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Communication

Bimetallic Reactivity Enabled by Ligand Flexibility in (β-Dialdiminato)iron Complexes

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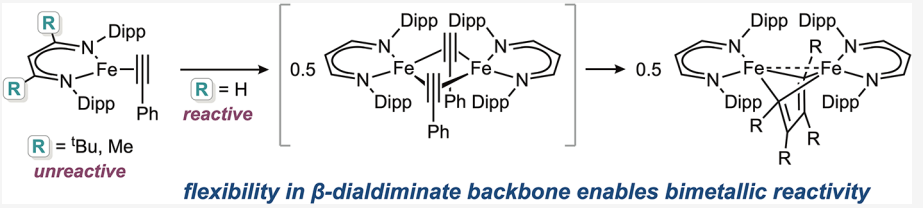


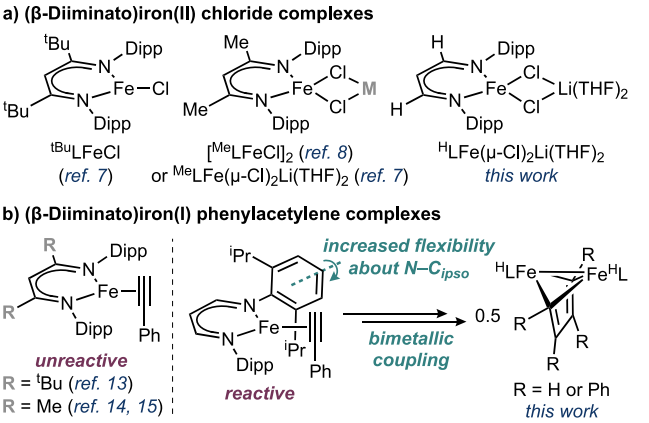
ABSTRACT: A group of iron complexes supported by a 2,6-diisopropylphenyl-substituted β-dialdiminate ligand have been prepared and characterized. The iron(II) chloride complex forms as the lithium chloride adduct that can be compared directly to its methyl-substituted β-diketiminate analog, revealing a more open iron center in the β-dialdiminate complex with a remarkable degree of rotation about the 2,6-diisopropylphenyl substituent. Exchange of chloride with phenylacetylide ligands generates a related four-coordinate organometallic complex. Interestingly, the iron(I) phenylacetylene complex is unstable in solution, undergoing bimetallic coupling to generate an isomeric mixture of bimetallacyclic complexes. We propose that this process stems from increased flexibility in the β-dialdiminate ligand backbone and highlights the exciting opportunities that are presented by this system.

Ancillary ligands are some of the most influential handles available for controlling behavior in a transition metal complex. Relatively small changes within the supporting scaffold can have large consequences on the steric and electronic environments at the metal center, which in turn can lead to significant effects on reactivity. As a result, ancillary ligand modification has become an indispensable tool in the development and optimization of reactions involving transition metals.

Our group is interested in the reactivity of (β-diiminato)iron complexes[1,2] and their application to iron-catalyzed synthetic transformations.[3,4] Prior work by the Holland group showed that the ostensibly remote iminyl substituent within the β-diketiminate backbone can have substantial effects on reaction outcome.[5,6] For example, the iron(II) chloride compound exists as a three-coordinate monomer in the *tert*-butyl-substituted system (Scheme 1a, ^{tBu}L = 3,5-bis(2,6-diisopropylphenylimino)-2,2,6,6-tetramethylheptyl)[7] but presents as a four-coordinate dimer[8] or lithium chloride adduct[7] when the backbone substituent is a methyl group (Scheme 1a, ^{Me}L = 2,4-bis(2,6-diisopropylphenylimino)pentyl). We were curious to explore the corresponding β-dialdiminate system (Scheme 1a, ^{H}L = 1,3-bis(2,6-diisopropylphenylimino)propyl) and its impact on the coordination environment and reactivity.

Previous studies of (β-dialdiminato)iron complexes demonstrated their application in the formation of a bimetallic compound containing an unsupported Fe−Fe bond[9] as well as the activation of white phosphorus (P_4).[10−12] In the latter case, reaction of the iron(I) species ^{H}LFe(PhMe) with P_4 leads to a dinuclear compound in which the two iron centers are bridged by diphosphorus ligands.[10] Further evaluation found that a

Scheme 1. Differences in Iron (a) Chloride and (b) Phenylacetylene Complexes Supported by β-Diiminate Ligands



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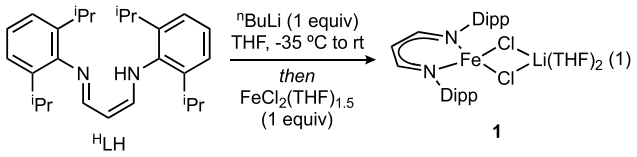
related but distinct bimetallic complex forms with the methyl-substituted system.[11]

Herein we report our study of iron complexes supported by a 2,6-diisopropylphenyl-substituted β-dialdiminate ligand (^{H}L, Scheme 1). We demonstrate that the four-coordinate iron(II) chloride lithium chloride adduct (Scheme 1a) exhibits remarkable flexibility in the ligand backbone (*vide infra*). We also show that the (β-dialdiminato)iron(I) phenylacetylene complex undergoes bimetallic coupling, in contrast to the stability of *tert*-butyl-substituted[13] and methyl-substituted[14,15] β-diketiminate analogs (Scheme 1b).[16]

Characterization of a β-Dialdiminate-Supported Iron Chloride Complex. Equation 1 details a two-step, one-pot protocol that



provides a direct route to the (β-dialdiminato)iron(II) chloride complex from the protonated ligand (^{H}LH). Reaction of *n*-butyllithium and ^{H}LH in tetrahydrofuran (THF) at −35 °C followed by warming to room temperature and addition of $FeCl_2(THF)_2$ led to the formation of a new paramagnetic product by ^{1}H NMR spectroscopy. The eight signals observed in the ^{1}H NMR spectrum (in addition to one signal not located) point to C_{2v} symmetry for this compound in solution. Magnetic susceptibility data signal an $S = 2$ ground state for this complex ($\mu_{eff} = 4.9(6)\mu_B$, Evans, 25 °C), consistent with a high-spin iron(II) center.

Analysis by X-ray diffraction allowed for the identification of the product of the reaction in eq 1 as the lithium chloride adduct HLFe(μ-Cl)$_2$Li(THF)$_2$ (**1**) (Figure 1). The geometry

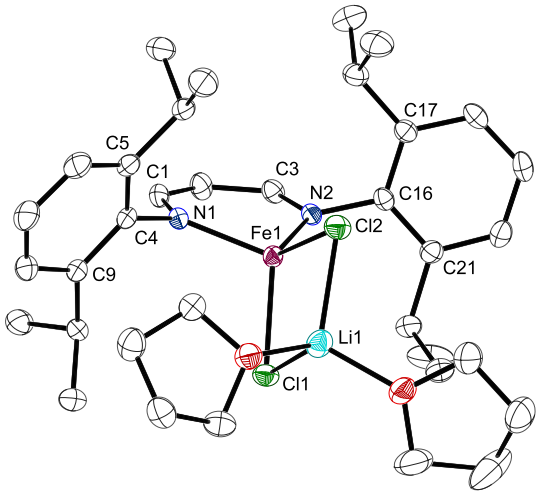


Figure 1. Molecular structure of **1** with ellipsoids drawn at the 50% probability level. Hydrogen atoms, disorder, and a solvent molecule have been omitted for clarity. Selected bond distances (Å), bond angles (deg), and torsion angles (deg) for **1**: Fe1−Cl1, 2.3394(4); Fe1−Cl2, 2.3307(3); Fe1−N1, 2.0094(10); Fe1−N2, 2.0024(10); Cl1−Fe1−Cl2, 97.935(12); N1−Fe1−N2, 91.84(4); N1−Fe1−Cl1, 109.80(3); N1−Fe1−Cl2, 123.62(3); N2−Fe1−Cl1, 124.02(3); N2−Fe1−Cl2, 111.98(3); C1−N1−C4, 116.28(9); C3−N2−C16, 115.38(9); C1−N1−C4−C5, −102.40(13); C1−N1−C4−C9, 79.16(14); C3−N2−C16−C17, −108.00(12); C3−N2−C16−C21, 73.66(13).

about the iron center in **1** can be described as pseudotetrahedral, with unequal N−Fe−Cl angles leading to an apparent twisting of the planes formed by N1, Fe1, and N2 and Cl1, Fe1, and Cl2 away from an expected perpendicular relationship by 10.7°. A general rotation of the ligand framework in the same direction completes the overall distortion observed about the metal center in **1**.

The effect of the relatively remote substituent in the backbone of the β-diiminate ligand on the overall molecular geometry can be explicitly observed through comparison of complex **1** to its methyl-substituted analog ^{Me}LFe(μ-Cl)$_2$Li(THF)$_2$ reported by the Holland group.[7] Figure 2 depicts an

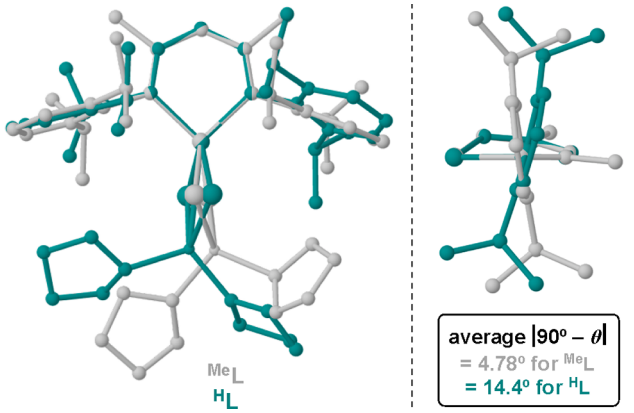


Figure 2. (left) Overlay of the molecular structures of ^{H}LFe(μ-Cl)$_2$Li(THF)$_2$ (**1**) and ^{Me}LFe(μ-Cl)$_2$Li(THF)$_2$.[7] (right) Side view focusing on the difference in rotation about the N−C$_{ipso}$ bond (θ = C$_{iminyl}$−N−C$_{ipso}$−C$_{ortho}$ torsion angle).

overlay of the molecular structures (left) with a focus on the view along the bond between the nitrogen and the ipso carbon of the aryl group (N−C$_{ipso}$, right). The influence of *tert*-butyl versus methyl substitution in (β-diketiminato)iron complexes has been described in terms of the angle between the iminyl carbon, nitrogen, and ipso carbon (C$_{iminyl}$−N−C$_{ipso}$),[17] and indeed, the iron center in complex **1** is more open by this measure, with an average C$_{iminyl}$−N−C$_{ipso}$ angle of 115.8° compared to 119.5° for the methyl analog. Perhaps more striking is the difference in rotation about the N−C$_{ipso}$ bond in these complexes. The steric constraints of the 2,6-diisopropylphenyl substituent often manifest as a nearly perpendicular relationship between the aryl group and the plane of the ligand backbone in (β-diketiminato)iron complexes. This is true for ^{Me}LFe(μ-Cl)$_2$Li(THF)$_2$, where the average deviation of the torsion angle among the iminyl carbon, nitrogen, ipso carbon, and ortho carbon (C$_{iminyl}$−N−C$_{ipso}$−C$_{ortho}$) from perpendicularity is only 4.78° (Figure 2, right). Remarkably, an almost 10° increase in rotation about the N−C$_{ipso}$ bond to 14.4° is observed for **1**, emphasizing the degree of flexibility exhibited by the β-dialdiminate system.

Ligand Exchange with Lithium Phenylacetylide. We explored the formation of an organometallic (β-dialdiminato)iron complex by evaluating the exchange reactivity of **1** with lithium phenylacetylide (LiCCPh). Crystallization from saturated pentane solution after the reaction of an equimolar solution of **1** and LiCCPh resulted in low yield of a new paramagnetic compound, as observed by ^{1}H NMR spectroscopy. The same complex is generated in higher yields when ≥2 equiv of the organolithium reagent is added to **1** (eq 2).

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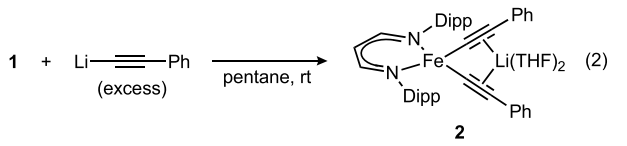


Molecular structure determination through X-ray crystallography identified the product of the reaction in eq 2 as the "ate" complex ^{H}LFe(μ-CCPh)$_2$Li(THF)$_2$ (**2**) (Figure 3),[18,19]

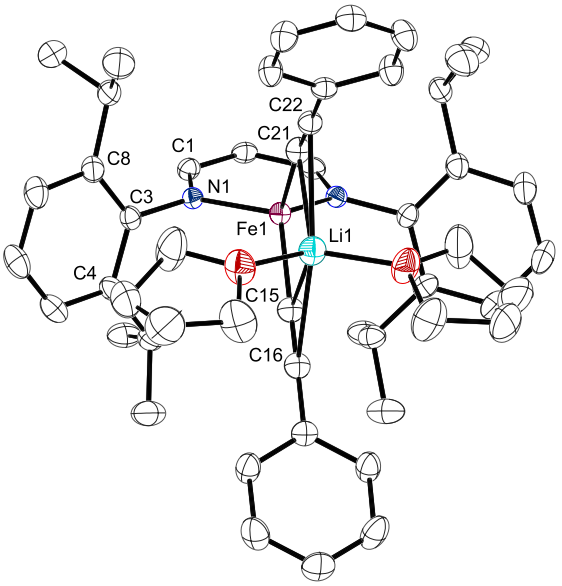


Figure 3. Molecular structure of **2** with ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å), bond angles (deg), and torsion angles (deg) for **2**: Fe1−C15, 2.054(4); Fe1−C21, 2.058(3); Fe1−N1, 2.013(2); C15−C16, 1.217(5); C21−C22, 1.214(5); C15−Fe1−C21, 101.67(18); N1−Fe1−N1′, 90.45(11); N1−Fe1−C15, 117.32(9); N1−Fe1−C21, 115.49(11); Fe1−C15−C16, 169.4(3); Fe1−C21−C22, 177.9(5); C1−N1−C3−C4, 83.0(3); C1−N1−C3−C8, −100.6(3).

consistent with the optimized reaction conditions. In contrast to **1**, the planes formed by N1, Fe1, and N1′ and C15, Fe1, and C21 exist in a perpendicular relationship in **2**, coinciding with a relatively smaller degree of rotation about the N−C$_{ipso}$ bond (average $|90° - \theta| = 8.80°$).

Bimetallic Cyclization of an Iron(I) Phenylacetylene Complex. We aimed to prepare a more reduced (β-dialdiminato)iron species by adding 1 equiv of phenylacetylene to the formally iron(I) compound ^{H}LFe(PhMe)[10] (Scheme 2). This reaction immediately generates a paramagnetic species that can be identified as ^{H}LFe(HCCPh) (**3**) (Scheme 2) by ^{1}H NMR spectroscopy through comparison to the analogous β-diketiminate complexes.[13,14] Compound **3** is unstable in solution and begins converting almost immediately to an isomeric mixture of three lower-symmetry compounds, two major and one minor, with complete conversion occurring after 24 h at room temperature. Filtration and concentration of the analogous reaction in pentane solvent allowed for isolation of single crystals suitable for analysis by X-ray diffraction from a saturated mixture at −35 °C in the second crop. Determination of the molecular structure revealed bimetallic complex **5a** (Scheme 2) in which both phenyl substituents occupy β-positions with respect to the metal center (Figure 4).

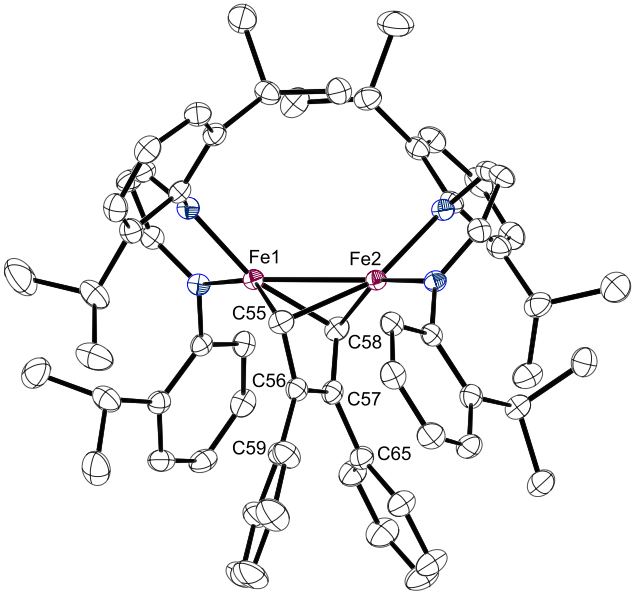
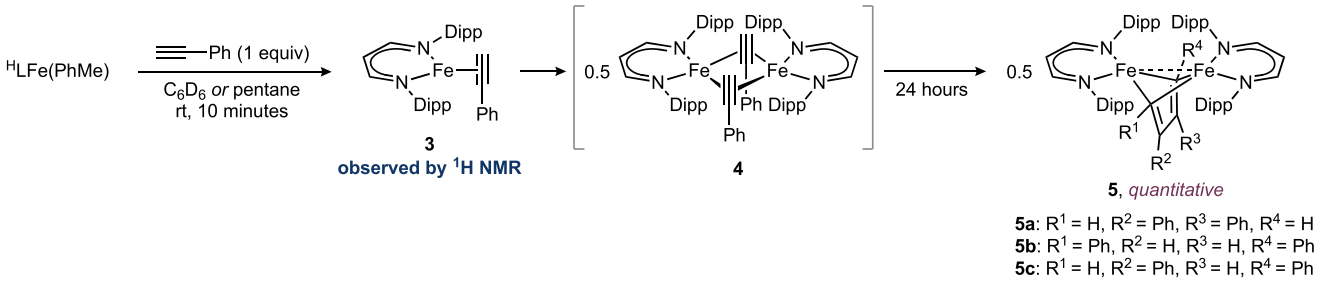


Figure 4. Molecular structure of **5a** with ellipsoids drawn at the 50% probability level. Hydrogen atoms, a solvent molecule, and two ligand isopropyl groups have been omitted for clarity. Selected bond distances (Å) and angles (deg) for **5a**: Fe1−Fe2, 2.5425(3); Fe1−C55, 1.9622(14); Fe1−C58, 1.9896(14); Fe2−C55, 2.1146(14); Fe2−C58, 2.0761(14); C55−C56, 1.393(2); C56−C57, 1.4869(19); C57−C58, 1.389(2); Fe1−C55−Fe2, 77.07(5); Fe1−C58−Fe2, 77.38(5); C55−Fe1−C58, 84.11(6); C55−Fe2−C58, 78.34(6); C55−C56−C57, 114.30(12); C56−C57−C58, 114.76(12); C55−C56−C59, 123.93(13); C58−C57−C65, 122.18(13).

A fortuitous crop of X-ray-quality crystals from a separate reaction were identified as the isomeric complex **5b** (Scheme 2) in which the phenyl groups are located in α-positions (Figure 5). We suspect that the asymmetric bimetallic coupling

Scheme 2. Formation of Bimetallacycles 5



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product **5c** (Scheme 2) represents the third component of the isomeric mixture that is observed by ^{1}H NMR spectroscopy.[20]

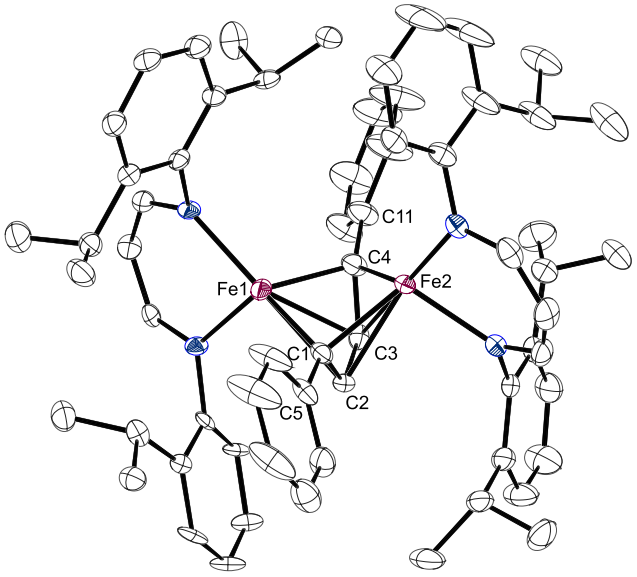

Figure 5. Molecular structure of **5b** with ellipsoids drawn at the 50% probability level. Hydrogen atoms, disorder, a solvent molecule, and two ligand isopropyl groups have been omitted for clarity. Selected bond distances (Å) and angles (deg) for **5b**: Fe1−C1, 2.029(3); Fe1−C4, 2.087(3); Fe2−C1, 2.098(3); Fe2−C4, 2.087(3); C1−C2, 1.398(4); C2−C3, 1.441(4); C3−C4, 1.397(4); Fe1−C1−Fe2, 87.72(10); Fe1−C4−Fe2, 87.79(11); C1−Fe1−C2, 84.93(11); C1−Fe2−C2, 84.42(11); C1−C2−C3, 118.2(2); C2−C3−C4, 119.0(2); C2−C1−C5, 125.4(2); C3−C4−C11, 123.4(3).

The formation of complex **5a** can be explained by the cyclization of two acetylene units across two (β-dialdiminato)-iron(I) moieties. Accordingly, the relative C−C bond distances observed in the solid-state structure are as expected for a 1,3-dien-1,4-diyl group (C55−C56 = 1.393 Å, C56−C57 = 1.487 Å, and C57−C58 = 1.389 Å). The illustration of **5a** in Figure 4 incorporates an Fe−Fe bond based on an interatomic distance of 2.543 Å between Fe1 and Fe2, amounting to a formal shortness ratio of 1.09 with respect to the sum of single-bond covalent radii of 2.33 Å for two iron atoms.[21] Complex **5b** exhibits an overall shift of the iron centers toward the internal carbons of the dienyl unit (C2 and C3), likely due to steric crowding imposed by the α-phenyl substituents. This deviation coincides with generally larger Fe−C bond distances and Fe−C−Fe bond angles, one consequence of which is a significant increase in the interatomic distance between iron atoms (2.8601(6) Å). This separation is large enough that an Fe−Fe bond is not included in the depiction of **5b** in Figure 5. It is possible that this contrast between **5a** and **5b** is more influenced by the relative steric constraints associated with the phenyl substituents rather than actual bonding interactions (or lack thereof). The underlying electronic structures and contributions of metal−metal bonding in these two compounds are currently under investigation.

The formation of bimetallacycles **5** from iron(I) phenylacetylene complex **3** is remarkable given that the analogous *tert*-butyl-substituted[13] and methyl-substituted[14,15] β-diketiminate complexes are stable.[16] We propose that this process initiates through dimerization of **3** to generate complex **4** (Scheme 2). Indeed, a similar sequence of transformations has been observed for a bulky iron(I) amido complex.[22] We propose that formation of **5** is a direct result of the flexible nature of the β-dialdiminate ligand that allows for the interaction of two monomers **3** to form dimer **4**, followed by bimetallic coupling. These observations emphasize the opportunities for new reactivity that are presented by this intriguing system.

Conclusion. Several (β-dialdiminato)iron complexes have been synthesized and analyzed by a variety of characterization techniques, including X-ray crystallography. Observation of the molecular structures of the iron(II) chloride and phenylacetylide complexes revealed greater flexibility in the β-dialdiminate ligand backbone in terms of rotation about the aryl substituent compared to β-diketiminate analogs. The iron(I) phenylacetylene complex was found to react by a bimetallic coupling process that forms an isomeric mixture of bimetallacyclic compounds, presumably as a result of the flexible nature of the ligand backbone.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.3c00296.

Complete experimental procedures, characterization data, spectra, and crystallographic information for **1**, **2**, **5a**, and **5b** (PDF)

Accession Codes

CCDC 2267851, 2267852, 2267906, and 2267907 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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(19) It is possible that in solution complex **2** is in equilibrium with the three-coordinate neutral complex HLFeCCPh, analogous to the product observed for the reaction of tBuLFeCl and LiCCPh (ref 8).

(20) The ^{1}H NMR spectrum of the reaction in C_6D_6 solution after 24 h indicates the presence of two major isomeric compounds as well as one minor species. This minor component is present in only trace amounts by ^{1}H NMR spectroscopy for the same reaction run in pentane solvent. We know from isolation and characterization of complex **5a** that it represents one of the major isomers of the mixture and is the favored product in pentane solvent. The ^{1}H NMR spectrum of the other major isomer is consistent with the structure of **5b** but could also be **5c**.

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