

Synthesis of a bulky bis(imino)pyridine compound: a methodology for systematic variation of steric bulk and energetic implications for metalation†

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A new bis(imino)pyridine compound, 2,6- $\{(2,6\text{-Me}_2\text{-C}_6\text{H}_3)\text{NC}(t\text{-Bu})\}_2\text{C}_5\text{H}_3\text{N}$ (**6**), has been synthesized with *t*-butyl substituents on the imino carbon atoms. The stepwise synthetic method for assembly of this compound is novel. Compound **6** and its synthetic precursor, mono(imino)pyridine **3**, have been characterized using single-crystal X-ray diffraction. Metalation attempts of **6** using iron(II) chloride under forcing conditions does not yield the desired iron(II) chloride complex; the use of refluxing acetic acid solvent provides a minimal amount of a paramagnetic species that has been characterized by NMR spectroscopy and magnetic susceptibility (NMR method). Computational methods have been used to evaluate the relative energies of three conformations of bis(imino)pyridine ligands with varying alkyl substitution at the imino carbon positions. The relative energies of these closed, open and open-planar conformations of **6** reveal a thermodynamic argument for the difficulty in metalation of **6**, as compared to related ligands with less steric hindrance at the imino carbon atoms.

Introduction

Bis(imino)pyridine ligands first came into the spotlight ten years ago when Brookhart^{1a} and Gibson^{2a} described the synthesis of iron and cobalt complexes bearing these ligands and their use as pre-catalysts for polyethylene formation. Follow-up studies by these research groups, as well as DuPont researchers, expanded the scope of these initial reports.^{1b-c,2b-c} Iron and cobalt catalysts incorporating the bis(imino)pyridine ligand have been used for ethylene oligomerization, homopolymerization, and copolymerization with α -olefins, as described in a 2006 review;³ some degree of success in α -olefin dimerization, oligomerization and polymerization has been reported by various groups.⁴

The backbone and substitution pattern of the bis(imino)pyridine ligand have been varied extensively, as described in two recent reviews.^{5,6} The two most common substitution patterns for this ligand (of the general formula: 2,6- $\{(2\text{-R}^2,4\text{-R}^4,6\text{-R}^3\text{-C}_6\text{H}_2)\text{NCR}^1\}_2\text{C}_5\text{H}_3\text{N}$) appear in Fig. 1. Ligand modifications have largely focused on substitution of the imino nitrogen atoms (with 2-, 2,6-, and 2,4,6- substituted aryl rings being most common), and on a more limited basis, the use of alkyl-,⁷ amino-,

or pyrrolyl-⁸ substituted imino nitrogen atoms. C_1 -symmetric bis(imino)pyridine ligands have been synthesized;^{4b,7a,7b,9} their asymmetry is derived from differentially substituted imino nitrogen atoms. Also, on a more limited basis, the central pyridyl ring has been altered to provide iron(II) pre-catalysts with low activity for ethylene polymerization.¹⁰

The range of functionality (R^1) for the imino carbon atoms is limited, and to date there are no reports of differential substitution of these imino carbon atoms to provide C_1 -symmetric ligands. Most often, R^1 is H or Me, since the corresponding ligands are synthetically derived from commercially available 2,6-diformylpyridine and 2,6-diacetylpyridine, respectively. The use of $R^1 = \text{Ph}$ has been reported by four research groups; moderate yields are achieved using standard condensation for ligand synthesis,^{11a} and improved yields are achieved using more forcing^{10,11b} or atypical^{7a} reaction conditions. One report describes the installation of heteroatom-substituted imino carbon atoms, specifically, where $R^1 = \text{OMe}$, SMe , $\text{O}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ or $\text{S}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$.¹² The latter three substituents yielded iron(II) pre-catalysts with ethylene polymerization activities comparable to the prototypical (2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$)-substituted ketimine analogue, [2,6- $\{(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{NCMe}\}_2\text{C}_5\text{H}_3\text{N}]\text{FeCl}_2$. Aliphatic R^1 substituents with increased steric bulk (relative to $R^1 = \text{Me}$) were singularly reported in 2007; pre-assembled bis(imino)pyridine ligands (where $R^1 = \text{Me}$) were treated with lithium diisopropylamide, followed by alkyl halide, to yield the following: $R^1 = \text{CH}_2\text{CH}_3$, $\text{CH}(\text{CH}_3)_2$, $\text{CH}_2\text{CH}_2\text{Ph}$, and $\text{CH}(\text{CH}_2\text{Ph})_2$.¹³ A notable feature of the corresponding iron(II) pre-catalysts is that as the steric bulk of R^1 increases, polyethylene molecular weight increases while maintaining catalyst productivity. The extension of Gibson's synthetic methodology to install a tertiary alkyl as R^1 was not reported, though one would anticipate continuation of the favorable trend of increased polyethylene molecular weight with comparable catalyst productivity.

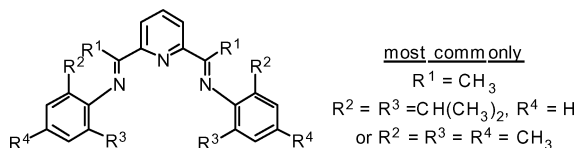


Fig. 1 Common substitution patterns for the bis(imino)pyridine ligand.

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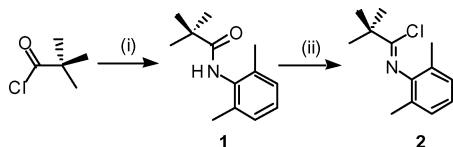
† CCDC reference numbers 702075 and 702076. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b815987d

In order to achieve the synthesis of a bis(imino)pyridine compound with $R^1 = t\text{-Bu}$, we developed a new synthetic route. In our hands, standard condensation of the appropriate *t*-butyl disubstituted 2,6-diketopyridine¹⁴ with substituted anilines or *N*-amino-pyrroles was unsuccessful. Furthermore, a range of modified reagents and reaction conditions were employed^{7a,8c,10,15} but at best the mono(imino)pyridine species was detected. In developing our current synthetic method, we took a cue from the *t*-butyl substituted β -diketiminate ligand employed by Holland as a component of three coordinate iron(II) complexes.¹⁶ We have utilized an imidoyl chloride as a synthetic intermediate, similar to their use in the preparation of sterically hindered β -diketiminate ligands.^{17,18} Our synthetic route also draws upon the recent literature for selective mono lithium–halogen exchange of 2,6-dibromopyridine.¹⁹

Results and discussion

Synthesis of bis(imino)pyridine 6

Preparation of *t*-butyl substituted amide, **1**, was achieved in a high yield by combination of pivaloyl chloride and 2,6-dimethylaniline in the presence of stoichiometric triethylamine (Scheme 1, step i), as described previously.^{20,21} Compound **1** was evaluated *via* single-crystal X-ray diffraction; suitable crystals of **1** were obtained from an anhydrous dichloromethane solution cooled to $-15\text{ }^\circ\text{C}$ for 8 d. The crystal structure for **1** was independently reported while our work was in progress; our crystallographic data is consistent with what appears in the literature.²²

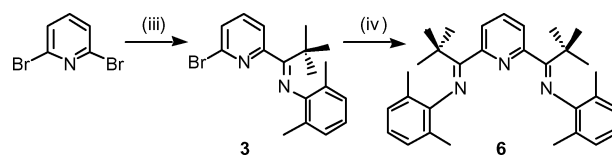


Scheme 1 Reagents and conditions: (i) 2,6-dimethylaniline, NEt_3 , CH_2Cl_2 , reflux, 1 h; (ii) POCl_3 , toluene, $22\text{ }^\circ\text{C}$, 15 h.

Using literature methods, a toluene solution of compound **1** was treated with phosphorous pentachloride to generate the *t*-butyl substituted imidoyl chloride, **2** (Scheme 1, step ii); small-scale synthesis and characterization of **2** was reported previously.²³ Ambient pressure distillation was used to remove toluene and the POCl_3 by-product from the product mixture, followed by standard vacuum distillation or Kügelrohr distillation to yield **2** as an off-white semi-solid. Alternatively, we have prepared **2** by stepwise treatment of a $0\text{ }^\circ\text{C}$ dichloromethane solution of **1** with 2,6-lutidine (1.66 equiv.) and oxalyl chloride (1.00 equiv.), similar to reported conditions for the synthesis of related imidoyl chlorides.²⁴

We utilized Peterson's method for selective mono-lithiation of 2,6-dibromopyridine¹⁹ as a model for our synthesis of brominated mono(imino)pyridine, **3** (Scheme 2, step iii). While Peterson demonstrated the successful addition of a variety of electrophiles to *in situ* generated 2-bromo-6-lithiopyridine, the use of an imidoyl chloride, such as **2**, as an electrophile was not described.

Mono-lithiation of a dichloromethane solution of 2,6-dibromopyridine at $-78\text{ }^\circ\text{C}$, followed by addition of 1.4 equiv. of **2** and slow warming to $22\text{ }^\circ\text{C}$ generates **3** (Scheme 2, step iii). Analytically pure, pale yellow microcrystalline **3** can be obtained



Scheme 2 Reagents and conditions: (iii) *n*-BuLi, CH_2Cl_2 , $-78\text{ }^\circ\text{C}$, 15 min; 1.4 equiv. **2**, -78 – $22\text{ }^\circ\text{C}$, 22 h; (iv) *n*-BuLi, THF, $-78\text{ }^\circ\text{C}$, 15 min; 1.0 equiv. **2**, -78 – $22\text{ }^\circ\text{C}$, 17 h.

via flash silica gel column chromatography. Benzene- d_6 is an optimal solvent for ^1H NMR spectroscopic analysis; chloroform- d gives overlapping pyridyl and phenyl proton resonances. NOE difference experiments were used to assign the three pyridyl proton resonances and homonuclear decoupling experiments were used to detect long range coupling between the methyl (attached to the phenyl rings) and the *ortho*-phenyl protons. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopic C=N chemical shift of 174.8 ppm (in benzene- d_6) and a C=N infrared stretching frequency of 1647 cm^{-1} provide further support for our structural assignment.

Single crystals of **3** for X-ray diffraction studies were obtained *via* slow evaporation of a 2.5% ethyl acetate–hexanes solution (v/v) of **3** over the course of 1 d. Most notably, the pyridyl and phenyl rings exhibit a nearly perpendicular arrangement, with a $\text{PlnA}–\text{PlnB}$ angle of $110.24(5)^\circ$ (see Fig. 2 and Table 1).

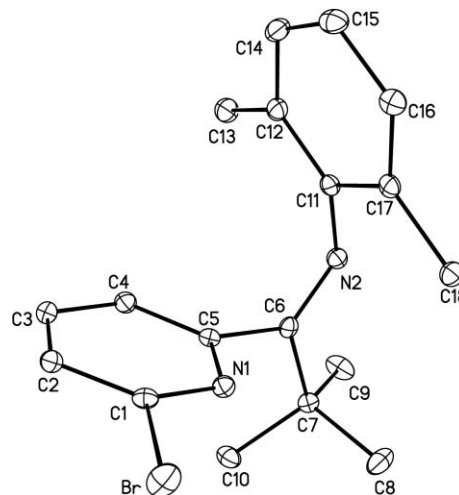


Fig. 2 X-Ray crystal structure of **3**. Hydrogen atoms are omitted for clarity.

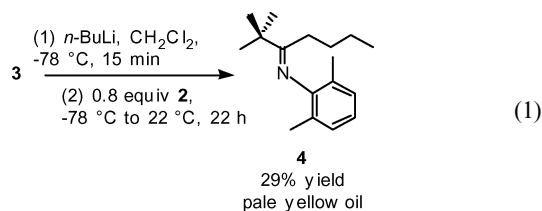
Our initial attempt to prepare the target bis(imino)pyridine compound followed our methodology for preparation of **3**; namely, lithium–halogen exchange at $-78\text{ }^\circ\text{C}$ using dichloromethane solvent, followed by addition of imidoyl chloride, **2**, as electrophile. These reaction conditions yielded product **4** (eqn (1)),

Table 1 Selected bond distances (\AA) and angles ($^\circ$) for **3**

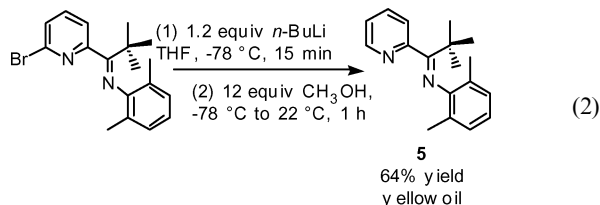
Br–C(1)	1.903(2)	N(1)–C(1)–Br	115.9(1)
C(5)–C(6)	1.510(2)	N(1)–C(5)–C(6)	117.1(1)
N(2)–C(6)	1.272(2)	C(5)–C(6)–C(7)	117.9(1)
N(2)–C(11)	1.427(2)	C(5)–C(6)–N(2)	122.8(1)
PlnA–PlnB ^a	110.24(5)	C(6)–N(2)–C(11)	121.0(1)

^a Where PlnA contains N(1), C(1), C(2), C(3), C(4) and C(5); PlnB contains C(11), C(12), C(14), C(15), C(16), and C(17).

consistent with alkylation of imidoyl chloride, **2**. Presumably, brominated mono(imino)pyridine **3** is not sufficiently soluble in dichloromethane solvent at $-78\text{ }^{\circ}\text{C}$ to facilitate lithium–halogen exchange, so instead, imidoyl chloride, **2**, is attacked by *n*-butyl lithium. Upon re-examination of NMR spectra for crude samples of **3**, we determined that **4** is also generated as a very minor by-product in formation of **3**.



The use of tetrahydrofuran as solvent, in place of dichloromethane, facilitates our desired lithium–halogen exchange for **3**. Treatment of **3** with *n*-butyl lithium in tetrahydrofuran solvent at $-78\text{ }^{\circ}\text{C}$ affords a bright yellow-orange solution immediately upon addition; quenching with excess methanol provides a pale yellow solution. Reaction work-up and purification *via* flash silica gel column chromatography provides a spectroscopically pure sample of compound **5** (eqn (2)), consistent with protonation of a lithiated intermediate.



Thus, lithiation of a tetrahydrofuran solution of **3** at $-78\text{ }^{\circ}\text{C}$, followed by addition of 1.0 equiv. of **2** and slow warming to $22\text{ }^{\circ}\text{C}$ generates **6** (Scheme 2, step iv). Compound **5** was detected as the major impurity in this reaction; pale yellow microcrystalline **6** was isolated in 54.2% yield after flash silica gel column chromatography. We postulate that our moderate yield is due to some product loss during silica gel column chromatography, though we found it to be a superior purification method in comparison to recrystallization. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopic C=N chemical shift of 175.9 ppm (in benzene- d_6) and the C=N infrared stretching frequency of 1651 cm^{-1} are consistent with the presence of a bis(imine).

A saturated solution of **6** in anhydrous pentane was cooled to $-15\text{ }^{\circ}\text{C}$ for 1 month to produce a single crystal suitable for X-ray diffraction (Table 2 and Fig. 3). As described in the literature for related alkyl or aryl substituted bis(imino)pyridine ligands,²⁵ the pyridyl and phenyl rings are nearly orthogonal, with a PlnA–PlnB angle of $116.22(4)^{\circ}$ and a PlnA–PlnC of $105.06(4)^{\circ}$ (where PlnA contains the pyridyl ring, PlnB contains the phenyl ring incorporating C(11) through C(16), and PlnC contains the phenyl ring incorporating C(24) through C(29)). Also, the imino C=N bonds are short ($1.275(2)$ and $1.270(2)$ Å, respectively), as observed for related bis(imino)pyridine ligands. The most striking aspect of this structure is that the imino C=N bonds are nearly orthogonal to the pyridyl ring, as indicated by the following dihedral angles: N(1)–C(1)–C(6)–N(2), $-46.7(2)^{\circ}$; N(1)–C(5)–C(19)–N(3), $-87.7(1)^{\circ}$. This conformation differs from the

Table 2 Selected bond distances (Å) and angles ($^{\circ}$) for **6**

N(1)–C(1)	1.345(2)	C(19)–N(3)–C(24)	123.9(1)
N(1)–C(5)	1.342(2)	N(1)–C(1)–C(6)	116.5(1)
C(1)–C(6)	1.510(2)	N(1)–C(5)–C(19)	115.5(1)
C(5)–C(19)	1.518(2)	N(1)–C(1)–C(2)	122.5(1)
N(2)–C(6)	1.275(2)	N(1)–C(5)–C(4)	122.7(1)
N(3)–C(19)	1.270(2)	C(1)–C(6)–N(2)	123.3(1)
C(6)–C(7)	1.537(2)	C(5)–C(19)–N(3)	123.2(1)
C(19)–C(20)	1.533(2)	N(2)–C(6)–C(7)	117.2(1)
C(1)–N(1)–C(5)	118.3(1)	N(3)–C(19)–C(20)	118.8(1)
C(6)–N(2)–C(11)	127.2(1)	PlnA–PlnB ^a	116.22(4)
		PlnA–PlnC ^a	105.06(4)

^a Where PlnA contains N(1), C(1), C(2), C(3), C(4) and C(5); PlnB contains C(11), C(12), C(13), C(14), C(15), and C(16); PlnC contains C(24), C(25), C(26), C(27), C(28), and C(29).

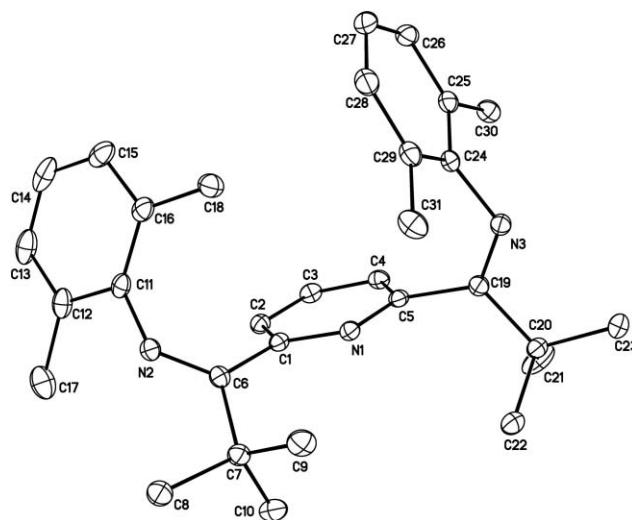


Fig. 3 X-Ray crystal structure of **6**. Hydrogen atoms are omitted for clarity.

reported structure for the methyl-substituted analogue, 2,6- $\{(2,6\text{-Me}_2\text{-C}_6\text{H}_3)\text{NCMe}\}_2\text{C}_5\text{H}_3\text{N}^{25b}$ (*vide infra*).

Attempted metalation of **6** with FeCl_2 and $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$

Literature reports have revealed that as the steric bulk at the imino carbon atoms increases (where R^1 is Me, Et, *i*-Pr or Ph, see Fig. 1), longer reaction times or forcing conditions are required for metalation. Gibson and co-workers have described metalation reactions using methyl substituted 2,6- $\{(2,6\text{-Me}_2\text{-C}_6\text{H}_3)\text{NCMe}\}_2\text{C}_5\text{H}_3\text{N}$ and R^1 substituted 2,6- $\{(2,4,6\text{-Me}_3\text{-C}_6\text{H}_2)\text{NCR}^1\}_2\text{C}_5\text{H}_3\text{N}$ (where R^1 is Me, Et, *i*-Pr or Ph), all with the same metalation agent (FeCl_2), solvent (*n*-butanol), and reaction temperature ($80\text{ }^{\circ}\text{C}$).^{2,10,13} In all cases, a color change is observed immediately upon mixing the ligand and FeCl_2 ; the resulting iron compounds are either blue (where R^1 is Me, Et or *i*-Pr) or green (where R^1 is Ph) in color. Where R^1 is methyl, the reaction was stopped after only 15 min;² where R^1 is phenyl a 30 min reaction time was used.¹⁰ Where R^1 is ethyl or isopropyl, a 12 h reaction time was reported.¹³ Brookhart described milder conditions for metalation of methyl substituted 2,6- $\{(2,6\text{-Me}_2\text{-C}_6\text{H}_3)\text{NCMe}\}_2\text{C}_5\text{H}_3\text{N}$ (use of either FeCl_2 or $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$, tetrahydrofuran solvent, ambient temperature, and several hours reaction time).¹

Attempted metalation of **6** under the following conditions gave no evidence of the desired iron(II) chloride metalated product: FeCl₂, *n*-hexanol solvent, reflux, 48 h; FeCl₂, *n*-butanol solvent, 80 °C, 14 h; FeCl₂, tetrahydrofuran solvent, reflux, 24 h; FeCl₂·4H₂O, tetrahydrofuran solvent, reflux, 20 h. In each case, the anticipated color change (to green, blue or purple) was not detected and unreacted **6** was recovered.

Under more forcing conditions (FeCl₂, acetic acid solvent, reflux, 3 h to 90 h), a color change was observed (a purple solution), but only upon concentration *in vacuo* (after 3 h reflux) or extended reaction times (>24 h reflux). Similar conditions were described by Chirik *et al.* for metalation of phenyl substituted 2,6-((2,6-*i*-Pr₂-C₆H₃)NCMe)₂C₅H₃N (reflux, 4 h).^{11b} For our metalation attempts using acetic acid solvent, small amounts of a purple, paramagnetic species were isolated upon reaction work-up (10–15 mg recovery, where 200–250 mg of **6** was used for metalation). ¹H NMR spectroscopic analysis using CD₂Cl₂ solvent reveals two broad downfield signals at 79.04 and 49.38 ppm that we tentatively assign as pyridyl proton resonances. Other resonances appear in the 12.95 to –32.24 ppm range, with a greater number of signals present than we would anticipate for a pure monomeric iron(II) chloride complex of **6**. Magnetic susceptibility measurements (Evans NMR method) give evidence of paramagnetism, though also suggest that impurities and/or multiple paramagnetic species are present. Recrystallization attempts using solvents such as acetone-*d*₆ and CD₂Cl₂ have led to precipitation of an iron(II) acetate species (presumably formed under metalation conditions). While these metalation conditions provide reproducible results, the poor recovery makes this reaction preparatively ineffective. We have considered the possibility that a given molecule of **6** may coordinate to more than one metal center, potentially yielding an oligomeric species. Nonetheless, experiments are under way to obtain X-ray quality single crystals of this purple, paramagnetic species.

Computational studies

Two facts led us to pursue computational studies for ligands of the form 2,6-((2,6-Me₂-C₆H₃)NCR¹)₂C₅H₃N (where R¹ is Me,

Et, *i*-Pr or *t*-Bu): (1) mild conditions are sufficient for metalation of methyl substituted 2,6-((2,6-Me₂-C₆H₃)NCMe)₂C₅H₃N with iron(II) chloride,¹ in contrast to *t*-butyl substituted **6**, and (2) methyl substituted 2,6-((2,6-Me₂-C₆H₃)NCMe)₂C₅H₃N adopts a different conformation in its crystalline form^{25b} than *t*-butyl substituted **6**. For each ligand, the energies of three conformers were calculated: closed (Fig. 3 gives the prototype for this conformer), open (the crystal structure of 2,6-((2,6-Me₂-C₆H₃)NCMe)₂C₅H₃N gives the prototype for this conformer), and open-planar (the crystal structure of [2,6-((2,4,6-Me₃-C₆H₂)NCMe)₂C₅H₃N]FeCl₂ gives the prototype for this conformer).^{2b} The closed, open, and open-planar conformers of **6** are illustrated in Fig. 4.

Based on the ease of metalation of the methyl substituted ligand and the energies presented in Table 3, the open conformer appears to be the reactive conformer for metalation. For comparison, the open conformers of methyl substituted 2,6-((2,6-Me₂-C₆H₃)NCMe)₂C₅H₃N and *t*-butyl substituted **6** are shown in Fig. 5. For both the methyl- and ethyl-substituted ligands, the open conformer is the more thermodynamically stable one. This agrees well with the previously reported crystal structure for the methyl-substituted ligand.^{25b} When the size of the alkyl chain is increased (*i.e.*, *i*-propyl and *t*-butyl), marked differences are observed in relative energies of the reactive conformation. The closed structure becomes more thermodynamically stable for the *i*-propyl and *t*-butyl substituted species, with a lower calculated energy for the *t*-butyl substituted species as compared to the

Table 3 Relative energies, in kcal mol^{–1}, of various conformations of **6** optimized at the B3LYP/6–31G(d) level of theory. Energies in parentheses were calculated at the MP2/cc-pVDZ level. Reorganization energies (ΔE_{reorg}) were evaluated in reference to the lowest energy conformation for a given substitution

	Closed	Open	Open-planar	ΔE_{reorg}
Methyl	7.9(2.6)	0.0	10.0 (10.9)	10.0 (10.9)
Ethyl	6.3(3.2)	0.0	14.2 (15.6)	14.2 (15.6)
<i>i</i> -Propyl	–4.1(–7.6)	0.0	14.2 (15.0)	18.3 (22.7)
<i>t</i> -Butyl	–9.6(–14.4)	0.0	11.1 (12.8)	20.7 (27.2)

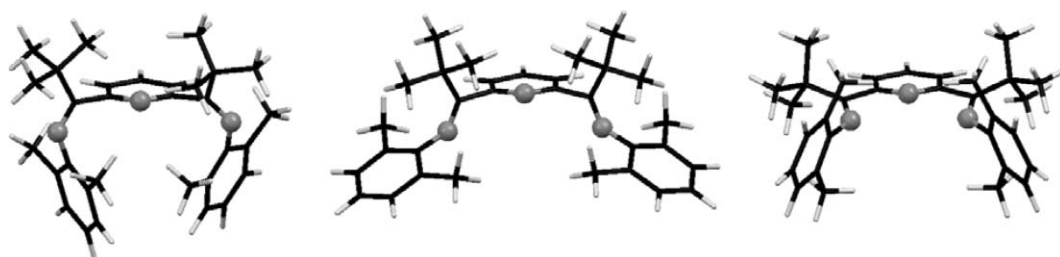


Fig. 4 Closed, open, and open-planar conformers of **6** (geometries were calculated at the B3LYP/6–31G(d) level).

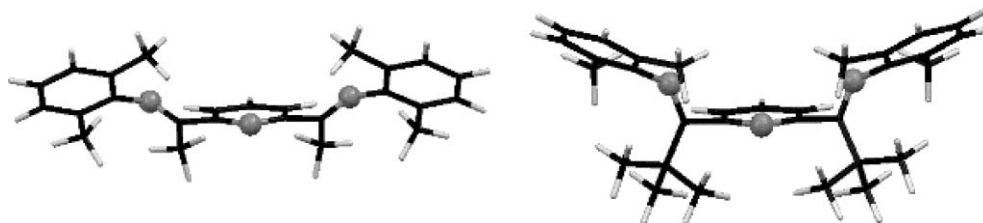


Fig. 5 Open conformers of methyl substituted 2,6-((2,6-Me₂-C₆H₃)NCMe)₂C₅H₃N and *t*-butyl substituted **6** (geometries were calculated at the B3LYP/6–31G(d) level).

i-propyl substituted species. This agrees with the crystal structure for **6** (Fig. 3) and may offer some insight into the difficulty in metalating this species. The *t*-butyl-substituted species also shows a significant geometrical difference compared to the other ligands in that the imino C–N bonds are almost perpendicular to the plane formed by the pyridine ring. This is most likely due to the steric strain the *t*-butyl groups would experience if the imino nitrogen atoms were in a configuration similar to that of the other ligands (*i.e.*, nearly planar with the pyridine ring).

Budzelaar and Zhu²⁶ recently published theoretical calculations on similar species in order to parameterize binding of these ligands to metal complexes. In their analyses, they broke down differential binding energies into three terms: σ -donation, π -donation, and reorganization energy associated with the open conformation of the ligand adopting the open-planar conformation. Their studies showed that, referenced to a structure almost identical to our methyl-substituted species, reorganization energies were typically lower or negligibly higher for structures with various substitutions on the imino carbons. However, they did not report reorganization energies based on closed conformations. For the *i*-propyl and *t*-butyl cases, this will significantly increase the reorganization energy. The *t*-butyl structure has the highest reorganization energy of the species considered, suggesting that metalation of this species will be the most difficult to accomplish.

Conclusions

A sterically hindered bis(imino)pyridine compound, 2,6- $\{(2,6\text{-Me}_2\text{-C}_6\text{H}_3)\text{NC}(t\text{-Bu})\}_2\text{C}_5\text{H}_3\text{N}$ (**6**), has been synthesized and characterized using single-crystal X-ray diffraction. Relative energies of three conformations of this species (closed, open, and open-planar) and the thermodynamic preference for the closed form give a potential explanation for the resistance of **6** towards metalation with iron(II) chloride. Similar calculations are under way in order to identify new, promising synthetic targets in the bis(imino)pyridine ligand family.

Experimental

General considerations

All chemical reactions were carried out under an atmosphere of argon using standard Schlenk techniques²⁷ unless otherwise noted. Argon gas was purified by passage over DrieriteTM. All chemicals were purchased from Aldrich and used as received unless otherwise noted. Chloroform-*d*, methylene chloride-*d*₂, benzene-*d*₆, and toluene-*d*₈ were purchased from Cambridge Isotope Laboratories and dried over molecular sieves (8–12 mesh, 4 Å, activated) before use. A MBraun Manual Solvent Purification System (MB-SPS) was used to obtain the following anhydrous solvents: toluene, tetrahydrofuran, diethyl ether, pentane and dichloromethane; solvents were submitted to three freeze–pump–thaw cycles before use when rigorously deoxygenated solvent was required.²⁸ Anhydrous *n*-hexanol and *n*-butanol were purchased from Aldrich (Sure/Seal bottleTM) and used as received. Molecular sieves (8–12 Mesh, 4 Å) were purchased from J. T. Baker and activated before use. Silica gel used for flash chromatography²⁹ was purchased from Aldrich (200–425 mesh). *n*-BuLi was purchased from Aldrich as a 1.6 M solution in hexanes (Sure/Seal bottleTM)

and titrated before use.³⁰ Before use, 2,6-dibromopyridine was recrystallized using 200 proof absolute ethanol.³¹

NMR spectra were recorded on a Varian Mercury spectrometer at 300 MHz (¹H) and 75 MHz (¹³C) at 298 K; all chemical shifts are referenced relative to the NMR solvent (either residual protio or ¹³C signals for the solvent peak(s)). The following abbreviations are used for NMR splitting patterns: pd (pseudo doublet), pt (pseudo triplet), and br s (broad singlet). MS data were obtained using an Applied Biosystems API2000 triple quadrupole mass spectrometer with electrospray ionization. MS samples, containing approximately 1 $\mu\text{g mL}^{-1}$ of analyte in methanol with 0.1% formic acid, were analyzed by direct infusion. Mass scans were performed from 20–300 *m/z*, and the signals were time-averaged over 2 min. Infrared spectra were recorded using a Perkin-Elmer Spectrum One FTIR System; samples were prepared by placing the compounds on a diamond attenuated total reflectance (ATR) plate in either solid or liquid form. Elemental analyses were performed at Atlantic Microlab, Inc. in Norcross, Georgia.

Multi-step synthesis of **6**

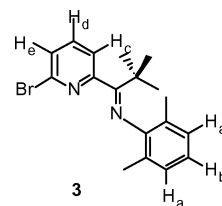
Preparation of *N*-(2,6-dimethyl-phenyl)-2,2-dimethyl-propionamide, **1.** The synthesis of this sterically hindered amide was achieved as described by literature methods.^{20–22} A solution of 2,6-dimethylaniline (24.8 mL, 200 mmol, 1.0 equiv.) and triethylamine (27.8 mL, 199 mmol, 1.0 equiv.) was prepared using dichloromethane (320 mL) in a 1 L round bottom flask, equipped with addition funnel. In a separate 500 mL round bottom flask, pivaloyl chloride (24.6 mL, 200 mmol, 1.0 equiv.) was dissolved in dichloromethane (80 mL) whilst stirring. The latter solution was added to the former solution *via* the addition funnel, and slow dropwise addition resulted in a cloudy white suspension. The reaction mixture was heated to reflux for 1 h, cooled to 22 °C and then extracted with water (2 \times 100 mL). The organic phase was dried over magnesium sulfate, and then filtered to yield a pale yellow solution. Removal of solvent *in vacuo* yielded a white powder (39.36 g, 95.9%). (Found: C 75.77, H 9.43, N 6.86%. Calcd for C₁₃H₁₉NO: C 76.06, H 9.33, N 6.82%). ν_{max} (ATR)/cm⁻¹: 3296 (N–H), 1646 (C=O). ¹H NMR (300 MHz, CDCl₃, 22 °C) δ /ppm: 1.37 (9H, s, C(CH₃)₃), 2.21 (6H, s, CH₃), 6.87 (1H, br s, N–H), 7.07 (3H, br s, C₆H₃). ¹H NMR (300 MHz, benzene-*d*₆, 22 °C) δ /ppm: 1.09 (9H, s, C(CH₃)₃), 2.05 (6H, s, CH₃), 6.03 (1H, br s, N–H), 6.95 (3H, m, C₆H₃). ¹³C NMR (75 MHz, CDCl₃, 22 °C) δ /ppm: 18.10 (CH₃), 27.56 (C(CH₃)₃), 39.01 (C(CH₃)₃), 126.55 (C₆H₃), 127.63 (C₆H₃), 134.26 (C₆H₃), 135.38 (C₆H₃), 176.52 (C=O). Single crystals of **1** suitable for X-ray diffraction were obtained from an anhydrous dichloromethane solution cooled to –15 °C for 8 d.

Preparation of *N*-(2,6-dimethyl-phenyl)-2,2-dimethyl-propionimidoyl chloride, **2.** The synthesis of this sterically hindered imidoyl chloride was achieved as described by literature methods.²³ Phosphorus pentachloride (11.51 g, 55.3 mmol, 1.0 equiv.) was slowly added to a yellow slurry of **1** (12.50 g, 60.9 mmol, 1.1 equiv.) in anhydrous toluene (125 mL) under a positive pressure of argon. The hydrogen chloride gaseous by-product was bubbled through a sodium hydroxide solution. The resulting opaque pale yellow slurry was stirred for 18.5 h at 22 °C. The product mixture was subjected to atmospheric pressure distillation under argon to remove toluene and the POCl₃ by-product, followed by vacuum distillation to collect the desired product as an off-white

semi-solid. (11.84 g, 86.9%). (Found: C 69.89, H 8.17, N 6.25%. Calcd for C₁₃H₁₈ClN: C 69.79, H 8.11, N 6.26%). ν_{\max} (ATR)/cm⁻¹: 1698 (C=N). ¹H NMR (300 MHz, CDCl₃, 22 °C) δ /ppm: 1.43 (9H, s, C(CH₃)₃), 2.06 (6H, s, CH₃), 6.96 (1H, m, C₆H₃), 7.04 (2H, pd, *J* = 7.4 Hz, C₆H₃). ¹H NMR (300 MHz, benzene-d₆, 22 °C) δ /ppm: 1.25 (9H, s, C(CH₃)₃), 2.03 (6H, s, CH₃), 6.96 (3H, m, C₆H₃). ¹³C NMR (75 MHz, CDCl₃, 22 °C) δ /ppm: 17.67 (CH₃), 28.53 (C(CH₃)₃), 43.85 (C(CH₃)₃), 123.73 (C₆H₃), 125.89 (C₆H₃), 127.60 (C₆H₃), 145.36 (C₆H₃), 155.45 (C=N). Alternatively, Kugelrohr distillation (95 °C, 1 Torr) may be used to collect the desired product. ³¹P NMR was used to qualitatively monitor the absence of the POCl₃ by-product. Purification *via* flash silica gel chromatography is not viable because it hydrolyzes **2**, thus reverting to **1**.

Preparation of [1-(6-bromo-pyridin-2-yl)-2,2-dimethyl-propylidene]-(2,6-dimethyl-phenyl)amine, 3. A 500 mL Schlenk flask was charged with 2,6-dibromopyridine (1.22 g, 5.15 mmol, 1.0 equiv.) and anhydrous dichloromethane (90 mL), then cooled to -78 °C using a dry ice-acetone bath. This solution was treated with 1.6 M *n*-butyllithium in hexanes (3.3 mL, 5.28 mmol, 1.0 equiv.). The resulting pale yellow solution was stirred at -78 °C for 15 min. Meanwhile, a 250 mL Schlenk flask was charged with **2** (1.58 g, 7.08 mmol, 1.4 equiv.) and anhydrous dichloromethane (5 mL). This solution of **2** was added to the reaction flask *via* cannula transfer to yield a yellow solution. The 250 mL Schlenk flask was washed with anhydrous dichloromethane (2 mL), and this wash was also transferred to the reaction flask *via* cannula transfer. Stirring of the reaction mixture continued at -78 °C and the cold bath was left intact to warm to 22 °C over the course of 22 h. The opaque pale yellow slurry was then filtered through a fine porosity glass filter, yielding a transparent yellow filtrate. Solvent was removed *in vacuo* for 3 h, providing a yellow semi-solid. The concentrated filtrate was dissolved in 2.5% ethyl acetate-hexanes (v/v, 2 mL) and dichloromethane (2 mL) and subjected to flash silica gel chromatography using 2.5% ethyl acetate-hexanes (v/v) as eluent. Combined fractions were dried *in vacuo* for 4 h to yield a pale yellow crystalline solid (1.48 g, 83.3%). (Found: C 62.89, H 6.26, N 7.85%. Calcd for C₁₈H₂₁BrN₂: C 62.61, H 6.13, N 8.11%). ν_{\max} (ATR)/cm⁻¹: 1647 (C=N). ¹H NMR (300 MHz, CDCl₃, 22 °C) δ /ppm: 1.38 (9H, s, C(CH₃)₃), 2.07 (6H, s, CH₃), 6.70 (2H, m, *Ar*), 6.81 (2H, m, *Ar*), 6.25 (2H, m, *Ar*). ¹H NMR (300 MHz, benzene-d₆, 22 °C) δ /ppm: 1.37 (9H, s, C(CH₃)₃), 2.11 (6H, s, CH₃), 6.25 (1H, pt, *J* = 7.7 Hz, H_d), 6.32 (1H, dd, *J* = 0.8 Hz, 7.7 Hz, H_c), 6.55 (1H, dd, *J* = 0.8 Hz, 7.7 Hz, H_c), 6.70 (1H, m, H_b), 6.79 (2H, pd, *J* = 7.4 Hz, H_a). ¹H NMR (300 MHz, toluene-d₈, 22 °C) δ /ppm: 1.35 (9H, s, C(CH₃)₃), 2.07 (6H, s, CH₃), 6.32 (2H, two overlapping m, *pyr*), 6.54 (1H, pd, *J* = 7.5 Hz, *pyr*), 6.65 (1H, m, H_b), 6.74 (2H, pd, *J* = 7.4 Hz, H_a). ¹H NMR (300 MHz, CD₂Cl₂, 22 °C) δ /ppm: 1.35 (9H, s, C(CH₃)₃), 2.03 (6H, s, CH₃), 6.68 (1H, m, H_b), 6.75 (1H, m, H_c), 6.79 (2H, pd, *J* = 7.4 Hz, H_a), 7.25 (1H, m, H_c), 7.30 (1H, m, H_d). ¹³C NMR (75 MHz, CDCl₃, 22 °C) δ /ppm: 18.35 (CH₃), 28.87 (C(CH₃)₃), 40.49 (C(CH₃)₃), 120.04, 122.54, 125.48, 126.96, 127.38, 137.27, 140.78, 147.67, 156.74, 175.21 (C=N). ¹³C NMR (75 MHz, benzene-d₆, 22 °C) δ /ppm: 18.74 (CH₃), 29.11 (C(CH₃)₃), 30.35 (C(CH₃)₃), 120.23, 123.08, 125.64, 127.03, *one aromatic resonance not detected*, 137.31, 141.20, 148.60, 157.22, 174.81 (C=N). NOE difference experiments were used to identify the three pyridyl proton signals.

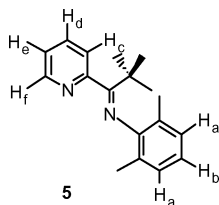
Homonuclear decoupling experiments were used to detect long range coupling between the phenyl-methyl protons and the *ortho*-phenyl ¹H NMR resonances. Single crystals of **3** suitable for X-ray diffraction were obtained *via* slow evaporation of a 2.5% ethyl acetate-hexanes (v/v) solution over the course of 1 d.



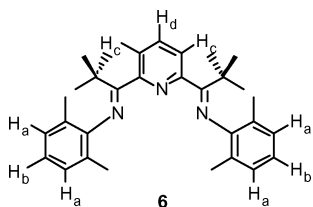
(1-Tert-butyl-pentylidene)-(2,6-dimethyl-phenyl)amine, 4. A 100 mL Schlenk flask was charged with **3** (0.71 g, 2.06 mmol, 1.0 equiv.) and anhydrous dichloromethane (15 mL), then cooled to -78 °C using a dry ice-acetone bath. This solution was treated with 1.6 M *n*-butyllithium in hexanes (0.96 mL, 1.54 mmol, 0.75 equiv.). The resulting pale yellow solution was stirred at -78 °C for 15 min. Meanwhile, a 50 mL Schlenk flask was charged with **2** (0.35 g, 1.58 mmol, 0.77 equiv.) and anhydrous dichloromethane (5 mL). This solution of **2** was added to the reaction flask *via* cannula transfer to yield a yellow solution. The 50 mL Schlenk flask was washed with anhydrous dichloromethane (2 × 5 mL), and these washes were also transferred to the reaction flask *via* cannula transfer. Stirring of the reaction mixture continued at -78 °C and the cold bath was left intact to warm to 22 °C over the course of 17.5 h. The resulting opaque pale yellow slurry was filtered through a fine porosity glass filter, yielding a transparent yellow filtrate. The solvent was removed *in vacuo* for 1 h, yielding a yellow oil. The concentrated filtrate was dissolved in 2.5% ethyl acetate-hexanes (v/v, 1 mL) and dichloromethane (0.5 mL) and subjected to flash silica gel chromatography using 2.5% ethyl acetate-hexanes (v/v) followed by 5.0% ethyl acetate-hexanes (v/v) as eluent. Combined fractions were dried *in vacuo* for 2.25 h to yield a pale yellow oil (0.11 g, 28.6%). ¹H NMR (300 MHz, benzene-d₆, 22 °C) δ /ppm: 0.57 (3H, t, *J* = 7.1 Hz, butyl CH₃), 0.89 (2H, sextet, *J* = 7.1 Hz, CH₂), 1.15 (2H, m, CH₂), 1.24 (9H, s, C(CH₃)₃), 1.96 (2H, m, CH₂), 2.04 (6H, s, CH₃), 6.90 (1H, m, C₆H₃), 7.02 (2H, pd, *J* = 7.4 Hz, C₆H₃). ¹³C NMR (75 MHz, benzene-d₆, 22 °C) δ /ppm: 13.65, 18.52, 23.62, 28.71, 28.93, 30.35, 41.16, 122.44, 124.98, *one aromatic resonance not detected*, 149.38, 178.69 (C=N). *m/z* (ESI) 246.4 ([M + H]⁺).

(2,6-Dimethyl-phenyl)-(2,2-dimethyl-1-pyridin-2-yl-propylidene)-amine, 5. Under an argon counter flow, a 100 mL flask was charged with **3** (0.114 g, 0.33 mmol, 1.0 equiv.) and 1.6 mL anhydrous tetrahydrofuran, then cooled to -78 °C using a dry ice-acetone bath. This bright yellow solution was treated with 1.29 M *n*-butyllithium in hexanes (0.307 mL, 0.40 mmol, 1.2 equiv.). The resulting vibrant yellow-orange solution was stirred at -78 °C for 1 h before the addition of methanol (0.160 mL, 3.9 mmol, 11.8 equiv.), providing a pale yellow solution. The removal of solvent *in vacuo* for 15 min produced a waxy pale yellow solid. The crude product was dissolved in 10% ethyl acetate-hexanes (4 mL, v/v) and dichloromethane (2 mL) and subjected to flash silica gel chromatography using 10% ethyl acetate-hexanes (v/v) as eluent. Combined fractions were dried *in vacuo* for 3.5 h to yield **5** as a yellow oil (0.0503 g, 63.6%). ν_{\max} (ATR)/cm⁻¹: 1645 (C=N). ¹H NMR (300 MHz, benzene-d₆,

22 °C) δ /ppm: 1.47 (9H, s, C(CH₃)₃), 2.19 (6H, s, CH₃), 6.30 (1H, ddd, J = 7.5 Hz, 4.9 Hz, 1.2 Hz, H_e), 6.56 (1H, dt, J = 7.7 Hz, 1.0 Hz, H_c), 6.66 (1H, td, J = 7.5 Hz, 1.7 Hz, H_d), 6.72 (1H, pt, J = 7.4 Hz, H_b), 6.82 (2H, pd, J = 7.4 Hz, H_a), 8.21 (1H, ddd, J = 4.9 Hz, 1.7 Hz, 1.0 Hz, H_f). ¹³C NMR (75 MHz, benzene-d₆, 22 °C) δ /ppm: 18.92 (CH₃), 29.33 (C(CH₃)₃), 40.87 (C(CH₃)₃), 121.45, 122.46, 122.77, 125.77, 127.86, one aromatic resonance not detected, 134.78, 148.60, 156.97, 176.46 (C=N). m/z (ESI) 267.5 ([M + H]⁺).



Preparation of 2,6-((2,6-Me₂-C₆H₃)NC(*t*-Bu))₂C₅H₃N, **6.** A 250 mL Schlenk flask was charged with **3** (0.77 g, 2.23 mmol, 1.0 equiv.) and anhydrous tetrahydrofuran (11 mL), then cooled to -78 °C for 20 min using a dry ice-acetone bath. This solution was treated, dropwise, with 1.6 M *n*-butyl lithium in hexanes (1.53 mL, 2.45 mmol, 1.1 equiv.). The resulting gold colored solution was stirred at -78 °C for 15 min. Meanwhile, an argon filled 100 mL round bottom flask was charged with **2** (0.51 g, 2.26 mmol, 0.98 equiv.) and anhydrous tetrahydrofuran (11 mL). This solution of **2** was added dropwise to the reaction flask *via* syringe to yield an orange solution. The 100 mL round bottomed flask was washed with anhydrous tetrahydrofuran (3 mL), and this wash was also transferred to the reaction flask *via* syringe. Stirring of the reaction mixture continued at -78 °C and the cold bath was left intact to warm to 22 °C over the course of 17 h. The solvent was removed *in vacuo* for 2.5 h, resulting in an orange semi-solid, which was then dissolved in 75 mL anhydrous pentane. The opaque yellow slurry was filtered through a fine porosity glass filter, yielding a transparent yellow filtrate. The solvent was removed *in vacuo* for 3 h, yielding a yellow semi-solid. The concentrated filtrate was dissolved in 1% ethyl acetate-hexanes (5 mL, v/v) and subjected to flash silica gel chromatography using 1% ethyl acetate-hexanes (v/v) as eluent. Combined fractions were dried *in vacuo* for 1 h to yield **6** as a pale yellow crystalline solid (0.55 g, 54.2%). (Found: C 81.43, H 8.78, N 8.79%. Calcd for C₃₁H₃₉N₃: C 82.07, H 8.66, N 9.26%). ν_{\max} (ATR)/cm⁻¹: 1651 (C=N). ¹H NMR (300 MHz, benzene-d₆, 22 °C) δ /ppm: 1.29 (18H, s, C(CH₃)₃), 2.09 (12H, s, CH₃), 6.36 (2H, pd, J = 7.5 Hz, H_c), 6.49 (1H, m, H_d), 6.70 (2H, m, H_b), 6.78 (4H, pd, J = 7.5 Hz, H_a). ¹³C NMR (75 MHz, benzene-d₆, 22 °C) δ /ppm: 19.08 (CH₃), 29.22 (C(CH₃)₃), 40.85 (C(CH₃)₃), 120.05, 122.65, 125.35, 127.90, 134.42, 148.82, 156.13, 175.87 (C=N). A saturated solution of **6** in anhydrous pentane was cooled to -15 °C for 1 month to produce a single crystal suitable for X-ray diffraction.



Attempted synthesis of iron(II) chloride complex of **6**

General metalation procedure using *n*-hexanol, *n*-butanol or tetrahydrofuran solvent. Under argon, a solution of **6** (1 equiv.) was treated with a pre-heated solution of FeCl₂ or FeCl₂·4H₂O (1 equiv., the solution was pre-heated to ensure complete dissolution). The reaction mixture was then heated between 14 and 48 h before removal of solvent under vacuum (*n*-butanol solutions were heated to 80 °C; *n*-hexanol and tetrahydrofuran solutions were heated to reflux). In each case, the anticipated color change (to green, blue or purple) was not detected, neither initially nor after concentration *in vacuo*. Inside the glove box, the residue was extracted with pentane and vacuum filtration provided a filtrate that was identified as unreacted **6** (structural assignment made *via* ¹H NMR spectroscopy). In each case, the precipitate isolated during vacuum filtration did not correspond to the desired iron(II) chloride complex of **6** (¹H NMR spectroscopy was used for analysis).

General metalation procedure using acetic acid solvent. Under argon, an acetic acid solution of **6** (1 equiv.) was added to solid FeCl₂ and the reaction mixture was then heated to reflux between 3 and 90 h before removal of solvent under vacuum (with gentle heating). The anticipated color change was first observed (a purple solution) either upon concentration *in vacuo* (after 3 h reflux) or extended reaction times (>24 h reflux). Inside the glove box, the residue was extracted with dichloromethane. Using vacuum filtration, the filtrate was collected and then concentrated to dryness under vacuum. Next, this residue was treated with pentane, and the purple, pentane-insoluble precipitate was collected and analyzed *via* ¹H NMR spectroscopy (in CD₂Cl₂) and magnetic susceptibility (Evans NMR method). Selected signals, ¹H NMR (300 MHz, CD₂Cl₂, 22 °C) δ /ppm: 79.04 (br s, *pyr*), 49.38 (br s, *pyr*), 12.95 (br s), 7.95–0.72 (overlapping signals), -6.74 (br s), -13.25 (br s), -14.26 (br s), -32.34 (br s). The other isolated species from reaction work-up (dichloromethane-insoluble material; pentane-soluble material) did not correspond to the desired iron(II) chloride complex of **6** (¹H NMR spectroscopy was used for analysis).

Crystal structure determinations

Crystallographic data are presented in Table 4. Single crystals of **3** and **6**, respectively, were mounted using Paratone[®] oil onto a glass fiber and cooled to the data collection temperature of 100 K. Data were collected on a Brüker-AXS Platform APEX II CCD diffractometer with 0.71073 Å MoK α radiation for compound **3**. Data were collected on a Brüker-AXS Kappa APEX II CCD diffractometer with 1.54178 Å CuK α radiation for compound **6**. Unit cell parameters were obtained from 90 data frames, 0.5° Φ , from three different sections of the Ewald sphere. The data-set was treated with SADABS absorption corrections based on redundant multi-scan data.³² All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contribution.

Computational methods

HF/6-31G(d) optimizations were performed and analytic harmonic frequencies were calculated to determine the nature of the stationary points observed. All geometries were then optimized

Table 4 Selected crystallographic and data collection parameters for compounds **3** and **6**

	3	6
Empirical formula	C ₁₈ H ₂₁ BrN ₂	C ₃₁ H ₃₉ N ₃
Formula weight	345.28	453.65
Crystal color	Colorless	Colorless
Habit	Block	Block
<i>T</i> /K	100(2)	100(2)
λ /Å	0.71073	1.54178
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	9.5839(5)	11.5027(4)
<i>b</i> /Å	9.2243(5)	11.6244(4)
<i>c</i> /Å	18.696(1)	20.8562(7)
α /°	90	90
β /°	91.430(1)	105.597(1)
γ /°	90	90
<i>V</i> /Å ³	1652.3(1)	2686.0(2)
<i>Z</i>	4	4
<i>D</i> _{calcd} /Mg m ⁻³	1.388	1.122
Absorption coefficient/mm ⁻¹	2.484	0.496
<i>F</i> (000)	712	984
Crystal size/mm ³	0.22 × 0.14 × 0.07	0.27 × 0.24 × 0.15
θ range of data collection/°	2.18–28.37	3.99–68.15
Index ranges	–11 ≤ <i>h</i> ≤ 12, –12 ≤ <i>k</i> ≤ 11, –23 ≤ <i>l</i> ≤ 24	–11 ≤ <i>h</i> ≤ 13, –13 ≤ <i>k</i> ≤ 11, –25 ≤ <i>l</i> ≤ 24
Reflections collected	11 499	19 189
Independent reflections	3812 [<i>R</i> _{int} = 0.0364]	4836 [<i>R</i> _{int} = 0.0221]
Completeness	99.2% to θ = 25.00°	99.5% to θ = 67.00°
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.8473 and 0.6086	0.9297 and 0.8785
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	3812/0/195	4836/0/317
Goodness-of-fit on <i>F</i> ²	1.048	1.065
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0320, <i>wR</i> ₂ = 0.0859	<i>R</i> ₁ = 0.0402, <i>wR</i> ₂ = 0.0990
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0360, <i>wR</i> ₂ = 0.0886	<i>R</i> ₁ = 0.0418, <i>wR</i> ₂ = 0.1001
Largest diffraction peak and hole	1.041 and –0.331 e Å ⁻³	0.208 and –0.196 e Å ⁻³

at the B3LYP/6–31G(d) level of theory with very little change observed in any of the geometries. Relative energies are reported for the B3LYP optimized structures and do not include zero-point energy corrections. MP2/cc-pVDZ energies were also calculated at the B3LYP/6–31G(d) optimized geometries. GAMESS³³ was used to optimize structures with the maximum gradient tolerance set to 0.0006 Hartree/Bohr. Default values were used for all other parameters.

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