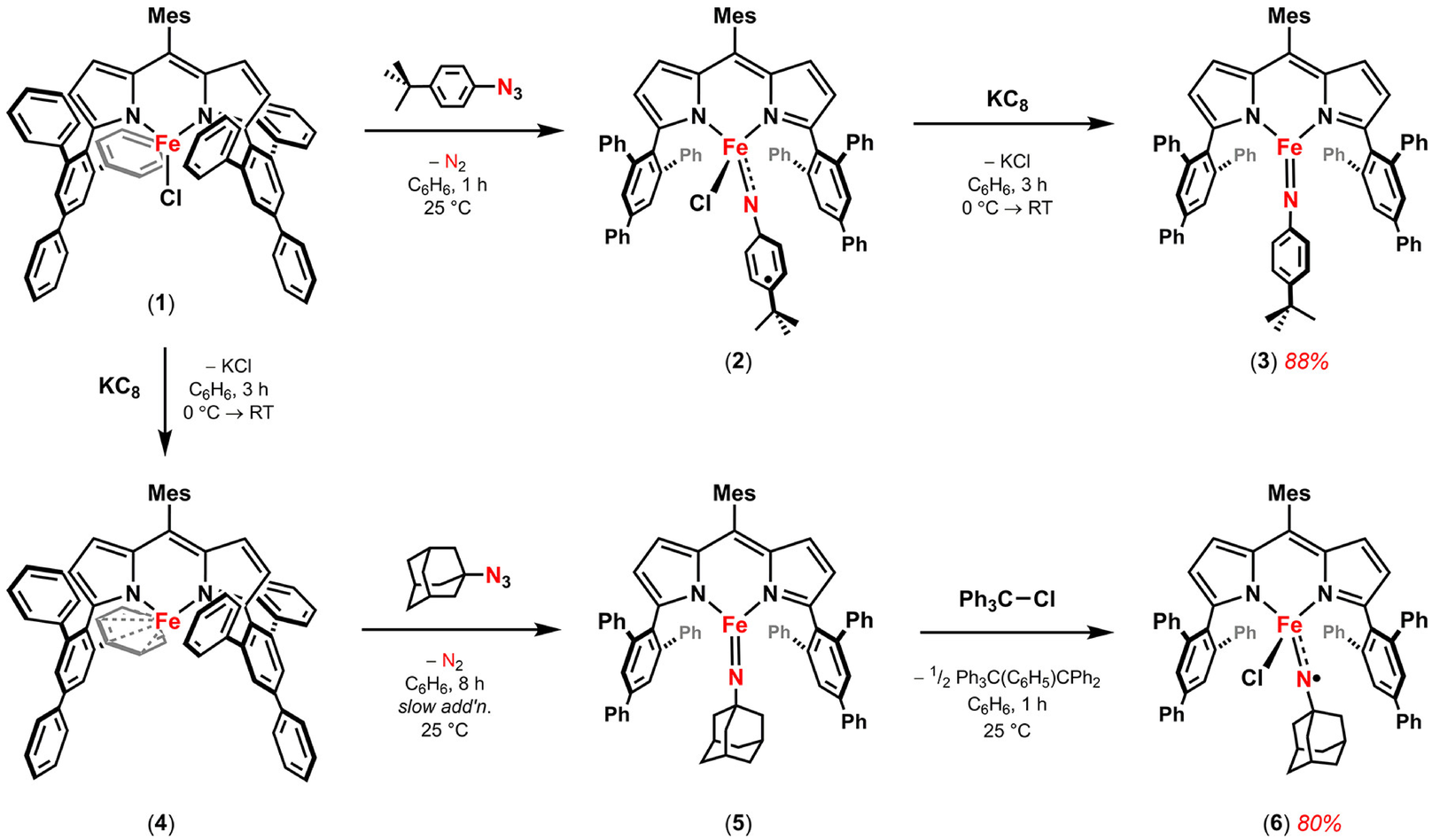




2017年，Betley报道了两种高自旋的Fe(III)=N配合物，从电子变化的角度说明了C-H胺化的反应历程。

Matthew J. T. Wilding, Diana A. Iovan, and Theodore A. Betley*. High-Spin Iron Imido Complexes Competent for C–H Bond Amination. J. Am. Chem. Soc. 2017, 139, 12043−12049.

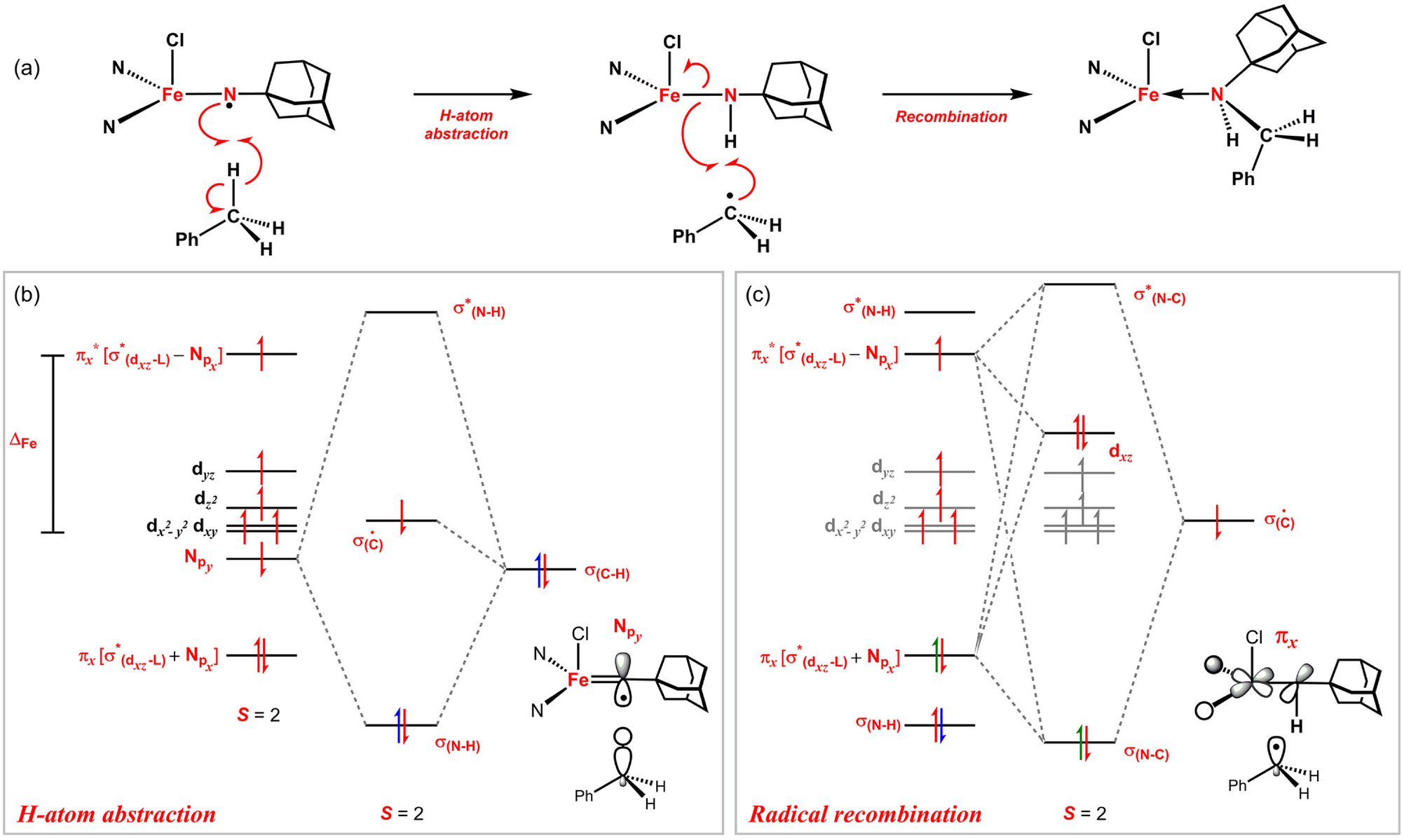
Fe=N



同年，他们对比两种不同价态Fe中间体的C-H胺化反应性，发现Fe(IV)=N中间体的活性相比Fe(III)=N中间体的活性更加优越。

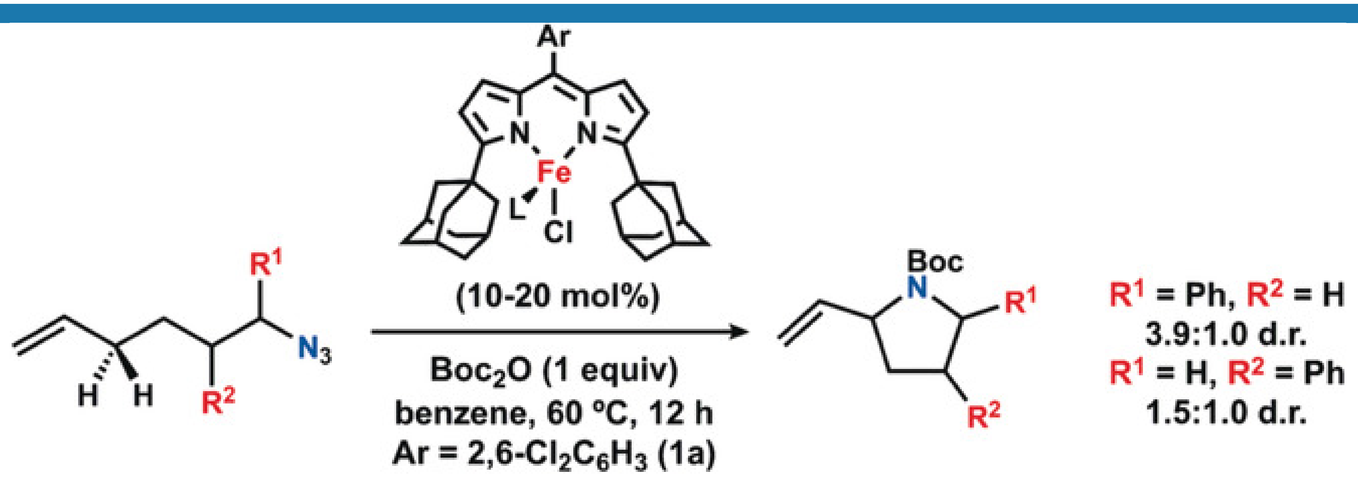
Matthew J. T. Wilding, Diana A. Iovan, Alexandra T. Wrobel, James T. Lukens, Samantha N. MacMillan, Kyle M. Lancaster, and Theodore A. Betley*. Direct Comparison of C−H Bond Amination Efficacy through Manipulation of Nitrogen-Valence Centered Redox: Imido versus Iminyl. J. Am. Chem. Soc. 2017, 139, 14757−14766.

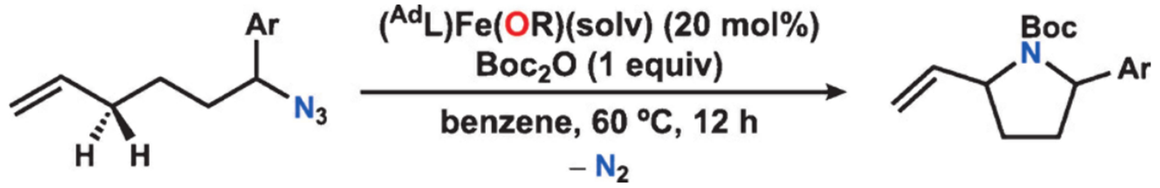
Fe=N



Matthew J. T. Wilding, Diana A. Iovan, Alexandra T. Wrobel, James T. Lukens, Samantha N. MacMillan, Kyle M. Lancaster, and Theodore A. Betley*. Direct Comparison of C−H Bond Amination Efficacy through Manipulation of Nitrogen-Valence Centered Redox: Imido versus Iminyl. J. Am. Chem. Soc. 2017, 139, 14757−14766.

Fe=N

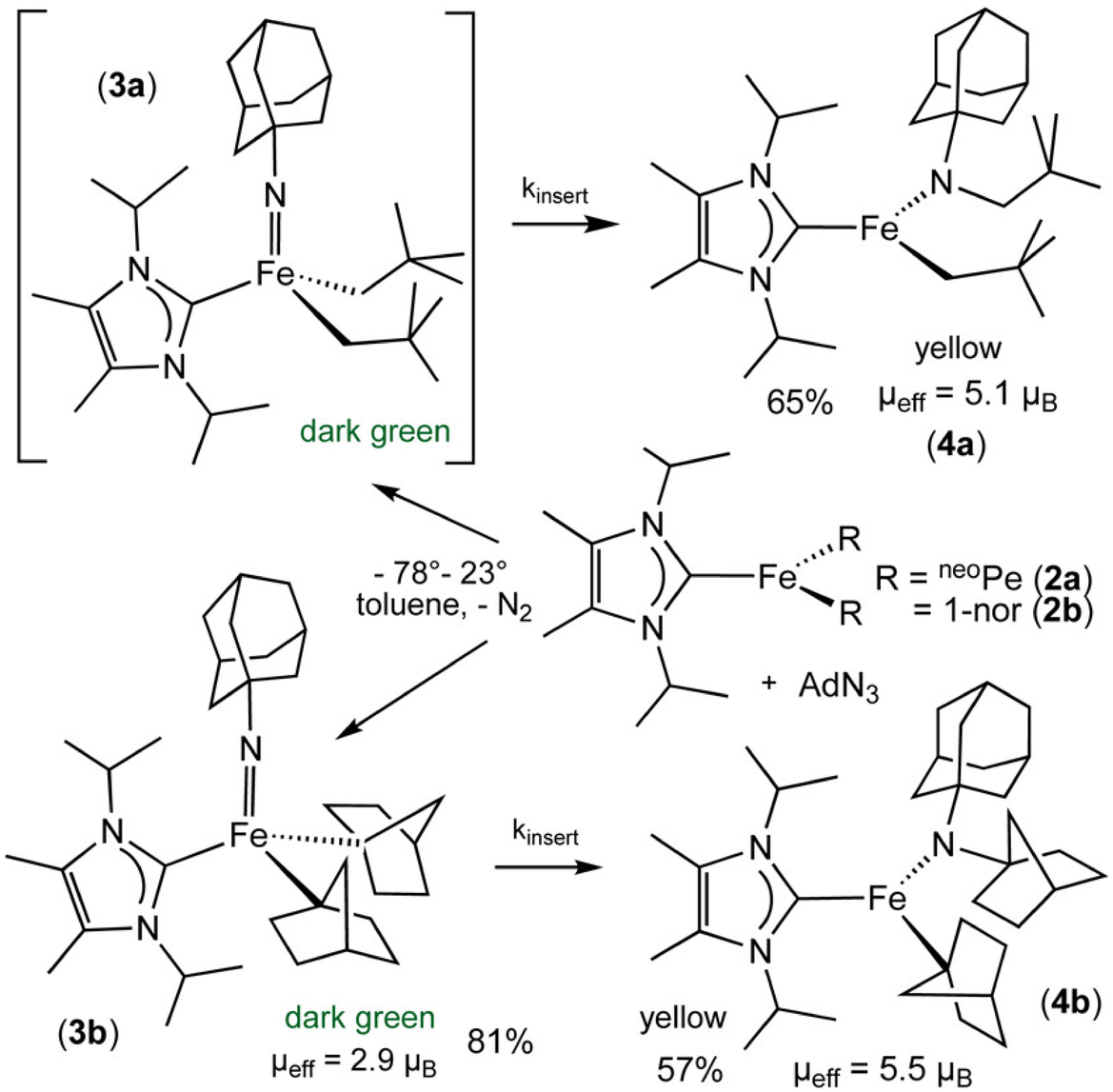




R	Complex	Yield [%]	d.r.[c]
$C(CF_3)(Me)Ph$	**6**	54[a]	13:1
$C(CF_3)Ph_2$	**7**	26[a]	6:1
Ph	**8**	67[a]	>20:1
o-$C_6H_3Cl_2$	**9**	42[b]	16:1
o-$C_6H_3Br_2$	**10**	42[b]	>20:1
o-$C_6H_3{}^{i}Pr_2$	**11**	49[b]	>20:1
p-C_6H_4F	**12**	66[a]	>20:1
p-C_6H_4OMe	**13**	82[a]	>20:1

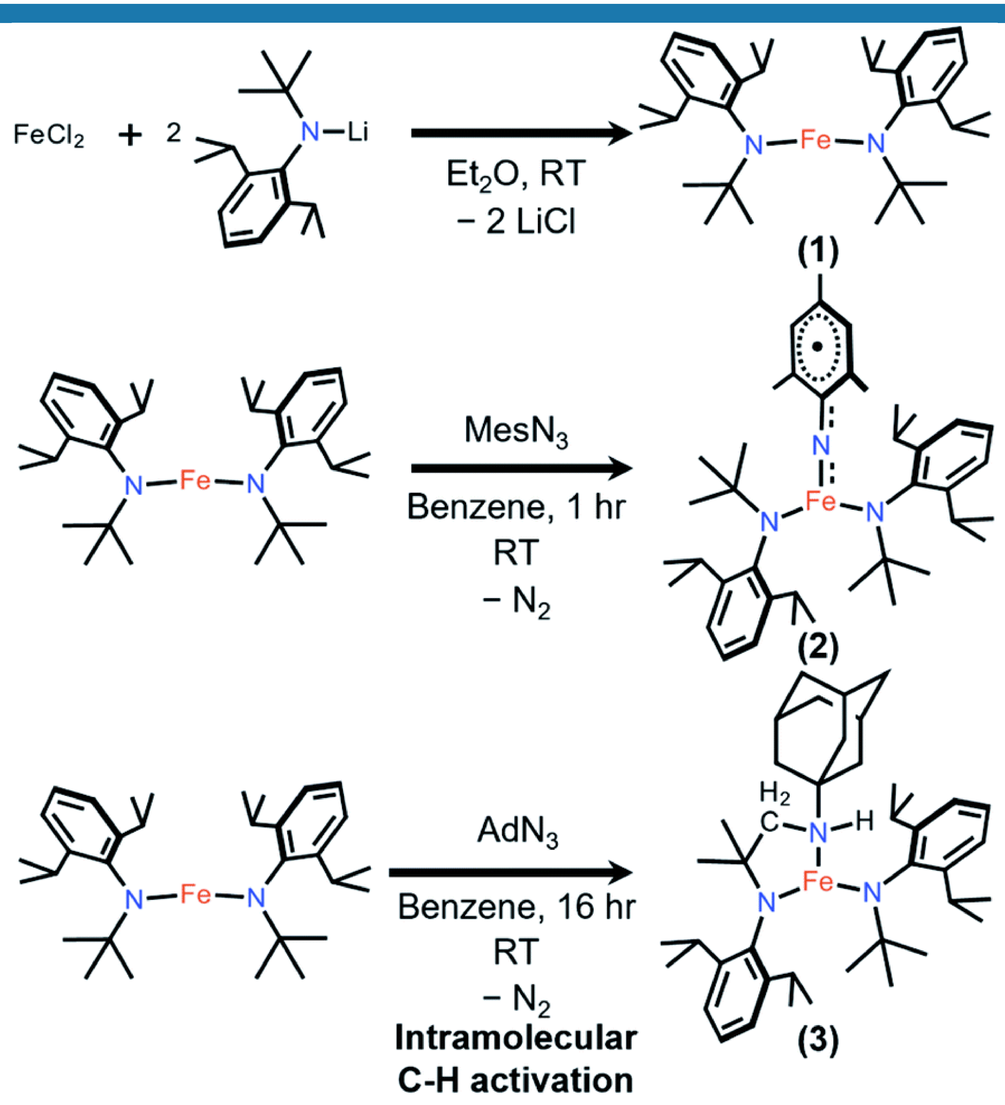
Diana A. Iovan, Matthew J. T. Wilding, Yunjung Baek, Elisabeth T. Hennessy, and Theodore A. Betley*. Diastereoselective C@H Bond Amination for Disubstituted Pyrrolidines. Angew. Chem. Int. Ed. 2017, 56, 15599 –15602.

Fe=N



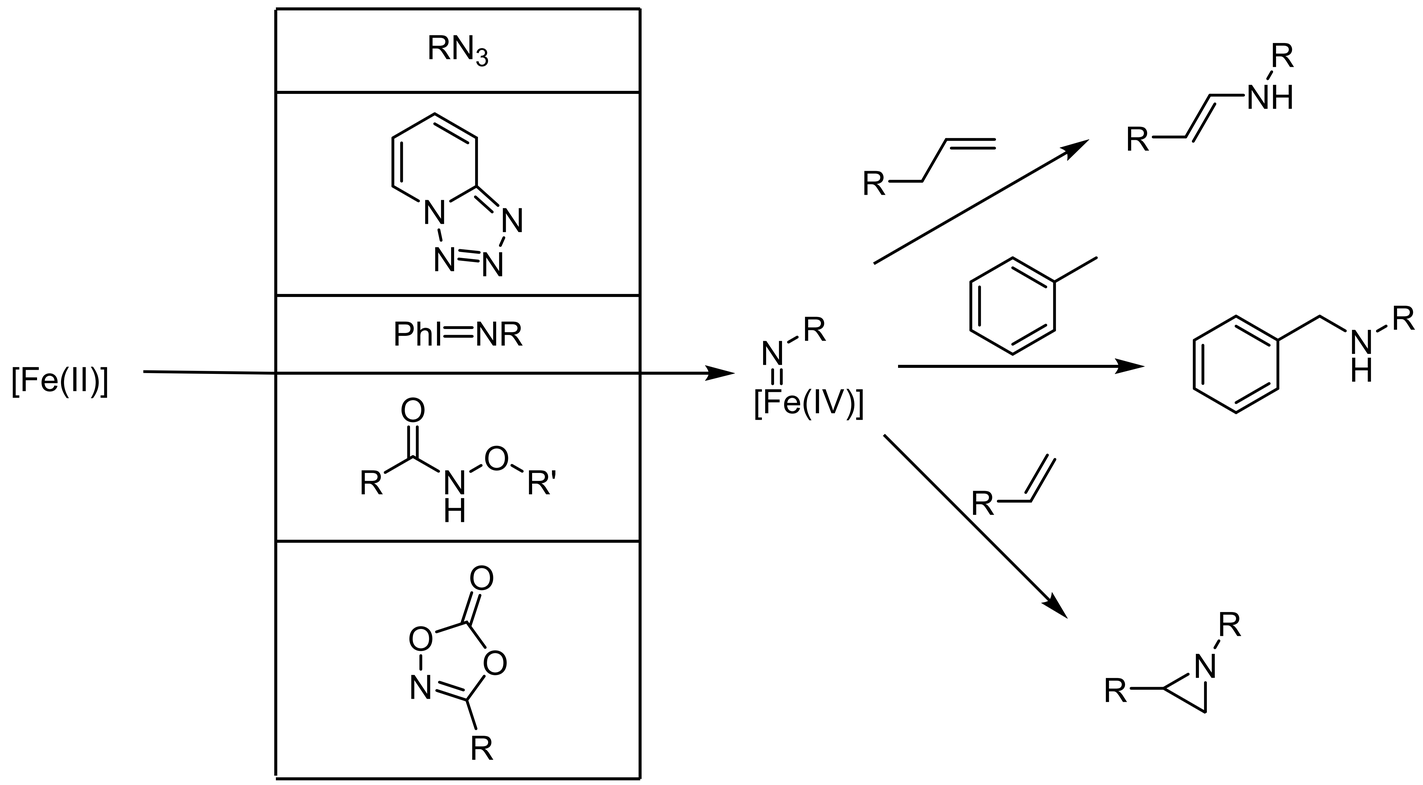
Brian P. Jacobs,† Peter T. Wolczanski,*, Quan Jiang, Thomas R. Cundari,*, and Samantha N. MacMillan*. Rare Examples of Fe(IV) Alkyl-Imide Migratory Insertions: Impact of Fe-C Covalency in (Me2IPr)Fe(=NAd)R2 (R = neoPe, 1-nor). J. Am. Chem. Soc. 2017, 139, 12145−12148.

Fe=N



Po-Chun Yang, Kuan-Po Yu, Chi-Tien Hsieh, Junjie Zou, Chia-Te Fang, Hsin-Kuan Liu, Chih-Wen Pao, Liang Deng, Mu-Jeng Cheng and Chun-Yi Lin*. Stabilization of a high-spin three-coordinate Fe(III) imidyl complex by radical delocalization. Chem. Sci., 2022, 13, 9637.

Fe=N Conclusion



The Yang Research Group
Precise Synthesis Lab at Tongji University

Thanks!