ORGANOMETALLICS

Synthesis, Structures, and Reactivity of Chelating Bis-N-Heterocyclic-Carbene Complexes of Iron(II)

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Supporting Information

ABSTRACT: Distorted tetrahedral (bis-carbene)FeX₂ complexes can be synthesized by direct metalation of chelating bisimidazolium salts, containing CH₂ or phenylene linkers, with Fe(N(SiMe₃)₂)₂(THF). For methylenebis(*N*-R-imidazole-2-ylidene) ((^RC)₂CH₂), the high-spin complexes ((^RC)₂CH₂)-FeX₂ (R = ⁱPr or 2,6-di-isopropylphenyl (DIPP), X = I or Br) are isolated in good to excellent yield. In contrast the phenylene-linked congener ((^{iPr}C)₂Ph)FeI₂ cannot be separated from two



co-products, one of which was characterized by X-ray crystallography and zero-field ⁵⁷Fe Mössbauer spectroscopy as the square-planar complex $[(({}^{\rm IPr}C)_2{\rm Ph})_2{\rm Fe}][I]_2$. The disparate reactivity toward Fe(N(SiMe_3)_2)_(THF) is due to the increase in linker length and decrease in linker flexibility of the phenylene-linked bis-carbene ligand relative to the methylene analogue. The short, flexible $-CH_2-$ linker projects the azole rings into the *xy* plane (defined as the carbene–Fe bond directions) and away from the pseudoaxial anionic substituent, whereas the inflexible phenylene linker ((${}^{\rm R}C)_2{\rm Ph}$) orientates both azole rings into the *z* direction, which in ((${}^{\rm R}C)_2{\rm Y}$)FeX₂ species (Y = CH₂ or phenylene) has the greatest steric crowding. Metallacycle distortion in tetrahedral ((${}^{\rm R}C)_2{\rm Ph}$)FeX₂ is necessary to project the azoles into the *xy* plane, destabilizing this geometry. Addition of CO to ((${}^{\rm DIPP}C)_2{\rm CH}_2$)FeI₂ forms *cis*-((${}^{\rm DIPP}C)_2{\rm CH}_2$)FeI₂ with NaSMe cleanly forms ((${}^{\rm DIPP}C)_2{\rm CH}_2$)FeI₂(SMe), while attempts to exchange the second iodide for ${}^{\rm -SMe}$ led to carbene dissociation.

INTRODUCTION

Individually the application of iron complexes¹⁻³ and N-heterocyclic carbenes $(NHCs)^{4-6}$ in organic synthesis and catalysis is becoming increasingly important. Despite the mutually attractive properties of Fe (low toxicity and high abundance) and NHCs (tunable sterics and the ability to stabilize a range of oxidation states due to strong σ donor and moderate π acceptor ability),⁷ catalytic applications using Fe-NHC complexes are currently rare.⁴ Notable exceptions have demonstrated that (NHC)Fe complexes are effective for catalyzing cross-coupling reactions,^{8–11} direct arene borylation,¹² hydrosilylation,¹³ and polymerization.^{14,15} These processes each require a coordinatively unsaturated Fe center during the catalytic cycle. However, (NHC)Fe complexes with coordination numbers less than 6 are relatively rare and generally contain NHCs appended with additional chelating ligands and/or anionic moieties. This scarcity of low-coordinate (NHC)Fe coincides with a growing body of evidence that the binding of carbenes to first-row transition metals can be weak, particularly in sterically crowded systems containing electron-rich transition metal centers.^{8,16–22,61} For iron even multidentate carbene-containing ligands have been reported to undergo dissociation from electron-rich Fe centers.¹⁶ Recently Grubbs et al. have utilized this phenomenon to catalyze the oligomerization of $Fe(COT)_2$ (COT = cyclo- octatetraene) with a monodentate carbene; the requirement for only catalytic carbene clearly indicates a reversible interaction with the Fe

center.^{17,18} More generally ligand dissociation is highly undesirable, often leading to irreversible catalyst deactivation. Overcoming this allows access to the useful reactivity manifold afforded by redox-active Fe centers ligated by strong carbene σ donor ligands. For example Smith and Meyer prevent carbene dissociation by using chelating tripodal tris-carbene ligands, containing either an anionic backbone or a coordinating amine Lewis base.^{23–27} These ligands have enabled the isolation of complexes containing iron in oxidation states ranging from +5 to +1, with the tris-carbene-Fe^I complex found to be extremely reducing, rapidly transforming an azido moiety to an Fe-imido.

For subsequent use as a catalytic precursor a facile synthetic route to robust carbene complexes of the general formula (carbene)₂FeX₂ (X = halide) was desired. While Grubbs et al. have previously reported a simple synthesis using monodentate NHCs and FeX₂, the propensity of monocarbenes to dissociate from electron-rich Fe centers led us to investigate the chelation of bis-carbenes to Fe.^{8,14} Bidentate carbenes will provide the entropically enhanced binding strength afforded by chelation while maintaining the flexibility inherent in an Fe precursor that is coordinatively unsaturated and ligated by two exchangeable anionic ligands, X (essential for example in radical rebound crosscoupling).²⁸ To the best of our knowledge, no complexes

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Figure 1. Dicationic components of the bis-imidazolium precursors 1-3. All are iodide salts.

containing bidentate carbenes chelating to a metal center in a tetrahedral geometry (as preferred by L_2FeI_2 complexes) have been reported to date. Previous work utilizing bis-carbenes has concentrated on square-planar and octahedral-based geometries, where the length and flexibility of the linker combined with the steric bulk of the N-substituents are key parameters controlling chelating ability.^{29,30} Herein we describe the synthesis of (bis-carbene)FeX₂ complexes containing phenylene and $-CH_2-$ carbene linkers. Key factors controlling the accessibility and stability of these distorted tetrahedral complexes were again found to be the linker length and flexibility. Initial reactivity studies demonstrate $-CH_2$ -linked bis-carbenes remain coordinated to iron during the ligation of further Lewis bases and halide salt metathesis, important for future catalytic applications.

RESULTS AND DISCUSSION

Precursor Syntheses. Ligand precursors containing two different ligand backbones, CH₂ and phenylene (termed (^RC)₂CH₂ and (^RC)₂Ph, respectively), were targeted to investigate the different binding propensities engendered by the formation of six- and seven-membered metallacycles, particularly how chelation is effected by ring strain and orientation of N-substituents (termed wingtips). For the CH₂ backbones an ⁱPr derivative and a bulkier analogue (2,6-di-isopropyl phenyl (DIPP)) were synthesized as the bis-imidazolium salts. Compounds 1-3 were isolated as the iodide salts using previously reported synthetic routes or modifications thereof (Figure 1).^{31–33}

Ligation of Fe with CH₂ Backbone Bis-carbene. The complexes $((^{R}C)_{2}CH_{2})FeI_{2}$ (R = ^{i}Pr , 4, and R = DIPP, 5) were readily synthesized in good to excellent yield by aminolysis of $Fe(N(SiMe_3)_2)_2(THF)$ with stoichiometric bis-imidazolium salt in THF.^{16,34} The dibromide $((^{DIPP}C)_2CH_2)FeBr_2$, 6, was also readily accessible in moderate isolated yield (40%) by initial deprotonation of the bis-imidazolium salt 2 with KH, addition of the free carbene to FeBr₂, and subsequent heating in toluene (80 °C, 20 h). The molecular structures of each (4 and 5 were recrystallized from THF/Et₂O and 6 from toluene) confirmed similar distorted tetrahedral geometries at Fe with Fe-C bond lengths (in the range 2.08 to 2.11 Å) consistent with other highspin four-coordinate Fe(II) carbene complexes.^{8,14} The highly distorted tetrahedral geometry at Fe allows for classification of one halide as pseudoapical (with C–Fe–X angles $\approx 100^{\circ}$) and one as pseudoequatorial (C-Fe-X angles approaching 120°), particularly for 5 and 6. The different degrees of deviation from ideal tetrahedral is quantified by the smaller displacement of Fe from the C–C– $X_{equatorial}$ plane for **5** and **6** compared to **4** (**4** = 0.846 Å, 5 = 0.752 Å, 6 = 0.776 Å). This disparity can be attributed to the more sterically crowded equatorial plane present in 4, arising from the N-ⁱPr substituents, which direct



Figure 2. ORTEP representation of complexes 4-6. Thermal ellipsoids are at 50%, and hydrogens are omitted for clarity. Inset, right: space-filling diagrams for 4 and 5 viewed along the C-C-I "equatorial plane". Nitrogen = blue, carbon = black, hydrogen = white, chloride = green, bromide = brown, and iron = red.

bulk inward toward the equatorial Fe-I. In comparison the aromatic rings of the DIPP wingtips are orthogonal to the equatorial plane, projecting less steric bulk into the equatorial plane (Figure 2 inset right).

Compounds 4–6 are however still grossly similar, with bite angles all in the region of 90°, comparable to other metal bis-carbene complexes containing a CH₂ backbone.^{29,35} The C–Fe–C angle in 4–6 is reduced compared to monodentate (carbene)₂FeX₂ compounds, while there is a concomitant increase in the X–Fe–X angle and the yaw angles (θ)²⁹ for 4–6 (Table 1, includes the monodentate carbene complexes (IPr)₂FeCl₂ and (IEt)₂FeMe₂ for comparison, IPr and IEt = 1,3-R₂-imidazole-2-ylidene, R = ⁱPr and Et, respectively). The closely comparable yaw angles for compounds 4–6 are smaller than those of ((^{tBu}C)₂CH₂)M complexes (θ = 13–14°), where the significant steric bulk of the ^tBu-N-substituent results in considerable steric crowding.

Comparison of key structural metrics of 4-6 with the more prevalent square-planar ((RC)2CH2)M complexes is informative. Steric interactions in the square-planar structures are minimized by the imidazole rings aligning out of the xy plane (defined as the C–M–C plane). This projects the wingtip bulk into the zplanes and significantly reduces the unfavorable steric interactions to other ligands in the xy plane. The degree of distortion of the imidazole ring out of the *xy* plane is termed the α angle⁸ and is in the range $40-57^{\circ}$ for $({}^{R}C)_{2}CH_{2}$ ligands in square-planar compounds. Compounds 4-6 with distorted tetrahedral geometries have reduced ligand bulk in the xy plane (defined as the C-Fe-C plane) but increased in the z planes compared to square-planar complexes. Consequentially 4–6 have smaller lphaangles (30.7°, 31.0°, and 31.7°, respectively) than observed in square-planar complexes. The lower α angle flattens the ligand and reduces the projection of the wingtip steric bulk into the z planes.

Compounds 4 and 6 are extremely poorly soluble in ether and hydrocarbon solvents, while slowly decomposing in chlorinated and protic solvents, frustrating complete characterization. Compound 5 however exhibited enhanced solubility, being partially soluble in arenes and readily soluble in THF and MeCN. The ¹H NMR spectrum of 5 (Figure 3, left) displays eight resonances, including two inequivalent ⁱPr methyl resonances of intensity 12, indicating restricted rotation around the N $-C_{aryl}$ and $C_{aryl}-C^{iPr}$ bonds, resulting in four methyl groups orientated in toward the Fe-I core. The absence of any intensity 1 resonances confirms the CH₂ protons are equivalent to boat conversion of the sixmembered metallacycle.³⁷ The solution magnetic moment

Table 1.	Structural Data	for 4–6 Compare	d to Nonchel	ating Ana	logues	$(NHC)_2FeX_2$
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linker (compound no.)	wingtip	Х	C-Fe-C angle (deg)	yaw angle $(deg)^b$	M–NHC (Å)	X—M—X (deg)
$CH_{2}(4)$	ⁱ Pr	Ι	91.1(3)	9.3	2.106(9), 2.109(8)	119.33(5)
$CH_2(5)$	DIPP	Ι	89.03(17)	8.7	2.075(4), 2.092(5)	118.28(2)
$CH_{2}(6)$	DIPP	Br	88.2(5)	8.0	2.107(12), 2.092(12)	121.29(8)
$(IPr)_2FeCl_2^{\ a}$	ⁱ Pr	Cl	102.05(6)	4.0	2.136(2), 2.130(2)	$112.95(2)^{c}$
$(IEt)_2 FeMe_2^a$	Et	Me	100.8(1)	2.3	2.132(3), 2.140(3)	$111.1(1)^d$

^{*a*} Monodentate carbenes (1,3-R₂-imidazole-2-ylidene). ^{*b*} Yaw angle, which is the in-plane distortion of the NHC imposed by metallacycle steric constraints, is defined as the difference between the two M-C-N angles divided by 2. ^{*c*} From ref 14. ^{*d*} From ref 8.



Figure 3. ¹H NMR of compound **5** in d_3 -MeCN, * = peaks due to residual protio MeCN and THF. Inset: zero-field ⁵⁷Fe Mössbauer spectrum of **5**. Right: temperature dependence of χ_M and $\chi_M T$ for **5** (χ_M = molar magnetic susceptibility). The red solid lines represent calculated values.³⁶

(Evans method) at 294 K in d_8 -THF of 5.2 μ_B is consistent with a high-spin S = 2 ground state, as expected for a distorted tetrahedral L₂FeX₂ environment.³⁸ Mössbauer spectroscopy on 5 (Figure 3 inset, isomer shift (i.s.) = 0.70 mm s⁻¹ and quadrupole shift splitting $(q.s.) = 3.74 \text{ mm s}^{-1}$ at 80 K, zero field) confirmed bulk purity and the presence of a single Fe(II) species in a distorted tetrahedral environment, with i.s. and q.s. parameters comparable to distorted tetrahedral (bis-phosphine)FeI₂ complexes.^{38,39} Variable-temperature (2-300 K) magnetic susceptibility measurements were made on a polycrystalline sample of **5** in an applied magnetic field of 0.1 T (Figure 3, right).³⁶ The room-temperature $\chi_{\rm M}T$ value of 3.4 cm³ K mol⁻¹ ($\mu_{\rm eff}$ = 5.2 $\mu_{\rm B}$) is in good agreement with the presence of a high-spin (S = 2)Fe(II) d⁶ center in 5. Upon cooling, $\chi_M T$ remains almost constant until 60 K, when it starts to decrease smoothly and then more rapidly below 26 K to reach 1.82 cm³ K mol⁻¹ at 2 K. At the same time, $\chi_M(T)$ increases on cooling from 0.011 cm³ mol⁻¹ at 300 K to 0.92 cm³ mol⁻¹ at 2 K. Fitting the susceptibility data above 30 K to the Curie–Weiss law ($\chi_{\rm M} = C/T - \theta$) gave $C = 3.43 \text{ cm}^3 \text{ K mol}^{-1}$ and $\theta = -0.57 \text{ K}$. The value of the Curie constant, C, implies an average g factor near 2.13, which is in good agreement with the distorted tetrahedral environment of Fe(II). The small and negative value of θ is consistent with weak intermolecular antiferromagnetic interactions in 5. Analysis of the low-temperature $\chi_{M}T(T)$ and magnetization data (ESI) gave a large value of D, implying considerable orbital angular momentum within the d⁶ configuration of Fe(II) as expected, and this was confirmed by EPR spectroscopy, which did not show any EPR transitions at 35 GHz microwave frequency, even at T = 5 K. The

closely comparable solid-state and solution $\mu_{\rm eff}$ values suggest a similar structure to that observed by X-ray diffraction for 5 persists in solution.

Ligation of Fe with Phenylene Backbone Bis-carbenes. Structurally characterized examples of metal complexes chelated with ortho-phenylene linked bis-carbenes are rare. 40,41 The previously reported octahedral complex trans-((^{nBu}C)₂Ph)RhI₂- $(\kappa^2$ -OAc) has key structural metrics comparable to compounds **4–6**, including a bite angle of 92.2° and an α angle of 33.4°,⁴⁰ while a yaw angle of only 2.0° implies there is no significant strain in the seven-membered metallacycle. However, attempts to access $((^{R}C)_{2}Ph)FeI_{2}$ by aminolysis of $Fe(N(SiMe_{3})_{2})_{2}(THF)$ with stoichiometric bis-imidazolium salt 3 in THF (or MeCN) were more complex than that using 1 or 2. ¹H NMR spectra contained diamagnetic resonances overlapped with eight observable paramagnetic resonances; the relative integrals of the latter were not consistent with a single complex. Single crystals from this mixture could be isolated, and characterization by X-ray diffraction revealed the formation of compound 7, $[((^{iPr}C)_2 -$ Ph)₂Fe]I₂, a dicationic species with a ligand:metal ratio of 2:1. The structure of 7 was disordered over two sites (with 57:43% relative occupancy), both possessing similar structural metrics, and as such, only the major component is discussed. The iron center in 7 is square planar (Figure 4, left, angles at Fe Σ = 359.94°) with disparate ligand bite angles of $82.6(6)^{\circ}$ and 88.5(6)°. The Fe-C distances (1.920(10) and 2.010(9) Å) are shorter than in high-spin Fe-carbene compounds but longer than in the diamagnetic Fe(II) square-planar complex [{bis(pyridylimidazol-2-ylidene)methane}Fe][PF₆]₂ (Fe–C = 1.801(9) Å).⁴² The two bis-carbenes linkers adopt a "trans"



Figure 4. Left: ORTEP representation of the major disordered cationic component (57%) of complex 7. Thermal ellipsoids are at 50%, and hydrogens are omitted for clarity. Inset center: space-filling diagrams (100% van der Waals) of 7, parallel and perpendicular to the *xy* plane (denoted in blue). Right: ⁵⁷Fe Mössbauer spectrum (80 K zero field, all parameters in mm s⁻¹ $\sigma \leq \pm 0.01$ mm s⁻¹ unless indicated otherwise in parentheses, individual doublets marked above spectra); component 1: i.s. = 0.68, q.s. = 3.82, hwhm = 0.16 (38% of total Fe), component 2: i.s. = 0.43, q.s = 0.94, hwhm = 0.31 (51 5% of total Fe), component 3: i.s. = 0.18(2) q.s. = 4.16(3), hwhm = 0.19 (11% of total Fe).

arrangement with one phenylene backbone orientated above and one below the square plane (Figure 4 inset center). The high α angle of 62.0° projects the majority of the wingtip steric bulk into the *z* planes, essential to attain a stable square-planar arrangement. This ligand arrangement results in sterically hindered axial sites (Figure 4 inset center), destabilizing ligand (e.g., iodide/MeCN) coordination. In contrast analogous (P–P)₂FeX₂ structures containing chelating phosphines adopt octahedral or square-based pyramid structures with no evidence for analogous $[(P-P)_2Fe]^{2+}$ square-planar complexes.^{39,43}

Attempts to produce bulk quantities of pure 7 for further study were complicated by variable elemental analyses across different batches despite identical reaction conditions. We attribute this to the isolation from solution (by precipitation) of different ratios of the complexes observed by ¹H NMR spectroscopy. Bulk material could be repeatedly produced that possessed elemental analysis consistent with 7 by extensive washing of isolated material with THF (in which 7 is extremely poorly soluble). However, on dissolution, the ¹H NMR spectra of this material was identical to the crude product, indicating numerous products. Mass spectroscopy in acetonitrile confirmed the presence of a number of Fe^{II} complexes, with positive ion peaks consistent with compound 7 present along with ions attributable to $[(({}^{iPr}C)_2Ph)_2FeI]^+$, $\{[(({}^{iPr}C)_2Ph)FeI_2] \cdot H\}^+, \text{ and } [(({}^{iPr}C)_2Ph)FeI]^+. \text{ Solid-state}$ ${}^{57}Fe Mössbauer spectroscopy (80 K, zero field, Figure 4, right)$ revealed the presence of three iron complexes, two major products, one with i.s. and q.s. consistent with a tetrahedral high-spin Fe(II) complex (assigned as $(({}^{iPr}C)_2Ph)FeI_2)$ and one consistent with a low-spin octahedral complex (i.s. = $0.68 \text{ mm s}^{-1} \text{ q.s.} = 3.82 \text{ mm}$ s^{-1} , and i.s = 0.43 mms⁻¹ q.s = 0.94 mm s⁻¹, respectively).^{38,39,43} One minor product was also present at \sim 10% and is assigned to 7, with parameters (i.s. = $0.18(2) \text{ mm s}^{-1}$, q.s. = $4.16(3) \text{ mm s}^{-1}$) closely comparable to square-planar S = 1 Fe(II) complexes ligated by strong σ donor and moderate π acceptor ligands, a ligand field consistent with four NHCs ligands.^{38,44} The identity of the octahedral compound is currently unknown, but the coordination of two iodides (or another ligand), forming octahedral ((^{iPr}C)₂Ph)₂FeI₂, is

disfavored due to the steric shielding of the axial sites of 7 and the observed paramagnetism of the related $(P-P)_2FeI_2$ complex.³⁹ Squid magnetometry on a sample with elemental analysis consistent with pure 7 was also inconsistent with the presence of only a square-planar Fe(II) S = 1 compound and resembled that of **5**. The results from Mössbauer spectroscopy imply ca. 40% of the sample is consistent with a tetrahedral high-spin Fe(II) compound and ca. 50% of the sample might be expected to be a low-spin (diamagnetic) octahedral Fe(II) compound of unknown molecular mass. This unknown compromises numerical analysis of the magnetic data, which are presented in the Supporting Information as mass susceptibility. Both analytical methods unambiguously confirm that the formation of a number of Fe^{II} species is not a solution phenomena.

Compound 7, with a ligand:Fe ratio of 2:1, has to be produced by carbene dissociation from an Fe complex, a process that may be initiated by solvent or anion coordination to $(({}^{iPr}C)_2Ph)FeI_2.{}^{39,43}$ No free carbene is present in the synthesis of 7 until deprotonation of the imidazolium precursor 3 by Fe(N(SiMe₃)₂)₂(THF), a process that invariably generates a M–C bond. Confirmation that $(({}^{iPr}C)_2Ph)$ will readily dissociate from Fe^{II} was provided by the addition of one equivalent of $(({}^{DIPP}C)_2CH_2)$ to the mixture containing 7 and $(({}^{iPr}C)_2Ph)FeI_2$ in THF. This resulted in the slow (due to the poor solubility of $(({}^{iPr}C)_2Ph)$ -ligated complexes in THF) formation of 5 as the major iron-containing product. Related substitution of the ethylene backbone bis-carbene $(({}^{tBu}C)_2Et)$ by $(({}^{tBu}C)_2CH_2)$ has been previously reported in a square-planar nickel complex and attributed to a reduction in ring strain on formation of the six-membered metallacycle relative to the sevenmembered metallacycle.²¹

Surmising that ligand strain may destabilize the distorted tetrahedral ((^{iPr}C)₂Ph)FeI₂ complex and lead to carbene dissociation and formation of 7, the structure of *trans*-((^{nBu}C)₂-Ph)RhI₂(κ^2 -OAc), which possesses the structural metrics expected in tetrahedral ((^{iPr}C)₂Ph)FeI₂, was revisited. Interestingly despite the insignificant yaw angles, strain in *trans*-((^{nBu}C)₂Ph)RhI₂(κ^2 -OAc) is indicated by the internal N–C–C angles of the seven-membered metallacycle being appreciably



Figure 5. ORTEP representation of the cationic portion of complex 8. Thermal ellipsoids shown at 50% probability. Inset right: the formation of 9 from the deprotonation of 3 in the absence of Fe salts.

larger than the ideal 120°. The strain in $(({}^{R}C_{2})Ph)$ can be quantified by the angle between the phenylene centroid and the two imidazolium centroids, which in an ideal system will approach 60° . For example in the imidazolium precursor 3 this value is 62.3°, ³⁶ while in the square-planar complexes $(({}^{Me}C)_2Ph)Rh$ - $(CO)_2$ and 7 it is 65.4° and 64.3°, respectively. In contrast in trans-(($^{nBu}C_2$)Ph)RhI₂(κ^2 -OAc) this intercentroid angle is 71.8°, indicating greater strain. With small ligand wingtips in trans-(($^{nBu}C_2$)Ph)RhI₂(κ^2 -OAc) this distortion can be attributed to strain in the metallacycle engendered by the axial iodide ligands enforcing a small α angle. This is significant, as the desired distorted tetrahedral complex (($^{iPr}C)_2Ph$)FeI₂ would require a similar α angle to *trans*-(($^{nBu}C)_2Ph$)RhI₂(κ^2 -OAc) (based on compounds 4-6) to minimize unfavorable steric interactions between the pseudoaxial halide and the ((^{iPr}C)₂Ph) ligand. Thus we propose the lack of flexibility inherent in the phenylene backbone combined with the requirement for a low α angle engendered by axial ligation in a distorted tetrahedral environment destabilizes $(({}^{1Pr}C)_2Ph)FeI_2$ sufficiently to result in reversible coordination of the carbene to iron. In contrast the $((^{n}C)_{2}CH_{2})$ bis-carbenes can adopt small α angles on chelation with little energetic penalty;^{5,29} thus $((^{DIPP}C)_2CH_2)FeI_2$ is stable to ligand dissociation even in the presence of Lewis bases (e.g., PMe₃ and MeCN) for 3 days (no new complexes were observed by ¹H NMR despite square-planar $((^{n}C)_{2}CH_{2})_{2}M$ structures being sterically accessible).^{21,45}

The synthesis commencing from 3 formally uses one equivalent of $Fe(N(SiMe_3)_2)_2(THF)$ only as a deprotonating agent, producing "FeI2" and HN(SiMe3)2 as byproducts that can be separated by repeated THF extraction. Attempts to form 7 cleanly by the low-temperature deprotonation of 3 with KH followed by subsequent addition of 0.5 equivalent of FeX2 instead led to ¹H and ¹³C $\{^{1}H\}$ NMR spectra indicative of a mixture of products arising from migration of isopropyl from N to C. N-C_{iPr} cleavage was unambiguously confirmed from the reaction of compound 3 with 0.5 equivalent of $FeCl_2$ and 2 equivalents of LiN(SiMe₃)₂ in THF at -78 °C. On warming and recrystallization from THF/pentane, a small quantity of poor-quality crystals was obtained of the planar monocationic compound 8 (Figure 5) as the iodide salt. The monocationic charge and structural metrics for compound 8 are consistent with one imidazole (C1-N1 = 1.362(13) Å and C1-N2 = 1.330(14) Å, N1-C1-N2 = $112.5(10)^{\circ}$) and one imidazolium ring (C2-N3 = 1.338(14) Å and C2-N4 = 1.329(14) Å, $N3-C2-N4 = 108.2(9)^{\circ}$ linked through a C-C single bond $(C1-C2 = 1.418(15) \text{ Å})^{46-48}$ with the caveat that the poorquality data lead to high uncertainties in bond lengths and angles. Carbene N-C cleavage has been recently reported by Deng et al., during the alkylation of (IEt)₂FeCl₂ with PhLi, and proposed to be an iron-mediated process proceeding via (IEt)₂ FePh(Cl).⁸ However, $N-C_{isopropyl}$ cleavage and C-C bond formation is also observed on deprotonation of 3 in the absence of any iron species (e.g., using two equivalents of KH or $LiN(SiMe_3)_2)$; thus the decomposition of 3 appears to follow the general Brønsted base initiated mechanism, possibly proceeding via a protonated dimer.⁴⁹ The intermediate produced on deprotonation of 3 with KH and formation of a C=C bond will then undergo subsequent [1,3]-sigmatropic rearrangement to form the observed compound 9 (Figure 5, inset right), analogous to related tetraamino-alkenes.⁵⁰ The instability of the free biscarbene $(({}^{iPr}C)_2Ph)$ is also consistent with previous synthetic routes to $(({}^{n}C)_{2}Ph)M$ complexes all proceeding by direct metalation of bis-imidazolium salts with a suitable metal precursor, with the free carbene not reported to the best of our knowledge. The preorganized geometric arrangement enforced by the rigid phenylene backbone is a key factor in C=C bond formation,⁵¹ with methylene and more relevantly ethylene backbone analogues stable and isolatable as the free bis-carbenes.^{21,52,53} The inaccessibility of the free bis-carbene $(({}^{iPr}C)_2Ph)$ combined with the lack of pure ((^{iPr}C)₂Ph)FeI₂ or 7 precluded these complexes from further reactivity studies, and subsequent work focuses on derivatizing 5.

Initial Reactivity Studies. Compound 5 will be useful only if the $\{((^{DIPP}C)_2CH_2)Fe\}$ moiety persists during addition of neutral ligands and/or salt metathesis. The addition of 1 atm of CO to a degassed THF solution of 5 resulted in a slow color change to violet. Monitoring the reaction by ¹H NMR spectroscopy revealed the gradual growth of a single new diamagnetic species as the major product, which displayed two CO bands at 2024 and 1974 cm^{-1} , along with the formation of a minor paramagnetic byproduct. The observation of two CO bands is consistent with a *cis* CO arrangement.^{54,55} In contrast analogous complexes with chelating diphosphines produce the trans-CO *cis*-iodide isomer, $(P-P)Fe(CO)_2I_2$.⁵⁶ Identification of $((^{DIPP}C)_2$ -CH₂)FeI₂(CO)₂, 10, as the cis-(CO)-cis-(I) or cis-(CO)-trans-(I) isomer was frustrated by the lack of suitable crystalline material. However, comparison of the CO stretching frequencies for 10 with (2,2'-bipyridyl)FeI₂(CO)₂ where both isomers have been characterized (the cis-(CO)-cis-(I) and cis-(CO)-trans-(I) isomers have ν CO of 2044/2004 and 2077/2033 cm⁻¹, respectively)⁵⁴ demonstrates that **10** is significantly more electron rich than 2,2'-bipyridyl. In contrast NHCs and pyridyl ligands have similar overall basicities toward $\{CpFe(CO)\}^+$ fragments, which has been attributed to greater Fe→NHC charge transfer compared to Fe→ pyridyl.⁵³ A decrease in metal to ligand π back-bonding from the {Fe(CO)₂I₂}



Figure 6. ORTEP representation of complex 11. Thermal ellipsoids are shown at 50% probability.

fragment to NHC (or pyridyl) can be expected due to the presence of two CO groups (with one or two carbonyls *trans* to NHCs, dependent on regioisomer). Thus the increased electron density at Fe in **10** is due to the superior σ donor properties of the NHC relative to pyridyls.⁵³

Pleasingly, metathesis of halide in 5 for the sterically small thiolate, SMe, is also facile by addition of one equivalent of NaSMe in THF. Recrystallization and structural analysis confirmed the formation of the distorted tetrahedral compound ((^{DIPP}C)₂CH₂)FeI(SMe), 11. Key structural metrics are comparable to 4-6, including a bite angle of $88.1(5)^\circ$, average yaw and α angles of 7.5° and 29.0°, and Fe-C bond lengths of 2.112(13) and 2.103(14) Å. The Fe-S distance in 11 (2.274(4) Å) is in the range expected for four-coordinate high-spin \tilde{Fe}^{II} thiolates.⁵⁷ It is also noteworthy that the SMe occupies the less sterically hindered pseudoequatorial site, while the bulky DIPP groups also prevent any dimerization through (μ -SMe). In solution (d_8 -THF) 11 is paramagnetic with a magnetic moment (294 K, Evans method) of 4.3 $\mu_{\rm B}$, most consistent with a distorted tetrahedral iron center. Compounds 5 and 11 are ligated by strong σ donor carbenes and good π donor ligands (iodide and thiolate) but while electron rich both show no evidence for carbene dissociation (stable in THF for days). The addition of a further equivalent of NaSMe to 11 however results in the formation of one new paramagnetic product with ligand resonances that are symmetry equivalent by ¹H NMR spectroscopy. This compound can be isolated in good yield (81% based on Fe) as a microcrystalline solid that has an elemental composition consistent with a $((^{\text{DIPP}}\text{C})_2\text{CH}_2)$:Fe:SMe ratio of 1:2:4, indicating carbene dissociation from iron has occurred. Dissolution of this microcrystalline material produced an identical ¹H NMR spectrum to the *in situ* product, and we tentatively assign it as $(MeS)Fe(\mu-MeS)_2(\mu-((\overset{DIPP}{D}C)_2CH_2))Fe(SMe)$, on the basis of analogy to the methylation of $((^{DIPP}C)_2CH_2)CrCl_2$ which afforded $((Me)Cr(\mu-Me)_2(\mu-((^{DIPP}C)_2CH_2))Cr(Me))$ by loss of bis-carbene.²⁰ The dissociation of $(^{^{DIPP}C})_2CH_2$ implies a weakened interaction between NHCs and the electron-rich Fe center, as the steric crowding in the targeted intermediate $(({}^{\rm DIPP}C)_2CH_2)Fe(SMe)_2$ will only be marginally greater than that in the stable complex 5. The latter shows no propensity for carbene dissociation, despite iodide generally being a better electron donor than thiolate. The stability of more crowded 10 can be rationalized by the enhanced Lewis acidity of the Fe center on coordination of π acidic carbonyls, strengthening the NHC-Fe bonds. Thus an electron-rich Fe center combined with sufficient steric crowding are both required for carbene dissociation.

Distorted tetrahedral FeX₂ compounds ligated by chelating carbenes are accessible in good yield provided the linker length is sufficiently short and flexible to project the azole rings predominantly into the sterically less crowded equatorial plane. Utilizing a nonflexible and longer linked bis-carbene that has a steric preference for high α angles (and thus square-planar structures) prevents the clean formation of (bis-carbene)FeX₂, leading to the formation of two co-products, one identified as the unusual square-planar S = 1 complex $[((^{iPr}C)_2Ph)_2Fe]I_2$, 7. The formation of 7 and the observed dissociation of $(^{DIPP}C)_2CH_2$ from Fe on addition of two equivalents of NaSMe to 5 indicate that the NHC—Fe bond is weaker than expected in these electron -rich Fe^{II} complexes. Thus ligand metallacycle strain and steric crowding must both be minimized in electron-rich (bis-carbene)-Fe^{II} complexes to ensure persistence of the (biscarbene)Fe moiety in future applications.

EXPERIMENTAL SECTION

General Considerations. All reactions were performed using standard glovebox or Schlenk line techniques, unless otherwise specified. Solvents used were either purified by an Innovative Technology PS-MD-5 solvent purification system or distilled from appropriate drying agents and degassed. Deuterated solvents were distilled from appropriate drying agents and degassed. N-Dipp-imidazole was prepared according to a published procedure³¹ and purified by sublimation. Methylenebis(N-ⁱPr-imidazolium) diiodide was prepared as described in the literature.³² o-Phenylenediimidazole was prepared according to the published procedure.33 All other materials were purchased from commercial vendors and used as received. NMR spectra were recorded with a Bruker AV-400 spectrometer (400 MHz ¹H; 100 MHz ¹³C; 162 MHz). ¹H NMR chemical shifts are reported in ppm relative to protio impurities in the deuterated solvents, and ¹³C NMR using the center line of CD_2Cl_2 (or other solvent as appropriate) as internal standard. Unless otherwise stated all NMR spectra are recorded at 293 K. Protio-solvent suppression experiments were performed on Varian Inova instruments (flame-sealed d_6 -dmso capillaries used to lock field) using pulse sequences written in-house by Prof. Gareth Morris. Elemental analysis of air-sensitive compounds was performed by London Metropolitan University service. Solution magnetic moments were recorded at 25 °C (unless otherwise stated) using the Evans method. 58,59 Mössbauer spectra were recorded in zero magnetic field at 80 and/or 298 K on an ES-Technology MS-105 Mössbauer spectrometer with a 100 MBq ⁵⁷Co source in a rhodium matrix at ambient temperature. Spectra were referenced against 25 µm iron foil at 298 K, and spectrum parameters were obtained by fitting with Lorentzian curves. Samples were prepared under a dry nitrogen atmosphere by grinding with boron nitride powder prior to mounting in the sample holder, and all errors are $<\pm 0.01$ mm s⁻¹ unless otherwise stated. SQUID measurements were carried out on microcrystalline material by enclosing the sample in an O-ring-sealed Kel-F capsule. The capsule was transferred to the sample holder in a glovebox, transported to the SQUID magnetometer (Quantum Design MPMS XL7) in a sealed Schlenk tube, and then rapidly transferred to the helium-purged sample space of the magnetometer. Corrections for diamagnetism were made using Pascal's constants, and the experimental magnetic data were also corrected for the diamagnetic contribution of the KelF capsule, which was measured in similar experimental conditions.

N-^I**Pr-imidazole**. Acetonitrile was added to a mixture of imidazole (1.36 g, 20 mmol) and potassium hydride (800 mg, 20 mmol) at 0 °C, and the reaction allowed to warm to RT with stirring for approximately 2 h (until visible gas evolution stopped). The sample was then cooled to 0 °C, and isopropyl iodide (2.99 mL, 5.1 g, 30 mmol) added.

The reaction mixture was stirred overnight at RT (further manipulations were carried out in an open laboratory), acetonitrile removed *in vacuo*, and the product extracted with dichloromethane to give a yellowish oil (2 g, 91%). The identity of the compound was confirmed by comparison with published NMR data (CDCl₃).⁶⁰

Methylenebis(*N***-Dipp-imidazolium) Diiodide, 2.** All manipulations were carried out in an open laboratory. *N*-Dipp-imidazole (1.9 g, 8.33 mmol) and methylene iodide (0.34 mL, 1.117 g, 4.17 mmol) were heated to reflux in acetonitrile (10 mL) in a high-pressure ampule overnight, resulting in a white suspension. This was concentrated to ca. 3 mL, 10 mL of diethyl ether was added, and this was briskly heated to reflux. The sample was cooled to room temperature, and the colorless solid was isolated by filtration, washed with diethyl ether, and dried *in vacuo* (2.36 g, 78%). If needed, further purification can be achieved by crystallization from acetonitrile/diethyl ether. The identity of the compound was confirmed by comparison with published NMR data for the analogous dibromide salt.¹⁹ Anal. Calcd: C = 51.39, H = 5.84, N = 7.73. Found: C = 51.49, H = 5.92, N = 7.63.

o-Phenylenebis(N-ⁱPr-imidazolium) Diiodide, 3. All manipulations were carried out in an open laboratory. o-Phenylenediimidazole (3 g, 14.29 mmol) and isopropyl iodide (5.7 mL, 9.7 g, 57.14 mmol) were heated to reflux in acetonitrile (15 mL) in a high-pressure ampule overnight, and the resulting yellow solution was concentrated and kept overnight at 3 °C. Colorless crystals were filtered off and dried in vacuo (4.3 g, 55%). X-ray quality crystals were grown by slow cooling of a saturated MeCN solution of compound 3 from reflux to RT. ¹H NMR (300 MHz, CD₃CN, 293 K) δ: 9.60 (s, 2H, NCHN), 7.93-7.84 (m, 2H +2H, C₆H₄), 7.61 (app. s, 2H, NCH₂CH₂N), 7.51 (app. s, 2H, NCH₂CH₂N), 4.74 (sept, 2H, CH(CH₃)₂, J_{H-H} = 6.69 Hz), 1.58 (d, 12H, CH(CH₃)₂, J_{H-H} = 6.78 Hz). ¹³C{¹H} NMR (75 MHz, CD₃CN, 293 K): not observed (2C, N-C-N), δ 136.84 (2C, C₂C₄H₄), 133.02 $(2C,\ C'_2C_4H_4),\ 128.82\ (2C,\ C''_2C_4H_4),\ 123.84\ (2C,\ NCHCHN),$ 122.11 (2C, NCHCHN), 54.56 (2C, CH(CH₃)₂), 22.26 (4C, CH-(CH₃)₂. Anal. Calcd: C = 40.37, H = 4.81, N = 9.91. Found: C = 39.44, H = 4.13, N = 10.01.

Methylenebis(*N***-Dipp-imidazole-2-ylidene).** THF (25 mL) was added at -78 °C to a mixture of methylenebis(*N*-Dipp-imidazole) diiodide (2 g, 2.76 mmol) and potassium hydride (221 mg, 5.52 mmol), and the reaction allowed to warm to RT overnight with stirring (*CAUTION: hydrogen evolution*). The resultant brown suspension was removed by filtration, and the THF solution removed under reduced pressure. Pentane (30 mL) was then added, and cooling to -78 °C for 1 h resulted in the formation of a precipitate that was filtered and dried to give a cream powder (1 g, 77%, 95% pure by NMR). The identity of the compound was confirmed by comparison with published NMR data.¹⁹

[Methylenebis(*N*-ⁱ**Pr-imidazole-2-ylidene)]diiodoiron(II), 4.** THF (50 mL) was added at -78 °C to methylenebis(*N*-ⁱ**Pr-imidazole**) diiodide (488 mg, 1 mmol) and bis(trimethylsilylamido)-(tetrahydrofuran)iron(II) (448 mg, 1 mmol), and the reaction mixture was allowed to slowly warm to RT overnight with stirring. The resultant yellow-brown solution was filtered, and the solvent was removed *in vacuo*. The resulting solid was washed with pentane (2 × 20 mL) and dried *in vacuo* to give a yellow-brown powder (310 mg, 57%). X-ray quality crystals were grown by slow diffusion of Et₂O into a THF solution of the compound at RT. ¹H NMR (400 MHz, THF+(CD₃)₂SO capillary, 293 K) δ : 57.5 (2H), 16.3 (2H), 13.8 (2H), 12.1 (2H), 1.4 (6H), 0.5 (6H). Anal. Calcd for C₁₃H₂₂I₂FeN₄: C = 28.70; H = 4.08; N = 10.30. Found: C = 28.61, H = 4.03, N = 10.17.

[Methylenebis(*N*-Dipp-imidazole-2-ylidene)]diiodoiron-(II), 5. THF (40 mL) was added at 0 °C to methylenebis(*N*-Dippimidazole) diiodide (1.527 g, 2.11 mmol) and bis(trimethylsilylamido)-(tetrahydrofuran)iron(II) (945 mg, 2.11 mmol), and the reaction mixture was allowed to slowly warm to RT overnight with stirring. The dark yellow-brown solution was concentrated to 1/4 of the initial volume, and pentane added (50 mL), causing precipitation of a yellowgreen powder. This was filtered, washed with pentane (2 × 25 mL), and dried *in vacuo*, yielding a yellow-green powder (1.6 g, 2.05 mmol, 97%). X-ray quality crystals were grown by slow diffusion of Et₂O into a THF solution of the compound. ¹H NMR (400 MHz, THF+(CD₃)₂SO capillary, 293 K) δ : 64.8 (2H), 30.4 (2H), 13.2 (2H, v br), 7.1 (2H), 6 (4H), -1.6 (12H), -5.6 (12H), -10.6 (4H). ¹H NMR (400 MHz, CD₃CN, 293 K), δ : 63.2 (2H), 28.5 (2H), 21 (2H, v br), 7.3 (2H), 6.3 (4H), -1.5 (12H), -5.4 (12H), -10.7 (4H). Evans (*d*₈-THF, toluene capillary, concentration approximately 0.05 g mL⁻¹, 400 MHz for ¹H, 125 MHz for ¹³C): averaged value 5.40 $\mu_{\rm B}$. Anal. Calcd for C₃₁H₄₀FeI₂N₄: C = 47.84, H = 5.18, N = 7.20. Found: C = 47.67, H = 5.32, N = 7.03.

[Methylenebis(*N*-Dipp-imidazole-2-ylidene)]dibromoiron(II), 6. Methylenebis(*N*-Dipp-imidazole-2-ylidene) (250 mg, 0.53 mmol) and iron(II) bromide (105 mg, 0.48 mmol) were heated at 70 °C in toluene (15 mL) for 20 h. The light brown precipitate was filtered, washed with Et₂O (2 × 10 mL), and dried *in vacuo* to yield a light brown powder (145 mg, 44%). X-ray quality crystals were grown by slow cooling of a refluxing C₆D₆ solution of the compound to RT. ¹H NMR (400 MHz, THF+(CD₃)₂SO capillary, 293 K) δ : 61.7 (2H), 25.9 (2H), 7.3 (2H), 6.7 (2H), 5.5 (4H), -1.4 (12H), -3.7 (12H), -8.9 (4H). Anal. Calcd for C₃₁H₄₀Br₂FeN₄: C = 54.41, H = 5.89, N = 8.19. Found: C = 54.08, H = 6.06, N = 8.08.

Compound 3 + Fe(N(SiMe₃)₂)₂(THF). A. MeCN (50 mL) was added to a mixture of *o*-phenylene(N-ⁱPr-imidazoline) diiodide (1 g, 1.82 mmol) and bis(trimethylsilylamido)(tetrahydrofuran)iron(II) (815 mg, 1.82 mmol) at RT and stirred overnight to yield a dark brown solution. This was filtered through a plug of Celite, MeCN was removed, and the resulting solid was washed with pentane (3 × 30 mL), then with THF (80 mL), and finally dried *in vacuo* to afford a pale brownish-green powder (490 mg, 60% yield based on ligand). X-ray quality crystals were grown by slow diffusion of Et₂O into a MeCN solution of the compound at RT.

Evans (CD₃CN, 293 K toluene capillary, concentration approximately 0.028 g/mL, 400 MHz for ¹H, 125 MHz for ¹³C): average value 6.28 μ_B . M/S: 604.9 (+ve CI, LigandFeI₂), 477.1 (+ve EI, LigandFeI), 322.2 (+ve NSI, Ligand₂Fe²⁺). Representative elemental analysis: found: C = 47.71, H = 4.84, N = 12.32 (for pure 7 C₃₆H₄₄FeI₂N₈ calculated: C = 48.13, H = 4.94, N = 12.47).

B. A J. Young's NMR tube was charged with *o*-phenylene(N-ⁱPrimidazoline) diiodide (24.6 mg, 0.045 mmol), bis(trimethylsilylamido)-(tetrahydrofuran)iron(II) (20 mg, 0.045 mmol), and THF (0.6 mL), and the contents were mixed for 4 days, at which point THF was removed and MeCN added. The ¹H NMR spectrum was analogous to that observed for the product from method **A**.

Compound 8. A Schlenk flask was charged with *o*-phenylene-(N-ⁱPr-imidazoline) diiodide (200 mg, 0.37 mmol), FeCl₂ (23 mg, 0.18 mmol), and 10 mL of THF and cooled to -78 °C. A THF solution of LiN(SiMe₃)₂ (122 mg, 0.72 mmol dissolved in 10 mL of THF) was added dropwise over 10 min. The resultant yellow solution was stirred at -78 °C for 2 h and warmed to 0 °C over 30 min with a gradual color change to red. Warming to 20 °C and stirring overnight resulted in a further color change to yellow. Filtration and slow diffusion of pentane yielded a significant quantity of yellow-brown powder and a limited number of small crystals, which on analysis by X-ray diffraction were the migration product **8**.

Compound 9. THF (15 mL) was added at -78 °C to a mixture of *o*-phenylenebis(*N*-ⁱPr-imidazolium) diiodide (55 mg, 0.1 mmol) and potassium hydride (8 mg, 0.2 mmol, analogous reactivity is observed using LiN(SiMe₃)₂), and the reaction mixture was allowed to slowly warm up to RT overnight with stirring to yield an orange-yellow solution. Filtration followed by solvent removal afforded an oily yellow residue (this could be crystallized by slow evaporation of a DCM/hexane

(1:5) solution to give yellow needles, unsuitable for single-crystal XRD due to their small size).

¹H NMR (400 MHz, C₆D₆, 293 K, assignments by 2D spectroscopy) δ: 7.24 (1H, d, ³*J*_{HH} = 1.6 Hz, imidazole C–H), 7.00 (1H, d, ³*J*_{HH} = 1.6 Hz imidazole), 6.90 (1H, m, phenylene C–H), 6.83 (1H, dd, ³*J*_{HH} = 8.4 Hz ¹*J*_{HH} = 1.6 Hz, phenylene C–H), 6.74 (1H, dd, ³*J*_{HH} = 8.0 Hz ¹*J*_{HH} = 1.6 Hz, phenylene C–H), 6.58 (1H, m, phenylene C–H), 5.96 (1H, d, ³*J*_{HH} = 2.8 Hz) 5.57 (1H, d, ³*J*_{HH} = 2.8 Hz), 4.73 (1H, pseudoseptet, ³*J*_{HH} = 6.4 Hz, NC_{iPr}–H), 2.31 (1H, pseudoseptet, ³*J*_{HH} = 7.2 Hz, CC_{iPr}H), 1.14 (3H, d, ³*J*_{HH} = 6.4 Hz, NCHCH₃) 1.05 (3H, d, ³*J*_{HH} = 7.2 Hz, CCHCH₃) 0.83 (3H, d, ³*J*_{HH} = 7.2 Hz, CCHCH₃) and 0.66 (3H, d, ³*J*_{HH} = 6.4 Hz, NCHCH₃) -8.9 (4H). ¹³C{¹H} NMR (128 MHz, C₆D₆, 293 K) δ: 140.4, 135.3, 130.6, 127.0, 122.4, 118.9, 116.2, 115.8, 115.7, 112.7, 112.2, 83.4, 47.7, 42.0, 22.4, 21.1, 16.7, 16.3. M/S (+ve ES): 301 (9 + Li⁺), 287 (9 – Me⁻ + H⁺ Li⁺).

[Methylenebis(*N*-Dipp-imidazole-2-ylidene)]dicarbonyldiiodoiron(II), 10. A J. Young's NMR tube was charged with [methylenebis-(*N*-Dipp-imidazole-2-ylidene)]diiodoiron(II) (20 mg, 0.026 mmol) and THF (0.6 mL). The resulting yellow-greenish solution was degassed by three freeze—pump—thaw cycles, and the contents were exposed to 1 atm of CO gas. Rotating the reaction mixture in the NMR tube overnight under 1 atm of CO resulted in formation of a brown-violet solution, at which point the contents were degassed and put under a dinitrogen atmosphere.

¹H NMR (300 MHz, THF+(CD₃)₂SO capillary, 293 K) δ: 8.09–6.83 (overlapping multiplets, 12H, $2 \times C_6H_3 + 2 \times NCHCHN + NCH_2N$), 2.72 (app. s, 2H, $CH(CH_3)_2$), 1.23 (app. s, 6H, $2 \times CH(CH_3)(CH_3)$), 1.14 (app. s, 6H, $2 \times CH(CH_3)(CH_3)$) (major diamagnetic components, these resonances could be assigned to [methylenebis(*N*-Dipp-imidazole-2ylidene)]dicarbonyldiiodoiron(II)); -6.8 (v br, 2H), -8.7 (v br, 2H) (unidentified minor paramagnetic compound). IR (THF solution against background of dry THF saturated with N₂, cm⁻¹): 2024, 1974.

Reaction of Compound 7 with Methylenebis(*N*-Dippimidazole-2-ylidene). A J. Young's NMR tube was charged with a mixture containing 7 and $(({}^{iPr}C)_2Ph)FeI_2$ (20 mg, 0.022 mmol), methylenebis(*N*-Dipp-imidazole-2-ylidene) (10.5 mg, 0.022 mmol), and THF (0.6 mL). Rotating the reaction mixture in the NMR tube for 2 days resulted in the formation of a brown suspension. The precipitate was allowed to settle, and the yellow-brown solution was carefully decanted into another J. Young's NMR tube and was subject to ¹H NMR analysis, which revealed [methylenebis(*N*-Dipp-imidazole-2ylidene)]diiodoiron(II) as the only product.

[Methylenebis(*N*-Dipp-imidazole-2-ylidene)](thiomethoxido)iodoiron(II), 11. THF (40 mL) was added at RT to a mixture of [methylenebis(*N*-Dipp-imidazole-2-ylidene)]diiodoiron(II) (250 mg, 0.32 mmol) and sodium thiomethoxide (22.4 mg, 0.32 mmol), and the reaction mixture stirred overnight. THF was removed *in vacuo* from the resulting dark yellow solution, and the solid residue washed with toluene (70 mL) to give a yellow-brown powder (150 mg). This was dissolved in THF (20 mL) followed by addition of Et_2O (10 mL) with mixing. On standing overnight, the precipitate that formed was filtered and discarded. The remaining dark yellow solution was dried *in vacuo* to afford a yellow-brown powder (70 mg, 31%).

¹H NMR (400 MHz, THF+(CD₃)₂SO capillary, 293 K) δ : 60.5, 47.0, 6.9, -3.5, -6.7, -10.8, -12.9, -20.4, -31.4. Evans (d_8 -THF, toluene capillary, concentration approximately 0.017 g/mL, 300 MHz for ¹H): averaged value 4.27 μ_B . Anal. Calcd for C₃₂H₄₃FeI₁N₄S₁: C = 55.02, H = 6.20, N = 8.02. Found: C = 54.85, H = 6.08, N = 7.89.

Compound 5 + 2 equiv of NaSMe. THF (50 mL) was added at RT to a mixture of [methylenebis(*N*-Dipp-imidazole-2-ylidene)]diiodoiron(II) (250 mg, 0.32 mmol) and sodium thiomethoxide (45 mg, 0.64 mmol), and the reaction mixture stirred overnight. THF was removed from the yellow suspension, the resulting bright yellow solid was washed with toluene (2×50 mL) followed by THF (25 mL), and the solid was then dried *in vacuo* to give a yellow powder (100 mg, 81% based on Fe assuming the solid is [methylenebis(N-Dipp-imidazole-2-ylidene)]bis-(μ_2 -thiomethoxido)bis(thiomethoxido)diiron(II)).

Crystallization could be achieved by slow diffusion of pentane into a THF solution (unsuitable for single-crystal XRD due to very poor diffraction properties); redissolving this crystalline material resulted in an identical NMR spectrum to the yellow powder.

¹H NMR (300 MHz, THF+(CD₃)₂SO capillary, 293 K) δ : 65.8, 40.0, 37.0, 35.3, 34.0, 0.0, -1.4, -3.4, -9.1 (v br). Anal. Calcd for C₃₅H₅₂-Fe₂N₄S₄: C = 54.68, H = 6.82, N = 7.29. Found: C = 54.83, H = 6.69, N = 7.48.

ASSOCIATED CONTENT

Supporting Information. Full experimental and crystallographic details are available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) Plietker, B. Iron Catalysis in Organic Chemistry; Wiley-VCH: Weinheim, 2008.

(2) Junge, K.; Schroder, K.; Beller, M. Chem. Commun. 2011, 47, 4849.

(3) Sun, C.-L.; Li, B.-J.; Shi, Z. J. Chem. Rev 2011, 111, 1293.

(4) Diez-Gonzalez, S.; Marion, N.; Nolan, S. P. Chem. Rev. 2009, 109, 3612.

(5) Corberan, R.; Mas-Marza, E.; Peris, E. Eur. J. Inorg. Chem. 2009, 1700.

(6) Herrmann, W. A. Angew. Chem., Int. Ed. 2002, 41, 1290.

(7) Hu, X.; Tang, Y.; Gantzel, P.; Meyer, K. Organometallics 2003, 22, 612.

(8) Xiang, L.; Xiao, J.; Deng, K. Organometallics 2011, 30, 2018.

(9) Bedford, R. B.; Betham, M.; Bruce, D. W.; Danopoulos, A. A.; Frost, R. M.; Hird, M. J. Org. Chem. **2006**, 71, 1104.

(10) Gao, H.; Y, C.; Tao, X.-P.; Xia, Y.; Sun, H.-M.; Shen, Q.; Zhang,
 Y. Organometallics 2010, 29, 4189.

(11) Hatakeyama, T.; Hashimoto, S.; Ishizuka, K.; Nakamura, M. J. Am. Chem. Soc. **2009**, 131, 11949.

(12) Hatanaka, T.; Ohki, Y.; Tatsumi, K. *Chem. Asian J.* 2010, *S*, 1657.
(13) Kandepi, V. V. K. M.; Cardoso, J. M. S.; Peris, E.; Royo, B.

Organometallics **2010**, 29, 2777.

(14) Louie, J.; Grubbs, R. H. Chem. Commun. 2000, 1479.

(15) Chen, M.-Z.; Sun, H.-M.; Li, W.-F.; Wang, Z.-G.; Shen, Q.; Zheng, Y. J. Organomet. Chem. 2006, 691, 2489.

(16) Danopoulos, A. A.; Pugh, D.; Smith, H.; Sassmannshausen, J. *Chem.—Eur. J.* **2009**, *15*, 5491.

- (17) Lavallo, V.; Grubbs, R. H. Science 2009, 326, 559.
- (18) Lavallo, V.; El-Batta, A.; Bertrand, G.; Grubbs, R. H. Angew. Chem., Int. Ed. 2011, 50, 268.
- (19) Kreisel, K. A.; Yap, G. P. A.; Theopold, K. H. Organometallics **2006**, *25*, 4670.
- (20) Kreisel, K. A.; Yap, G. P. A.; Theopold, K. H. *Chem. Commun.* 2007, 1510.
- (21) Douthwaite, R. E.; Haussinger, D.; Green, M. L. H.; Silcock,
- P. J.; Gomes, P. T.; Martins, A. M.; Danopoulos, A. A. Organometallics 1999, 18, 4584.
- (22) Crudden, C. M.; Allen, D. P. *Coord. Chem. Rev.* 2004, 248, 2247.
 (23) Vogel, C. S.; Heinemann, F. W.; Khusniyarov, M. M.; Meyer, K. *Inorg. Chim. Acta* 2010, 364, 226.
- (24) Vogel, C.; Heinemann, F. W.; Sutter, J.; Anthon, C.; Meyer, K. Angew. Chem., Int. Ed. 2008, 47, 2681.
- (25) Scepaniak, J. J.; Vogel, C. S.; Khusniyarov, M. M.; Heinemann, F. W.; Meyer, K.; Smith, J. M. *Science* **2011**, *331*, 1049.
- (26) Scepaniak, J. J.; Young, J. A.; Bontchev, R. P.; Smith, J. N. Angew. Chem., Int. Ed. 2009, 48, 3158.
- (27) Nieto, I.; Ding, F.; Bontchev, R. P.; Wang, H.; Smith, J. M. J. Am. Chem. Soc. 2008, 130, 2716.
- (28) Hatakeyama, T.; Hashimoto, T.; Kondo, Y.; Fujiwara, Y.; Seike, H.; Takaya, H.; Tamada, Y.; Ono, T.; Nakamura, M. *J. Am. Chem. Soc.* **2010**, *132*, 10674.
- (29) Poyatos, M.; Mata, J. A.; Peris, E. *Chem. Rev* 2009, 109, 3677.
 (30) Leung, C. H.; Incarvito, C. D.; Crabtree, R. H. *Organometallics* 2006, 25, 6099.
- (31) Liu, J.; Chen, J.; Zhao, J.; Zhao, Y.; Li, L.; Zhang, H. Synthesis 2003, 17, 2661.
- (32) Venkatachalam, G.; Heckenroth, M.; Neels, A.; Albrecht, M. Helv. Chim. Acta 2009, 92, 1034.
- (33) Zhang, S.; Yang, S.; Lan, J.; Yang, S.; You, J. Chem. Commun. 2008, 6170.
- (34) Danopoulos, A. A.; Tsoureas, N.; Wright, J. A.; Light, M. E. Organometallics 2004, 23, 166.
- (35) Morvan, D.; Capon, J.-F.; Gloaguen, F.; Le-Goff, A.; Marchivie, M.; Michaud, F.; Schollhammer, P.; Talarmin, J.; Yaouanc, J.-J. *Organo-metallics* **2007**, *26*, 2042.
 - (36) See Supporting Information.
- (37) Mata, J. A.; Poyatos, M.; Peris, E. Coord. Chem. Rev. 2007, 251, 841.
- (38) Hawrelak, E. J.; Bernskoetter, W. H.; Lobkovsky, E.; Yee, G. T.; Bill, E.; Chirik, P. J. *Inorg. Chem.* **2005**, *44*, 3103.
- (39) Barclay, J. E.; Leigh, G. J.; Houlton, A.; Silver, J. J. Chem. Soc., Dalton Trans. 1988, 2865.
- (40) Albrecht, M.; Crabtree, R. H.; Mata, J.; Peris, E. *Chem. Commun.* 2002, 32.
- (41) Canac, Y.; Lepetit, C.; Abdalilah, M.; Duhayon, C.; Chauvin, R. J. Am. Chem. Soc. **2008**, 130, 8406.
- (42) Liu, B.; Xia, Q.; Chen, W. Angew. Chem., Int. Ed. 2009, 48, 5513.
- (43) Barclay, J. E.; Hills, A.; Hughes, D. L.; Leigh, G. J. J. Chem. Soc., Dalton Trans. 1988, 2871.
- (44) Muller, G.; Sales, J.; Vinaixa, J.; Tejada, J. Inorg. Chim. Acta 1982, 60, 227.
- (45) Heckenroth, M.; Neels, A.; Stoeckli-Evans, H.; Albrecht, M. Inorg. Chim. Acta 2006, 359, 1929.
 - (46) Athey, P. S.; Kiefer, G. E. J. Org. Chem. 2002, 67, 4081.
- (47) Ostermeier, M.; Limberg, C.; Ziemer, B.; Karunkaran, V. Angew. Chem., Int. Ed. 2007, 46, 5329.
- (48) Heckenroth, M.; Neels, A.; Garnier, M. G.; Aebi, P.; Ehlers, A. W.; Albrecht, M. *Chem.—Eur. J.* **2009**, *15*, 9375.
- (49) Alder, R. W.; Blake, M. E.; Chaker, L.; Harvey, J. N.; Paolini, F.; Schutz, J. Angew. Chem., Int. Ed. **2004**, 43, 5896.
 - (50) Chamizo, J. A.; Lappert, M. F. J. Org. Chem. 1989, 54, 4684.
- (51) Taton, T. A.; Chen, P. Angew. Chem., Int. Ed. Engl. 1996, 35, 1011.

- (52) Wells, K. D.; Ferguson, M. J.; McDonald, R.; Cowie, M. Organometallics 2008, 27, 691.
- (53) Mercs, L.; Labat, G.; Neels, A.; Ehlers, A.; Albrecht, M. Organometallics 2006, 25, 5648.
- (54) Li, B.; Liu, T.; Popescu, C. V.; Bilko, A.; Darensbourg, M. Y. Inorg. Chem. **2009**, 48, 11283.
- (55) Breuer, J.; Fruhauf, H.-W.; Smeets, W. J. J.; Spek, A. L. Inorg. Chim. Acta **1999**, 291, 438.
- (56) Zhang, Z.-Z.; Zhang, J.-K.; Zhang, W.-D.; Xi, H.-P.; Cheng, H.; Wang, H.-G. J. Organomet. Chem. **1996**, *515*, 1.
- (57) Pohl, S.; Opitz, U.; Haase, D.; Saak, W. Z. Anorg. Allg. Chem. 1995, 621, 1140.
 - (58) Evans, D. F. J. Chem. Soc. 1959, 2003.
 - (59) Sur, S. K. J. Magn. Reson. 1989, 82, 169.
- (60) Perry, M. C.; Cui, X.; Powell, M. T.; Hou, D.-R.; Reibenspies, J. H.; Burgess, K. J. Am. Chem. Soc. 2003, 125, 113.
- (61) Layfield, R. A.; McDouall, J. J. W.; Scheer, M.; Schwarzmaier,
 C.; Tuna, F. Chem. Commun. DOI: 10.1039/C1CC14576B.