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Communication

# Catalytic Carbodiimide Guanylation by a Nucleophilic, High Spin Iron(II) Imido Complex

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**ABSTRACT:** Reduction of the three-coordinate iron(III) imido [$Ph_2B(^tBuIm)_2Fe{=}NDipp$] (**1**) affords [$Ph_2B(^tBuIm)_2Fe{=}NDipp$][K(18-C-6)$THF_2$] (**2**), a rare example of a high-spin ($S$ = 2) iron(II) imido complex. Unusually for a late metal imido complex, the imido ligand in **2** has nucleophilic character, as demonstrated by the reaction with $DippNH_2$, which establishes an equilibrium with the bis(anilido) complex [$Ph_2B(^tBuIm)_2Fe(NHDipp)_2$][K(18-C-6)$THF_2$] (**3**). In an unusual transformation, formal insertion of $^iPrN{=}C{=}N^iPr$ into the Fe=N(imido) bond yields the guanidinate [$Ph_2B(^tBuIm)_2Fe(^iPrN)_2CNDipp$][K(18-C-6)$THF_2$] (**4**). Reaction of **4** with excess $DippNH_2$ provides **3**, along with the guanidine $(^iPrNH)_2C{=}NDipp$. As suggested by these stoichiometric reactions, **2** is an efficient catalyst for the guanylation of carbodiimides, converting a wide range of aniline substrates under mild conditions.

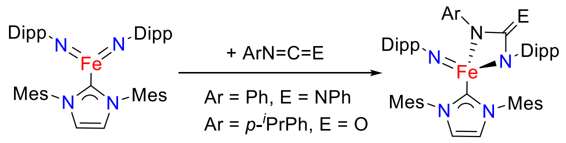
As dictated by relative d-orbital energies, nucleophilic imido ligands are typically associated with early transition metals.[1−3] As a result, the reactivity of early transition metal imido complexes is often distinct from that of their late metal congeners, which are usually more electrophilic. For example, the [2 + 2] cycloaddition between an M=NR bond and an unsaturated substrate hinges on the nucleophilicity of the imido ligand, making it a characteristic reaction of early metal imidos,[3] but rarely observed for late metals.

The [2 + 2] cycloaddition reaction forms the basis of a range of useful catalytic transformations for early metal imido complexes, including alkyne carboamination,[4,5] alkyne hydroamination,[6,7] and the assembly of pyrroles from alkynes and amines.[7,8] Despite this utility, these catalysts often have limited substrate scope, which may be partly related to the Lewis acidity of the early transition metal. For example, catalytic pyrrole formation by Ti-catalyzed [2 + 2 + 1] reactions fail for alkynyl esters and tethered alkyl ethers, likely due to the oxygen donors blocking access to the oxophilic metal.[9]

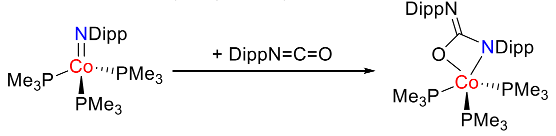
Building on our insights from iron catalyzed alkene isomerization,[10] we hypothesize that this limitation can be addressed by high spin late metal imido catalysts that weakly bind Lewis basic functional groups. While there are now multiple examples of isolable high spin late transition metal imido complexes,[11−23] [2 + 2] cycloadditions involving these complexes are rare. Indeed, only a limited number of stoichiometric [2 + 2] reactions have been observed, including for the low spin complexes [(IMes)Fe(NDipp)$_2$],[24] [$(PMe_3)_3Co{=}NDipp$],[25] and [$(^tBu_2PCH_2CH_2P^tBu_2)Ni{=}NR$][26] (Scheme 1). In addition, the noble metal imido complexes [$Cp^*Ir{=}N^tBu$][27] and [$(^tBu_2PCH{=}CHNCH{=}CHP^tBu_2)Ir{=}N^tBu$][28] have been reported to undergo [2 + 2] reactions with heterocumulenes. To the best of our knowledge, there are no examples of [2 + 2] catalysis involving late metal imido complexes.

**Scheme 1. Selected Examples of [2 + 2] Cycloaddition Reactions Involving Late Transition Metal Imido Complexes**

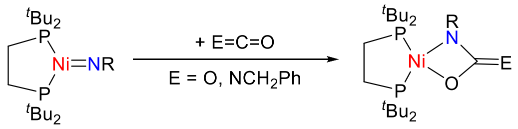
a. Iron imido complex (Deng, ref.24)



b. Cobalt imido complex (Deng, ref.25)



c. Nickel imido complex (Hillhouse, ref.26)



This paper reports a rare example of a high-spin iron(II) imido complex [$Ph_2B(^tBuIm)_2FeNDipp$][K(18-C-6)$THF_2$] (**2**). This complex has nucleophilic character at the imido ligand and reacts with a carbodiimide to yield a guanidinate complex, likely via a formal [2 + 2] cycloaddition reaction. The

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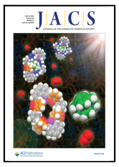

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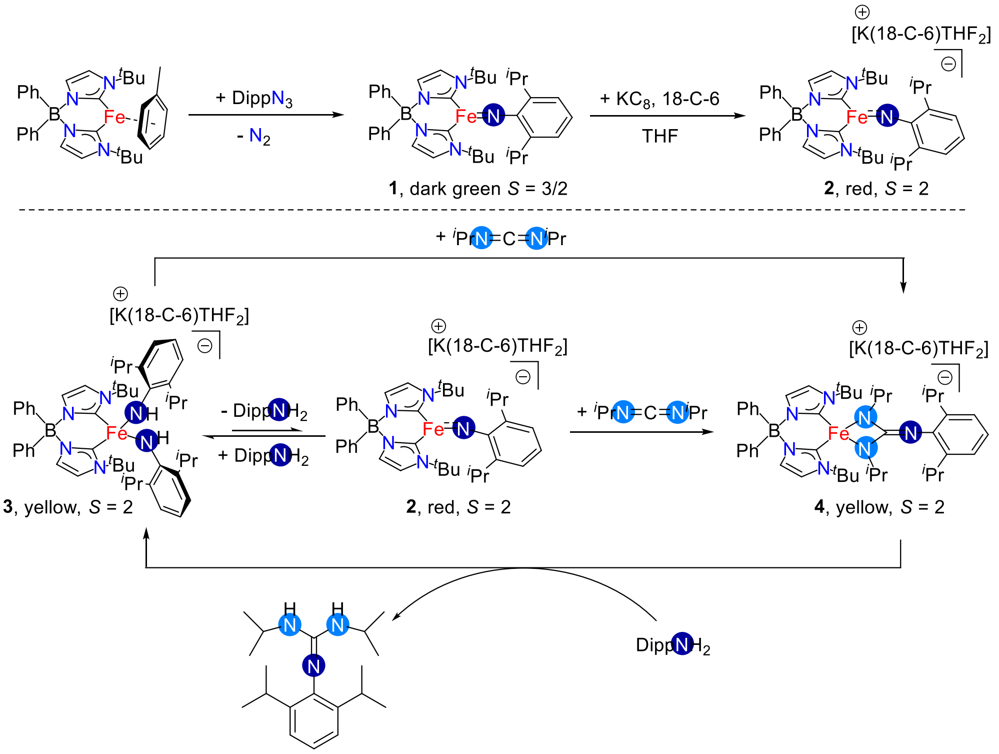
**Scheme 2. Synthesis and Reactivity of Iron(II) Imido Complex 2**



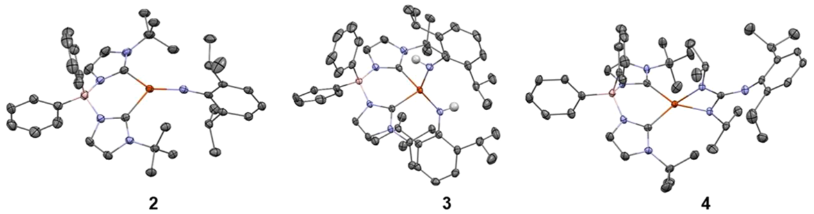


**Figure 1.** Molecular structures of complexes **2**−**4**, as determined by single crystal X-ray diffraction. Ellipsoids are shown at 50% probability level. Counterions, solvent molecules and most hydrogen atoms are omitted for clarity. Pink, dark gray, orange, and blue ellipsoids represent boron, carbon, iron, and nitrogen atoms, respectively.

stoichiometric reactivity establishes **2** as a catalyst for carbodiimide guanylation, which occurs for a range of substrates and under mild conditions.

The dark green iron(III) imido complex $Ph_2B(^tBuIm)_2Fe{=}NDipp$ (**1**) is formed in 66% yield from the reaction of iron(I) complex $Ph_2B(^tBuIm)_2Fe(\eta^6\text{-toluene})$[29] with 1 equiv of $DippN_3$ (Scheme 2). The molecular structure of **1**, as determined by single crystal X-ray diffraction (Figure S1), reveals a trigonal planar iron center (sum of angles = 359°) with the Fe−N (1.708(2) Å) bond distance and Fe−N−C angle (172.3(2)°) that are comparable to three-coordinate $S$ = 3/2 iron(III) imido complexes.[30−35] The solution magnetic moment, as determined by Evans' method ($\mu_{eff}$ = 4.2(2) $\mu_B$), combined with the zero-field $^{57}$Fe Mössbauer spectrum ($\delta$ = 0.25 mm/s and $\Delta E_Q$ = 1.32 mm/s at 200 K), supports the $S$ = 3/2 iron(III) formulation.

Complex **1** is readily reduced by $KC_8$ in the presence of 18-crown-6 to provide red $[Ph_2B(^tBuIm)_2FeNDipp][K(18\text{-}C\text{-}6)THF_2]$ (**2**) in 80% yield (Scheme 2). Complex **2** crystallizes with two independent molecules in the asymmetric unit, both of which have similar bond metrics.[36] The solid-state molecular structure of **2** reveals an anionic iron imido complex in which the trigonal planar iron center is retained (sum of angles = 355°, Figure 1). Reduction leads to elongation of the Fe−N bond (1.779(2) Å), which is over 0.1 Å longer than in those of four-coordinate ($S$ = 0) iron(II) imido complexes,[21,37−39] despite **2** having a lower coordination number. The Fe−N distance is also longer than that in the two coordinate ($S$ = 2) iron(II) imido complex $[(IPr)Fe(NAr^{Trip})]$ ($Ar^{Trip}$ = 2,6-bis(2′,4′,6′-triisopropylphenyl)-phenyl) (1.7151(16) Å).[21] These structural data suggest a high spin ($S$ = 2) iron(II) formulation for **2**. Indeed, the Fe−C(carbene) bond distances in **2** (2.077(3)−2.087(2) Å) are similar to other $S$ = 2 iron(II) bis(carbene)borate complexes.[10,29,40−42]

The zero-field $^{57}$Fe Mössbauer spectrum supports the oxidation and spin state assignment, with spectral parameters ($\delta$ = 0.46 mm/s and $\Delta E_Q$ = 1.45 mm/s at 80 K) that compares well with the three-coordinate $S$ = 2 iron(II) complexes $[LFeCH_3]$[43] (L = $\beta$-diketiminate, $\delta$ = 0.48 mm/s and $\Delta E_Q$ = 1.74 mm/s at 4.2 K), $[Ph_2B(^tBuIm)_2FeCH_2{}^tBu]$[10] ($\delta$ = 0.34 mm/s and $\Delta E_Q$ = 1.41 mm/s at 80 K) and $[(IPr_2Me_2)Fe(\sigma\text{-}CPh{=}CPh_2)_2]$[44] ($\delta$ = 0.33 mm/s and $\Delta E_Q$ = 2.20 mm/s at 200 K).[45] As expected for this spin state, the solution $^1$H NMR spectrum is paramagnetically shifted, and the Evans' solution magnetic moment ($\mu_{eff}$ = 5.0(1) $\mu_B$) is consistent with $S$ = 2 iron(II). In contrast to **1**, complex **2** is insoluble in nonpolar

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solvents such as pentane and toluene, consistent with its ionic formulation.

The electronic structure of the anionic iron complex in **2** has been probed by DFT calculations (B3LYP/def2-TZVP/SVP). Structural optimization of the full complex provides bond metrics that reproduce those found in the solid-state structure (Table S2). Natural orbital analysis of the electronic structure reveals doubly occupied orbitals with significant σ- and π-bonding character between iron and the imido ligand (Figure 2, Figure S48). The highest, singly occupied orbitals have iron−nitrogen π* character, which serves to decrease the multiple bond character of the iron−nitrogen bond. The remaining singly occupied orbitals are predominantly iron based (Figure S48). As a consequence of this electronic structure, the computed spin density is mainly located on the iron center (Mulliken spin density +3.58), with non-negligible spin density (+0.22) on the imido nitrogen atom (Figure S47).

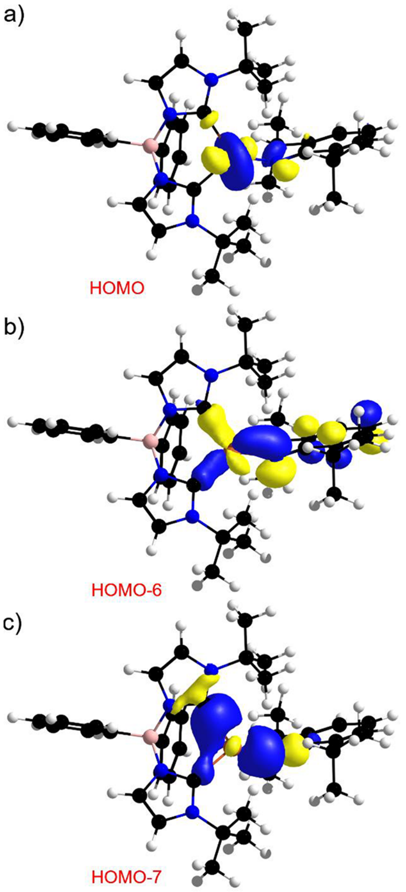


**Figure 2.** Selected orbitals showing the Fe=N σ and π interactions that are in the C−Fe−C plane; (a) π* HOMO; (b) π-bonding HOMO−6; (c) σ-bonding HOMO−7. Natural orbitals shown with isodensity = 0.05.

In light of the negative charge on the complex, we anticipated that the imido ligand in **2** to have nucleophilic character. In accord with this expectation, **2** reacts with 1 equiv of $DippNH_2$ to provide yellow $[Ph_2B(^tBuIm)_2Fe(NHDipp)_2]$-$[K(18\text{-}C\text{-}6)THF_2]$ (**3**) in 88% yield (Scheme 2). The molecular structure of **3**, as determined by single crystal X-ray diffraction (Figure 1), reveals a four-coordinate iron center ($\tau = 0.9$)[46] bound by the bis(carbene)borate ligand and two anilido ligands.[47] The Fe−C (2.133(2) and 2.125(2) Å) and Fe−N bond distances (2.050(2) and 2.024(2) Å) are similar to those in related $S = 2$ iron(II) complexes.[48] The $^{57}$Fe Mössbauer spectral parameters ($\delta = 0.76$ mm/s and $\Delta E_Q = 3.13$ mm/s at 80 K) also support the $S = 2$ iron(II) formulation. The complex has also been characterized in solution by $^1$H NMR spectroscopy and Evans' magnetic moment ($\mu_{eff} = 5.4(2)\ \mu_B$). Complex **3** can be independently synthesized by reaction of the iron(II) chloride complex $[Ph_2B(^tBuIm)_2FeCl(THF)]$[29] with 2 equiv of DippNHK in the presence of 18-crown-6.

Interestingly, $DippNH_2$ can be clearly observed in the $^1$H NMR spectrum of crystalline samples of **3**, suggesting the equilibrium:

$$\mathbf{3} \leftrightarrows \mathbf{2} + H_2NDipp$$

Using mesitylene as the internal standard, the equilibrium constant was determined by $^1$H NMR spectroscopy to be $K_{eq} \approx 8 \times 10^{-3}$ mol/L at room temperature. While common for early metal complexes,[49−51] the formation of an imido ligand by amine loss from the corresponding diamido complex is unusual for iron.[39,52]

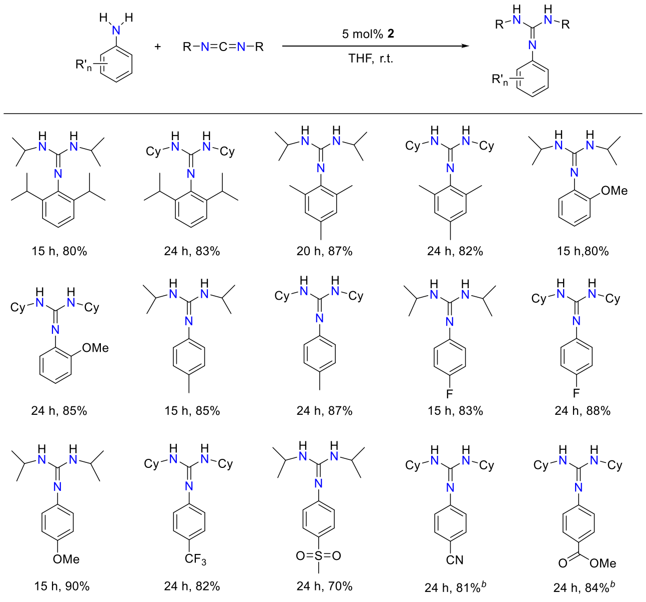
The evidence for a nucleophilic imido ligand in **2** prompted us to investigate its activity toward substrates known to be active in [2 + 2] cycloaddition reactions. In an initial demonstration, we find that **2** reacts with equimolar $^i$PrN=C=N$^i$Pr to provide the yellow complex $[Ph_2B(^tBuIm)_2Fe$-$(^iPrN)_2CNDipp][K(18\text{-}C\text{-}6)THF_2]$ (**4**) in 92% yield (Scheme 2). The molecular structure of **4** reveals a four-coordinate iron center ($\tau = 0.8$)[46] that is coordinated by the bis(carbene)-borate and a newly formed guanidinate ligand (Figure 1). The Fe−N (2.031(2) and 1.998(2) Å) and Fe−C (2.126(2) and 2.119(2) Å) bond distances are similar to those for $S = 2$ iron(II) complexes.[48] The $S = 2$ assignment is further supported by the zero-field $^{57}$Fe Mössbauer spectrum ($\delta = 0.62$ mm/s and $\Delta E_Q = 4.20$ mm/s at 80 K). The complex has also been characterized in solution by $^1$H NMR spectroscopy and Evans' magnetic moment ($\mu_{eff} = 5.0(1)\ \mu_B$).

The molecular structure of **4** can be described as the result of $^i$PrN=C=N$^i$Pr insertion into the iron imido bond. This contrasts with early transition metal imido complexes, which react with carbodiimides to provide the corresponding [2 + 2] azametallocyclobutanes.[3,53] Nonetheless, the formation of **4** can be rationalized according to a reaction sequence in which an initial formal [2 + 2] cycloaddition reaction between **2** and $^i$PrN=C=N$^i$Pr is followed by [1,3]-Fe migration.[54] It is worth noting that, with the exception of $[(IMes)Fe$-$(NDipp)_2]$,[24] iron imido complexes are typically unreactive toward carbodiimides. Indeed, carbodiimides are often formed as the products of nitrene transfer from iron imido complexes to isonitriles.[31]

As expected from the equilibrium between **3** and **2**, complex **4** can also be formed from the reaction of **3** with excess $^i$PrN=C=N$^i$Pr. Moreover, **3** is formed from the reaction of excess $DippNH_2$ with **4**, which also provides equimolar *N*-2,6-diisopropylphenyl-*N*′,*N*″-diisopropylguanidine, as characterized by $^1$H NMR spectroscopy and GC-MS.

Together, the stoichiometric reactions suggest **2** as a catalyst for carbodiimide guanylation. Guanidines find widespread application, e.g. building blocks toward complex organic compounds, superbase catalysts and versatile supporting ligands.[55,56] We observe smooth conversion of equimolar $^i$PrN=C=N$^i$Pr and $DippNH_2$ to *N*-2,6-diisopropylphenyl-*N*′,*N*″-diisopropylguanidine in the presence of 5 mol % **2**, with

### Table 1. Catalytic Carbodiimide Guanylation[a]



[a] Reaction conditions: aniline (1 mmol), carbodiimide (1.1 mmol) with 5 mol % **2** at room temperature in 2 mL of THF. The yields are isolated yields based on aniline. The formation of $DippNH_2$ is also observed by GC-MS when other anilines are used. [b] NMR yields using mesitylene as the internal standard.

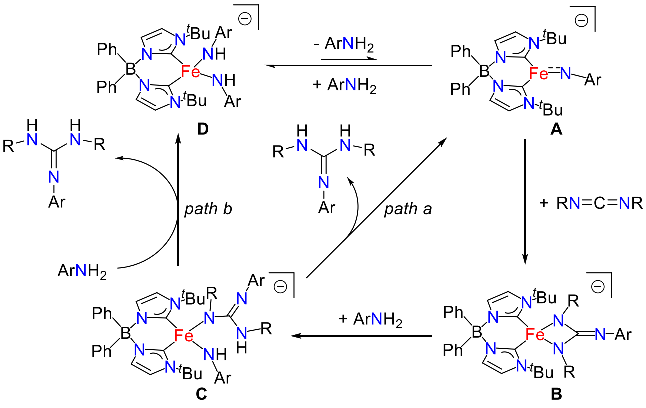
complete conversion occurring over hours at room temperature. More generally, **2** catalyzes the room temperature formation of a variety of guanidines from both $^iPrN{=}C{=}N^iPr$ and CyN=C=NCy (Table 1). We observe that anilines bearing both electron-withdrawing and electron-donating substituents are active in the reaction. Even anilines with potentially coordinating groups are successful substrates for the reaction. In all cases, high isolated yields of the guanidine products are obtained. It worth noting that **1** does not catalyze these guanylation reactions under the same conditions.

In addition to the remarkable substrate scope, the mild conditions of the catalytic guanylation reaction are notable. While a number of early transition metal imido complexes have been reported to catalyze the guanylation of carbodiimides, heating is required to drive most of these reactions.[6,53,57,58] It is also worth noting that while the simple iron salts have been reported to catalyze certain guanylation reactions, this is only above 120 °C, with no activity at lower temperatures.[59] The nature of the catalytically active species in these reactions is unknown. By contrast, **2** catalyzes the guanylation reaction at room temperature, even for very bulky substrates (e.g., $DippNH_2$).

In accord with the stoichiometric transformations described above, both **3** and **4** catalyze the guanylation of $^iPrN{=}C{=}N^iPr$ by $DippNH_2$. However, the rate of reaction is notably slower when **3** is used as the catalyst, with full conversion only occurring after 48 h at room temperature. This suggests that catalysis is initiated by the formation of **2** from **3**. In addition, no catalysis by **2** is observed for a 20:1 mol ratio of $DippNH_2$ to $^iPrN{=}C{=}N^iPr$, suggesting that the carbodiimide does not insert into the Fe−N bonds of **3**.

Based on our observations, we propose a catalytic cycle for carbodiimide guanylation (Scheme 3). Starting from imido **A**, the carbodiimide inserts into the Fe=N bond to provide **B**. Subsequent reaction with 1 equiv of $ArNH_2$ provides

### Scheme 3. Proposed Mechanism of Catalytic Carbodiimide Guanylation



intermediate **C**. From here, there are two possible routes to the guanidine product. In path a, internal proton transfer in **C** releases the guanidine while regenerating **A**. In path b, **C** is protonated by another equivalent of $ArNH_2$ to form bis(anilido) **D** concomitant with guanidine release. The imido complex **A** is then regenerated by the proton transfer equilibrium involving $ArNH_2$. Since the rate of catalysis is slower when **3** is used as the catalyst instead of **2** or **4**, this suggests that path a is more likely. We have so far been unable to prepare **C**, as the reaction of **4** with 1 equiv of $DippNH_2$ results in 50% conversion to **3**.

In summary, we have isolated a rare example of a high-spin ($S$ = 2) iron(II) imido complex. The imido ligand has properties that are more akin to early metal imido complexes, including nucleophilic character, as demonstrated by the proton transfer reaction with $DippNH_2$ and a carbodiimide insertion reaction, which likely involves a formal [2 + 2] cycloaddition reaction. The imido complex is an efficient catalyst for the guanylation of carbodiimides, providing high yields of product under mild conditions. The broad substrate scope demonstrates the advantageous properties of a high spin, late metal imido complex for this catalytic reaction.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c02068.

Full experimental and computational details (PDF)
Atomic coordinate information (XYZ)

### Accession Codes

CCDC 2064486−2064489 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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## Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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## ■ REFERENCES

(1) Mindiola, D. J. Oxidatively Induced Abstraction Reactions. A Synthetic Approach to Low-Coordinate and Reactive Early Transition Metal Complexes Containing Metal-Ligand Multiple Bonds. *Acc. Chem. Res.* **2006**, *39*, 813−821.

(2) Heyduk, A. F.; Zarkesh, R. A.; Nguyen, A. I. Designing Catalysts for Nitrene Transfer Using Early Transition Metals and Redox-Active Ligands. *Inorg. Chem.* **2011**, *50*, 9849−9863.

(3) Kawakita, K.; Kakiuchi, Y.; Tsurugi, H.; Mashima, K.; Parker, B. F.; Arnold, J.; Tonks, I. A. Reactivity of Terminal Imido Complexes of Group 4−6 Metals: Stoichiometric and Catalytic Reactions Involving Cycloaddition with Unsaturated Organic Molecules. *Coord. Chem. Rev.* **2020**, *407*, 213118.

(4) Ruck, R. T.; Zuckerman, R. L.; Krska, S. W.; Bergman, R. G. Carboamination: Additions of Imine C═N Bonds Across Alkynes Catalyzed by Imido Zirconium Complexes. *Angew. Chem., Int. Ed.* **2004**, *43*, 5372−5374.

(5) Aneetha, H.; Basuli, F.; Bollinger, J.; Huffman, J. C.; Mindiola, D. J. $Ti(NMe_2)_4$ and $[HNMe_2Ph][B(C_6F_5)_4]$: A Convenient Blend for Effective Catalytic Carboamination of Alkynes. *Organometallics* **2006**, *25*, 2402−2404.

(6) Johnson, J.; Bergman, R. G. Imidotitaniumcomplexes as Hydroamiation Catallysts: Substantially Enhanced Reactivity from an Unexpected Cyclopentadienide/Amide Ligand Exchange. *J. Am. Chem. Soc.* **2001**, *123*, 2923−2924.

(7) Ramanathan, B.; Keith, A. J.; Armstrong, D.; Odom, A. L. Pyrrole Syntheses Based on Titanium-Catalyzed Hydroamination of Diynes. *Org. Lett.* **2004**, *6*, 2957−2960.

(8) Barnea, E.; Majumder, S.; Staples, R. J.; Odom, A. L. One-Step Route to 2,3-Diaminopyrroles Using a Titanium-Catalyzed Four-Component Coupling. *Organometallics* **2009**, *28*, 3876−3881.

(9) Gilbert, Z. W.; Hue, R. J.; Tonks, I. A. Catalytic Formal [2 + 2+1] Synthesis of Pyrroles from Alkynes and Diazenes via Ti(II)/Ti(IV) Redox Catalysis. *Nat. Chem.* **2016**, *8*, 63−68.

(10) Lutz, S. A.; Hickey, A. K.; Gao, Y.; Chen, C. H.; Smith, J. M. Two-State Reactivity in Iron-Catalyzed Alkene Isomerization Confers Sigma-Base Resistance. *J. Am. Chem. Soc.* **2020**, *142*, 15527−15535.

(11) King, E. R.; Hennessy, E. T.; Betley, T. A. Catalytic C−H Bond Amination From High-Spin Iron Imido Complexes. *J. Am. Chem. Soc.* **2011**, *133*, 4917−4923.

(12) Laskowski, C. A.; Miller, A. J.; Hillhouse, G. L.; Cundari, T. R. A Two-Coordinate Nickel Imido Complex That Effects C−H Amination. *J. Am. Chem. Soc.* **2011**, *133*, 771−773.

(13) King, E. R.; Sazama, G. T.; Betley, T. A. Co(III) Imidos Exhibiting Spin Crossover and C−H Bond Activation. *J. Am. Chem. Soc.* **2012**, *134*, 17858−17861.

(14) Hennessy, E. T.; Liu, R. Y.; Iovan, D. A.; Duncan, R. A.; Betley, T. A. Iron-Mediated Intermolecular N-Group Transfer Chemistry with Olefinic Substrates. *Chem. Sci.* **2014**, *5*, 1526−1532.

(15) Du, J.; Wang, L.; Xie, M.; Deng, L. A Two-Coordinate Cobalt(II) Imido Complex with NHC Ligation: Synthesis, Structure, and Reactivity. *Angew. Chem., Int. Ed.* **2015**, *54*, 12640−12644.

(16) Iovan, D. A.; Betley, T. A. Characterization of Iron-Imido Species Relevant for N-Group Transfer Chemistry. *J. Am. Chem. Soc.* **2016**, *138*, 1983−1993.

(17) Wilding, M. J. T.; Iovan, D. A.; Betley, T. A. High-Spin Iron Imido Complexes Competent for C−H Bond Amination. *J. Am. Chem. Soc.* **2017**, *139*, 12043−12049.

(18) Wilding, M. J. T.; Iovan, D. A.; Wrobel, A. T.; Lukens, J. T.; MacMillan, S. N.; Lancaster, K. M.; Betley, T. A. 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.

(19) Yao, X. N.; Du, J. Z.; Zhang, Y. Q.; Leng, X. B.; Yang, M. W.; Jiang, S. D.; Wang, Z. X.; Ouyang, Z. W.; Deng, L.; Wang, B. W.; Gao, S. Two-Coordinate Co(II) Imido Complexes as Outstanding Single-Molecule Magnets. *J. Am. Chem. Soc.* **2017**, *139*, 373−380.

(20) Carsch, K. M.; DiMucci, I. M.; Iovan, D. A.; Li, A.; Zheng, S. L.; Titus, C. J.; Lee, S. J.; Irwin, K. D.; Nordlund, D.; Lancaster, K. M.; Betley, T. A. Synthesis of A Copper-Supported Triplet Nitrene Complex Pertinent to Copper-Catalyzed Amination. *Science* **2019**, *365*, 1138−1143.

(21) Cheng, J.; Liu, J.; Leng, X.; Lohmiller, T.; Schnegg, A.; Bill, E.; Ye, S.; Deng, L. A Two-Coordinate Iron(II) Imido Complex with NHC Ligation: Synthesis, Characterization, and Its Diversified Reactivity of Nitrene Transfer and C−H Bond Activation. *Inorg. Chem.* **2019**, *58*, 7634−7644.

(22) Baek, Y.; Das, A.; Zheng, S. L.; Reibenspies, J. H.; Powers, D. C.; Betley, T. A. C-H Amination Mediated by Cobalt Organoazide Adducts and the Corresponding Cobalt Nitrenoid Intermediates. *J. Am. Chem. Soc.* **2020**, *142*, 11232−11243.

(23) Reckziegel, A.; Pietzonka, C.; Kraus, F.; Werncke, C. G. C−H Bond Activation by an Imido Cobalt(III) and the Resulting Amido Cobalt(II) Complex. *Angew. Chem., Int. Ed.* **2020**, *59*, 8527−8531.

(24) Wang, L.; Hu, L.; Zhang, H.; Chen, H.; Deng, L. Three-Coordinate Iron(IV) Bisimido Complexes with Aminocarbene Ligation: Synthesis, Structure, and Reactivity. *J. Am. Chem. Soc.* **2015**, *137*, 14196−14207.

(25) Liu, Y.; Du, J.; Deng, L. Synthesis, Structure, and Reactivity of Low-Spin Cobalt(II) Imido Complexes $[(Me_3P)_3Co(NAr)]$. *Inorg. Chem.* **2017**, *56*, 8278−8286.

(26) Mindiola, D. J.; Waterman, R.; Iluc, V. M.; Cundari, T. R.; Hillhouse, G. L. Carbon−Hydrogen Bond Activation, C−N Bond Coupling, and Cycloaddition Reactivity of a Three-Coordinate Nickel Complex Featuring a Terminal Imido Ligand. *Inorg. Chem.* **2014**, *53*, 13227−13238.

(27) Glueck, D. S.; Hollander, F. J.; Bergman, R. G. Synthesis, Structure, and Reactivity of a Monomeric Pentamethylcyclopentadienyliridium(III) Imido Complex. *J. Am. Chem. Soc.* **1989**, *111*, 2719−2721.

(28) Kinauer, M.; Diefenbach, M.; Bamberger, H.; Demeshko, S.; Reijerse, E. J.; Volkmann, C.; Wurtele, C.; van Slageren, J.; de Bruin, B.; Holthausen, M. C.; Schneider, S. An Iridium(III/IV/V) Redox Series Featuring a Terminal Imido Complex with Triplet Ground State. *Chem. Sci.* **2018**, *9*, 4325−4332.

(29) Hickey, A. K.; Lee, W. T.; Chen, C. H.; Pink, M.; Smith, J. M. A Bidentate Carbene Ligand Stabilizes a Low-Coordinate Iron(0) Carbonyl Complex. *Organometallics* **2016**, *35*, 3069−3073.

(30) Eckert, N. A.; Vaddadi, S.; Stoian, S.; Lachicotte, R. J.; Cundari, T. R.; Holland, P. L. Coordination-Number Dependence of Reactivityin an Imidoiron(III) Complex. *Angew. Chem., Int. Ed.* **2006**, *45*, 6868−6871.

(31) Cowley, R. E.; Eckert, N. A.; Elhaik, J.; Holland, P. L. Catalytic Nitrene Transfer from an Imidoiron(III) Complex to form Carbodiimides and Isocyanates. *Chem. Commun.* **2009**, 1760−1762.

(32) Cowley, R. E.; DeYonker, N. J.; Eckert, N. A.; Cundari, T. R.; DeBeer, S.; Bill, E.; Ottenwaelder, X.; Flaschenriem, C.; Holland, P. L. Three-Coordinate Terminal Imidoiron(III) Complexes: Structure, Spectroscopy, and Mechanism of Formation. *Inorg. Chem.* **2010**, *49*, 6172−6187.

(33) Cowley, R. E.; Eckert, N. A.; Vaddadi, S.; Figg, T. M.; Cundari, T. R.; Holland, P. L. Selectivity and Mechanism of Hydrogen Atom Transfer by an Isolable Imidoiron(III) Complex. *J. Am. Chem. Soc.* **2011**, *133*, 9796−9811.

(34) Cowley, R. E.; Holland, P. L. C-H Activation by a Terminal Imidoiron(III) Complex to Form a Cyclopentadienyliron(II) Product. *Inorg. Chim. Acta* **2011**, *369*, 40−44.

(35) Cowley, R. E.; Holland, P. L. Ligand Effects on Hydrogen Atom Transfer from Hydrocarbons to Three-Coordinate Iron Imides. *Inorg. Chem.* **2012**, *51*, 8352−8361.

(36) The two molecules have similar metrical parameters, with the most significant difference being the Fe−N−C angle (165.11(7)° and 172.64(19)°).

(37) Brown, S. D.; Peters, J. C. Ground-State Singlet $L_3Fe$-($\mu$-N)-$FeL_3$ and $L_3Fe(NR)$ Complexes Featuring Pseudotetrahedral Fe(II) Centers. *J. Am. Chem. Soc.* **2005**, *127*, 1913−1923.

(38) Moret, M. E.; Peters, J. C. Terminal Iron Dinitrogen and Iron Imide Complexes Supported by a Tris(phosphino)borane Ligand. *Angew. Chem., Int. Ed.* **2011**, *50*, 2063−2067.

(39) Aldrich, K. E.; Fales, B. S.; Singh, A. K.; Staples, R. J.; Levine, B. G.; McCracken, J.; Smith, M. R., III; Odom, A. L. Electronic and Structural Comparisons between Iron(II/III) and Ruthenium(II/III) Imide Analogs. *Inorg. Chem.* **2019**, *58*, 11699−11715.

(40) Lee, W. T.; Jeon, I.; Xu, S.; Dickie, D. A.; Smith, J. M. Low-Coordinate Iron(II) Complexes of a Bulky Bis(carbene)borate Ligand. *Organometallics* **2014**, *33*, 5654−5659.

(41) Hickey, A. K.; Lutz, S. A.; Chen, C. H.; Smith, J. M. Two-state Reactivity in C-H Activation by a Four-coordinate Iron(0) Complex. *Chem. Commun.* **2017**, *53*, 1245−1248.

(42) Hickey, A. K.; Greer, S. M.; Valdez-Moreira, J. A.; Lutz, S. A.; Pink, M.; DeGayner, J. A.; Harris, T. D.; Hill, S.; Telser, J.; Smith, J. M. A Dimeric Hydride-Bridged Complex with Geometrically Distinct Iron Centers Giving Rise to an S = 3 Ground State. *J. Am. Chem. Soc.* **2019**, *141*, 11970−11975.

(43) Andres, H.; Bominaar, E. L.; Smith, J. M.; Eckert, N. A.; Holland, P. L.; Munck, E. Planar Three-Coordinate High-Spin $Fe^{II}$ Complexes with Large Orbital Angular Momentum: Mossbauer, Electron Paramagnetic Resonance, and Electronic Structure Studies. *J. Am. Chem. Soc.* **2002**, *124*, 3012−3025.

(44) Liu, Y.; Wang, L.; Deng, L. Three-Coordinate Iron(II) Dialkenyl Compound with NHC Ligation: Synthesis, Structure, and Reactivity. *Organometallics* **2015**, *34*, 4401−4407.

(45) The small differences in isomer shift are attributed, at least in part, to the second-order Doppler shift correction.

(46) $\tau$ = 1 for tetrahedral geometry, $\tau$ = 0 for square planar geometry. Yang, L.; Powell, D. R.; Houser, R. P. Structural Variation in Copper(I) Complexes with Pyridylmethylamide Ligands: Structural Analysis with a New Four-coordinate Geometry Index, $\tau_4$. *Dalton Trans.* **2007**, 955−964.

(47) The anilido protons were found by crystallographical method.

(48) Wang, X.; Mo, Z.; Xiao, J.; Deng, L. 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.

(49) Walsh, P. J.; Baranger, A. M.; Bergman, R. G. Stoichiometric and Catalytic Hydroamination of Alkynes and Allene by Zirconium Bisamides $Cp_2Zr(NHR)_2$. *J. Am. Chem. Soc.* **1992**, *114*, 1708−1719.

(50) Krinsky, J. L.; Anderson, L. L.; Arnold, J.; Bergman, R. G. Oxygen-Centered Hexatantalum Tetradecaimido Cluster Complexes. *Inorg. Chem.* **2008**, *47*, 1053−1066.

(51) Gavenonis, J.; Tilley, T. D. Tantalum Alkyl and Silyl Complexes of the Bulky (Terphenyl)imido Ligand $[2,6\text{-}(Mes)_2C_6H_3N{=}]^{2-}$ $([Ar^*N{=}]^{2-})$. Generation and Reactivity of $[(Ar^*N{=})(Ar^*NH)\text{-}Ta(H)(OSO_2CF_3)]$, Which Reversibly Transfers Hydride to an Aromatic Ring of the Arylamide Ligand. *Organometallics* **2002**, *21*, 5549−5563.

(52) Verma, A. K.; Nazif, T. N.; Achim, C.; Lee, S. C. A Stable Terminal Imide on Iron. *J. Am. Chem. Soc.* **2000**, *122*, 11013−11014.

(53) Ong, T.-G.; Yap, G. P. A.; Richeson, D. S. Catalytic Construction and Reconstruction of Guanidines: Ti-Mediated Guanylation of Amines and Transamination of Guanidines. *J. Am. Chem. Soc.* **2003**, *125*, 8100−8101.

(54) Takemoto, Y.; Ishii, K.; Ibuka, T.; Miwa, Y.; Taga, T.; Nakao, S.; Tanaka, T.; Ohishi, H.; Kai, Y.; Kanehisa, N. Stereospecific 1,3-Migration of an $Fe(CO)_3$ Group on Acyclic Conjugated Polyenes: Application to Remote and Iterative Asymmetric Induction. *J. Org. Chem.* **2001**, *66*, 6116−6123.

(55) Alonso-Moreno, C.; Antinolo, A.; Carrillo-Hermosilla, F.; Otero, A. Guanidines: From Classical Approaches to Efficient Catalytic Syntheses. *Chem. Soc. Rev.* **2014**, *43*, 3406−3425.

(56) Zhang, W. X.; Xu, L.; Xi, Z. Recent Development of Synthetic Preparation Methods for Guanidines via Transition Metal Catalysis. *Chem. Commun.* **2015**, *51*, 254−265.

(57) Montilla, F.; Pastor, A.; Galindo, A. Guanylation of Aromatic Amines Catalyzed by Vanadium Imido Complexes. *J. Organomet. Chem.* **2004**, *689*, 993−996.

(58) Romero-Fernandez, J.; Carrillo-Hermosilla, F.; Antinolo, A.; Alonso-Moreno, C.; Rodriguez, A. M.; Lopez-Solera, I.; Otero, A. Oxo- and Imido-alkoxide Vanadium Complexes as Precatalysts for the Guanylation of Aromatic Amines. *Dalton Trans.* **2010**, *39*, 6419−6425.

(59) Pottabathula, S.; Royo, B. First Iron-catalyzed Guanylation of Amines: A Simple and Highly Efficient Protocol to Guanidines. *Tetrahedron Lett.* **2012**, *53*, 5156−5158.