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Combined Effects of Backbone and N-Substituents on Structure, Bonding, and Reactivity of Alkylated Iron(II)-NHCs

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Abstract

Iron and *N*-heterocyclic carbenes (NHCs) have proven to be a successful pair in catalysis, with reactivity and selectivity being highly dependent on the nature of the NHC ligand backbone saturation and *N*-substituents. Four (NHC)Fe(1,3-dioxan-2-ylethyl)₂ complexes have been isolated and spectroscopically characterized to correlate their reactivity to steric effects of the NHC from *both* the backbone saturation and *N*-substituents. Only in the extreme case of SIPr where NHC backbone and *N*-substituent steric effects are the largest is there a major structural perturbation observed crystallographically. The addition of only two hydrogen atoms is sufficient for a drastic change in product selectivity in the coupling of 1-iodo-3-phenylpropane with (2-(1,3-dioxan-2-yl)ethyl)magnesium bromide due to resulting structural perturbations to the precatalyst. Mössbauer spectroscopy and magnetic circular dichroism enabled the correlation of covalency and steric bulk in the SIPr case to its poor selectivity in alkyl–alkyl cross-coupling with iron. Density functional theory calculations provided insight into the electronic structure and molecular orbital effects of ligation changes to the iron center. Finally, charge donation analysis and Mayer bond order calculations further confirmed the stronger Fe–ligand bonding in the SIPr complex. Overall, these studies highlight the importance of considering both *N*-substituent and backbone steric contributions to structure, bonding, and reactivity in iron-NHCs.

Graphical Abstract

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Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00466.

Supplementary data including ⁵⁷Fe Mössbauer and NMR spectra, details of DFT calculations, and X-ray crystal structure data (PDF) Cartesian coordinates (XYZ)

Accession Codes

CCDC 1855763 and 1855764 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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INTRODUCTION

The ability to synthetically manipulate ligand additives for catalysis has enabled the development of a large selection of commercially available organometallic precatalysts and ligands for use in catalytic reactions. *N*-heterocyclic carbenes (NHCs) are a particularly popular class of ligand additives and have been used in a vast number of catalytic reactions as organocatalysts,^{1,2} and in tandem with transition metals^{3–9} and Group 13 elements.^{1,2,10} NHCs are available in the form of stable salts with a large number of different *N*-substituents, central ring size, and even central ring functionalization, making them very easy to access and work with.^{2,11} Furthermore, “smart NHCs” are under development which are redox-switchable, bifunctional, or hemilabile and have even been shown to exhibit backbone reactivity.¹² Due to their structural diversity, NHCs have been utilized in many catalytic transformations including hydro-silylation, olefin metathesis, C–H activation, and, of particular note, cross-coupling reactions.²

The value of the NHC functionality is seen in some of the earliest reports of NHC cross-coupling with precious metals. The first Kumada cross-coupling reaction using NHCs was developed by Nolan and co-workers and showed a dependence on the bulkier IPr in catalysis over IMes (Scheme 1, right) for the successful coupling of aryl iodides with aryl Grignard reagents using palladium, but no backbone variations were explored.¹³ Alternatively, Beller and co-workers reported the first aryl–alkyl cross-coupling reactions having success with IMes as a ligand additive instead of IPr in the presence of palladium.¹⁴ A simple *N*-substituent change allowed for the cross-coupling of two different sets of reagents.

Along with their popularity in precious metal catalysis, NHCs have been used in a multitude of iron catalyzed reactions.^{15,16} In cross-coupling, aryl–aryl,^{17–20} aryl–alkenyl,²¹ alkyl–aryl,^{22–30} aryl–alkyl,³¹ and alkyl–alkyl³² transformations have all been achieved using a variety of NHCs (Scheme 1). In a popular example, Nakamura and co-workers reported in 2007 the Kumada coupling of aryl Grignard reagents with aryl halides using iron, nickel, and cobalt fluorides.^{17,18} Here, SIPr is the most effective NHC for catalysis, outperforming IPr with 98% yield compared to only 25% cross-coupled product (Scheme 1). In this case, and in several other reactions using NHCs and iron, a change in backbone saturation drastically alters selectivity.^{27,31}

To better understand the selectivity of certain NHCs for different catalytic reactions, previous studies have explored the reactivity and electronic structure of independently

synthesized iron-NHC compounds. For example, Deng and co-workers have investigated aryl and alkyl iron-NHCs,^{33–37} and Tonzetich and co-workers have explored the electronic structure and bonding effects in (NHC)FeX_n and aryl containing species.^{38–40} More recently, the first direct observation of an *in situ* formed reactive iron-NHC complex was reported by the Neidig group.⁴¹ These studies, however, do not address the combined effects of NHC backbone structure and *N*-substitutions on electronic structure and bonding of reactive iron species in great detail.

In this study, IMes, SIMes, IPr, and SIPr (Scheme 1, right) were used for the independent synthesis of iron-alkyl compounds to create a complete set of variations in both backbone and *N*-substituents. The effects of these changes on reactivity, electronic structure, and bonding are identified using gas chromatography (GC), X-ray diffraction, ⁵⁷Fe Mössbauer spectroscopy, magnetic circular dichroism (MCD), and density functional theory (DFT) and show that iron-NHC reactivity can be influenced by steric effects deriving from both *N*-substituents and backbone saturation effects.

RESULTS AND DISCUSSION

Changes in Catalytic Activity Resulting from NHC Variations.

As described previously, catalytic reactions with iron have used different NHCs with varying levels of success depending on *N*-substituent steric effects or backbone saturation. Recently, reactivity differences due to changes in *N*-substituents were solidified in a study from the Neidig group.⁴¹ (IMes)Fe(1,3-dioxan-2-ylethyl)₂ (1^{IMes}) was identified as a reactive iron species with chelating dioxane moieties on the alkyl ligands in the coupling of (2-(1,3-dioxan-2-yl)ethyl)-magnesium bromide with 1-iodo-3-phenylpropane.⁴¹ In this alkyl–alkyl cross-coupling reaction originally reported by Cárdenas,³² bulkier NHCs like SIPr and even more sterically encumbering bisphosphine ligands resulted in low cross-coupled product yield (Scheme 1).³² Therefore, reactivity differences were yet again solely attributed to the change in NHC *N*-substituent. Preliminary results using alternative nucleophiles were also explored,⁴¹ but poor cross-coupled yields were observed for all reactions that did not contain a rigid, dioxane-type chelating moiety and are therefore not discussed in this NHC focused work.

Since initial alkyl–alkyl cross-coupling studies did not include detailed catalytic data for the use of a series of NHCs with varying *N*-substituents *and* backbone saturation under optimized reaction conditions, the catalytic performances of IPr, SIPr, IMes, and SIMes were evaluated using a modified procedure from Cárdenas and co-workers³² as reported previously;⁴¹ Table 1 highlights these results. The use of IMes as a ligand additive results in the highest amount of cross-coupled product at 78% yield. Consistent with original reports, SIMes produces almost identical results as the only perturbation to ligand structure is in the saturation of the backbone. When an *N*-substituent change is made in the case of SIPr, a severe drop in cross-coupled product yield to only 23% is observed. The change from mesityl to diisopropylphenyl causes a loss of chelation in one of the alkyl ligands on iron for the isolated precatalyst with SIPr compared to IMes.⁴¹ Since backbone saturation has almost no effect on the reactivity of the mesityl NHCs, IPr was expected to have similarly poor catalytic performance to SIPr when used in this alkyl–alkyl cross-coupling reaction.

However, the use of IPr results in the formation of 69% cross-coupled product, greatly outperforming SIPr, suggesting that the loss of reactivity seen with SIPr is more complex than a simple argument of added *N*-substituent steric bulk.

Structural Characterization of (NHC)Fe(1,3-dioxan-2-ylethyl)₂ Compounds.

The unexpected high selectivity observed for the IPr/SIPr couple inspired further characterization of the precatalysts formed during the reaction protocol to directly identify any structural changes caused by either backbone saturation or *N*-substituent variation. In the alkyl–alkyl cross-coupling of (2-(1,3-dioxan-2-yl)ethyl)magnesium bromide with 1-iodo-3-phenylpropane, (NHC)Fe(1,3-dioxan-2-ylethyl)₂ type species were found to form *in situ* during the precatalyst formation step of the reaction where excess Grignard reagent is added to iron and NHC·HCl in THF at 50–60 °C. The IMes derivative, 1^{IMes} (Figure 1A), was shown to have two hemilabile alkyl ligands from the Grignard reagent. Therefore, initial efforts focused on the isolation of SIMes and IPr derivatives.

To form (SIMes)Fe(1,3-dioxan-2-ylethyl)₂, complex 2^{SIMes}, 4 equiv of (2-(1,3-dioxan-2-yl)ethyl)magnesium bromide was added in one portion to 1 equiv each of Fe(OAc)₂ and SIMes·HCl at room temperature. Following cooling to –80 °C, yellow crystals suitable for X-ray diffraction were obtained. The structure of 2^{SIMes} (Figure 1B) is described as a distorted 5-coordinate iron complex ($\tau_5 = 0.43$) with two chelating oxygen moieties from the alkyl ligands, a similar geometry to that of 1^{IMes} ($\tau_5 = 0.52$).⁴² Oxygen interactions are at 2.5069(15) and 2.4553(14) Å to the iron center, slightly elongated in comparison with 1^{IMes}. Fe–C bonds to the alkyl ligands are 2.106(2) and 2.101(2) Å, and the Fe–SIMes bond is 2.124(2) Å in length, consistent with the bischelated compound 1^{IMes} (Table S1).

The IPr precatalyst was isolated in a similar way to complex 2^{SIMes}: 6 equiv of (2-(1,3-dioxan-2-yl)ethyl)magnesium bromide was added to 1 equiv each of Fe(OAc)₂ and IPr·HCl at room temperature. After cooling to –80 °C, yellow crystals suitable for X-ray diffraction were acquired. Consistent with its comparable reactivity to 1^{IMes} and 2^{SIMes}, 3^{IPr} (Figure 1C) is also described as a distorted 5-coordinate ($\tau_5 = 0.49$) iron complex with two chelating dioxane alkyl rings with oxygen interactions at 2.49068(13) and 2.44736(14) Å. Fe–C bond lengths to the alkyl groups are at 2.1125(19) and 2.11558(19) Å, and the Fe–IPr bond length is 2.1571(17) Å (Table S1). The stabilizing chelation of both alkyl groups through oxygen observed in 1^{IMes}, 2^{SIMes}, and 3^{IPr} reduces the opportunity for β -H elimination during catalysis and is consistent with their high selectivity.

This series of bisalkyl iron compounds is completed with the comparison to the structure of the SIPr derivative, complex 4^{SIPr} (Figure 1D). This precatalyst was found to have the structure (SIPr)Fe(1,3-dioxan-2-ylethyl)₂ with pseudo tetrahedral geometry ($\tau_4 = 0.82$) where only one alkyl group is chelated to iron through oxygen, attributed to the added steric bulk of the diisopropylphenyl groups as opposed to mesityl in 1^{IMes} and 2^{SIMes}. The Fe–NHC bond length is shortened to 2.0920 (10) Å, and the single chelated oxygen is at a distance of 2.3130(9) Å from the iron center. Loss of reactivity was initially assigned to the steric bulk of the *N*-substituents, but with the addition of complex 3^{IPr} to this series, it is clear that this is not the only origin of structural perturbations in alkyl iron complexes. So, in cross-coupling reactions where NHC backbone variation correlates to product selectivity

such as in the biaryl system developed by Nakamura, it is important to consider the electronic *and* steric effects of backbone variations.

Interestingly, although 3^IPr is also a bischelate through the two dioxane oxygen atoms, the steric bulk of the diisopropylphenyl groups appears to cause one of the dioxane rings to be severely canted relative to those of 1^IMes and 2^{SI}Mes. When the RMS (root-mean-square) plane of the dioxane rings relative to the plane normal to the Fe–NHC bond is considered, the tilt of the dioxane rings in these complexes can be quantified. These results are shown in Table 2.

The first “set” of chelated dioxane rings have similar orientations relative to the plane described above. In the case of 2^{SI}Mes and 4^{SI}Pr, which both have saturated NHC backbones, this angle is ~10° greater than in 1^IMes and 3^IPr (Table 2), indicating that the simple addition of two hydrogens to the NHC structure can be enough to modify substrate interaction with an iron center. In the case of the second “set” of chelated dioxane rings, the distortion in 3^IPr has a value of 74.1°, whereas 1^IMes shows an almost identical angle to that of the first chelated ring. Complex 2^{SI}Mes also shows a change in ring tilt from 39.7° to 11.3°, further confirming that backbone saturation can affect chelation to iron.

To address the varying degrees of alkyl bischelation in compounds 1^IMes to 4^{SI}Pr, the steric components of each iron compound were quantified as a function of NHC using SambVca 2.0.⁴³ While the Tolman cone angle is a useful method for quantifying steric properties in monodentate phosphine ligands, the percent buried volume (% V_{bur}) allows for the sterics of the NHC ligand that project toward the metal center to be quantified.⁵ Complex 4^{SI}Pr shows the highest % V_{bur} for the NHC ligand of 44.6%, while 3^IPr has a % V_{bur} of only 34.1%. When the steric maps⁴⁴ are considered (Figure 1E), 4^{SI}Pr clearly shows the distortion of an isopropylphenyl group at approximately 1.4 Å to the iron center which creates the increase in % V_{bur} . 3^IPr lacks this tilted isopropylphenyl ring and shows a maximum distance of approximately 2.2 Å from the iron center in its steric map. 1^IMes and 2^{SI}Mes show nearly identical results to 3^IPr with respect to maximum distance of the NHC substituents to the iron center and % V_{bur} .

The steric mapping and % V_{bur} for 4^{SI}Pr are consistent with its loss of alkyl chelation observed crystallographically and subsequent decrease in cross-coupled product selectivity when compared with 3^IPr. In fact, when the two NHC segments are directly superimposed, structural differences can be even more readily visualized (Figure 2A). Shown in red, the SIPr ligand clearly displays a “bent” side arm isopropyl group that would be closer to the metal center and potentially block a reactive site on iron. When 1^IMes and 2^{SI}Mes are overlaid in the same way, it is clear that the side arm groups are oriented in a much more planar way than in 4^{SI}Pr (Figure 2B) and are very similar to one another. These representations show the significance of both NHC backbone and *N*-substituent manipulations in the reactivity, characteristics, and stability of intermediates in iron catalysis.

Another ligand system employed in the alkyl–alkyl cross-coupling system discussed here is Xantphos (4,5-bis(diphenylphosphino)-9,9-dimethylxanthene). In this case, only 27% cross-

coupled product is observed, similar to the 23% yield with SIPr,³² making it clear that ligand bulk plays an important role in this alkyl–alkyl cross-coupling reaction. Since Xantphos is utilized in the two other alkyl–alkyl cross-couplings with iron reported by Nakamura⁴⁵ and Chai,⁴⁶ we wanted to confirm that steric hindrance around an iron center across ligand classes was cause enough for it to be less productive in the coupling of (2-(1,3-dioxan-2-yl)ethyl)magnesium bromide with 1-iodo-3-phenylpropane. When (Xantphos)FeCl₂⁴⁷ was treated with the same % V_{bur} calculation methods as the NHC-alkyl complexes reported here, a value of 54.6% was determined and the steric map indicates two major regions of Xantphos phenyls within 0.5 Å of the iron center (Figure S4). These ligand distances are even closer than those observed for 4^{SIPr}, and further demonstrate that ligand systems with sufficient steric bulk can prevent substrate chelation to iron and decrease selectivity in this alkyl–alkyl cross-coupling system.

Spectroscopic Characterization of (NHC)Fe(1,3-dioxan-2-ylethyl)₂ Compounds.

With the completion of the structural analysis of this series of iron-NHC complexes, Evans method, ⁵⁷Fe Mössbauer spectroscopy, and MCD experiments were used to investigate the effects of backbone saturation and variation in side *N*-substituents on the electronic structure of these molecules.

In the case of Evans method analysis of the isolated crystalline 2^{SIMes} in THF-*d*₈, the μ_{eff} value of 4.9(0.2) μ_{B} is consistent with an *S* = 2 iron(II) center like in 1^{IMes} and 4^{SIPr}.⁴¹ 5 K solid Mössbauer of isolated crystalline material further confirms the spin state of the iron center with δ = 0.54 mm/s and E_{Q} = 2.56 mm/s (Table 3, Figure S1). The Evans method of the isolated crystalline 3^{IPr} in THF-*d*₈ results in an artificially low μ_{eff} value of 4.4(2) μ_{B} from the expected 4.9 μ_{B} for *S* = 2 iron(II) due to the variable presence of cocrystallized magnesium salts. However, 5 K Mössbauer spectroscopy of isolated crystalline 3^{IPr} results in a single quadrupole doublet with parameters of δ = 0.58 mm/s and E_{Q} = 2.36 mm/s (Table 3, Figure S1), consistent with an *S* = 2 iron(II). This is further consistent with the Mössbauer parameters and high spin iron(II) states for 1^{IMes}, 2^{SIMes}, and 4^{SIPr} (Table 3). A slight decrease in isomer shift is observed in 4^{SIPr} which corresponds to the shorter bond lengths and variation in ligand environment observed crystallographically.

The 5 K, 7 T NIR MCD spectra of complexes 1^{IMes} through 4^{SIPr} complement the electronic structure insights observed in the Mössbauer data. In the case of the mesityl based NHC complexes, 1^{IMes} shows C-term MCD transitions at 5310 and 7600 cm^{−1} (Figure 3(1^{IMes}) and Table 3), and 2^{SIMes} at 5400 and 7630 cm^{−1} (Figure 3(2^{SIMes}), Table 3). The average ligand field energies of these compounds (6455 cm^{−1} and 6515 cm^{−1} for 1^{IMes} and 2^{SIMes}, respectively) are consistent with their longer Fe–C_{NHC} bond distances observed crystallographically and Mössbauer parameters when compared with 4^{SIPr} (7140 cm^{−1}). The MCD transitions for 1^{IMes} and 2^{SIMes} both show negative intensity at similar relative intensities. This indicates that the change in saturation from double to single bond on the NHC ring backbone has little effect on the electronic structure of the iron complex, consistent with a previous study by Tonzetich and co-workers where backbone manipulations to IMes were explored.³⁸ Only in the case of 4, where the combined steric

effects of the saturated backbone and isopropylphenyl groups prevent the chelation of two alkyl oxygens, is there a significant change in electronic structure and bonding at iron.

Complex 3^{IPr} displays two temperature-dependent, C-term, ligand field transitions at <5000 and 8060 cm^{-1} (Figure 3(3^{IPr}), Table 3). The SIPr derivative has ligand field transitions at 5800 and 8480 cm^{-1} (Figure 3(4^{SIPr}), Table 3). In the case of 4^{SIPr} , the C-term intensities produce pseudo A-terms created by two slightly overlapping C-terms of opposite intensity which is not observed for 3^{IPr} . The change in iron site geometry from pseudo 5-coordinate, 3^{IPr} , to pseudo 4-coordinate, 4^{SIPr} , would be expected to be a sufficient change to cause this shift in ligand field energy. In fact, the average ligand field energy is significantly larger for 4^{SIPr} than what can be approximated for 3^{IPr} (7140 and 6530 cm^{-1} , respectively). A larger ligand field energy corresponds with 4^{SIPr} having more covalent ligands. This is observed in the shorter bond lengths from Fe–C_{SIPr} and Fe–C_{alkyl}, and in the decreased value of Mössbauer parameters compared with the other three complexes studied here.

Electronic Structure and Bonding Analysis.

Spin unrestricted DFT calculations using the B3LYP functional and def2-TZVP basis set were carried out to further analyze the electronic structure and bonding in 2^{SIMes} and 3^{IPr} . Previously reported calculations for 1^{IMes} and 4^{SIPr} were repeated using the same updated basis set and functional for consistency in the series and more comparable calculated geometries to crystallographic data (see the Supporting Information). Molecular orbitals in the gas phase were also explored, focusing on the occupied and unoccupied frontier molecular orbitals (FMOs) of the β orbital manifold to determine major bonding contributions.

Figure 4 gives the calculated FMO energy diagrams for the β manifolds of (IMes)Fe(1,3-dioxan-2-ylethyl)₂ (1^{IMes}), (SIMes)-Fe(1,3-dioxan-2-ylethyl)₂ (2^{SIMes}), (IPr)Fe(1,3-dioxan-2-ylethyl)₂ (3^{IPr}), and (SIPr)Fe(1,3-dioxan-2-ylethyl)₂ (4^{SIPr}). All complexes share a similar FMO ordering and composition around the HOMO/LUMO gap. As a representative example, 3^{IPr} has a ground state consisting of one occupied FMO, $\beta 180$, with 94% Fe d orbital character (HOMO, d_{xy}). The LUMO shows significant π bonding with the NHC carbene C ($\beta 181$, d_{yz} , π carbene). In fact, 26% of the FMO composition is located at the carbene C. Fe d character is also observed in $\beta 187$ (LUMO +6, 74% d_{xz}), $\beta 188$ (LUMO+7, 67% d_{z^2}), $\beta 194$ (LUMO+13, 23% d_{yz}), and $\beta 199$ (LUMO+18, 55% $d_{x^2-y^2}$). Note that two FMOs possess d_{yz} character, and in each case also have significant π interactions with the NHC carbene C.

Mayer bond order and charge donation analyses were carried out from optimized geometry coordinates to quantify the bonding interactions across this series of iron compounds. Table 4 highlights the bonding interactions of the metal centers of the NHC-iron-alkyl complexes with each ligand. The Fe–C bond orders to the carbons of the alkyl ligands are nearly identical for the two alkyl ligands in 1^{IMes} at 0.691 and 0.692. For each remaining complex, one of the two Fe–C bonds to the alkyl ligand is slightly larger than the other. This is most pronounced for 4^{SIPr} where the bond orders are at 0.662 and 0.769, likely due to the presence of only one metallacycle with a dioxane moiety when compared with the other three molecules. Consistent with the comparable Fe–C bonding in these complexes, charge

donation analysis from the alkyl ligands to the Fe-NHC portion of the molecule is similar for all complexes (Table 4). Fe–O bond orders however are comparable and very weak for each molecule, including complex 4^{SIPr} . Previously, the monoalkylated analog, (IMes)FeBr(THF) (1,3-dioxan-2-ylethyl), was found to have a Mayer bond order of 0.224 to the oxygen of the hemilabile alkyl ligand,⁴¹ which suggests that the origin of the single chelated alkyl moiety in 4^{SIPr} is due to the total steric effects of the SIPr ligand. 4^{SIPr} continues to stand out when the Fe–NHC bond is considered as well, with a Mayer bond order of 0.771 which is nearly 0.1 greater than all other NHCs.

CONCLUSIONS

The evaluation of four alkylated iron-NHC compounds has provided insight on the implications of both backbone and *N*-substituent variations of traditional *N*-heterocyclic carbenes on precatalyst structure. Mössbauer spectroscopy, MCD, and DFT have indicated the effects that are possible because of NHC structure manipulation on the chelation ability of iron alkyl complexes. These techniques have shown that changes in NHC structure do little to affect the electronic structure and bonding in these types of compounds apart from when the steric effects of the NHC backbone saturation and *N*-substituent are combined in the case of 4^{SIPr} . Only in this case is the structure of the reactive iron complex altered to reduce chelation of the alkyl substrate and prevent the production of cross-coupled product. Therefore, in cross-coupling systems where backbone saturation affects product selectivity, even the addition of two hydrogen atoms can be a potential steric effect in addition to any *N*-substituent steric effects that might also be present. Extension of this study to other metal centers and chelating alkyl substituents will provide further understanding of the powerful effects of these subtle changes to the metal-NHC complex, enabling improved catalyst design.

EXPERIMENTAL SECTION

General Considerations.

All general experimental methods and characterization, including collection and refinement of X-ray data, may be found in the Supporting Information. (IMes)Fe(1,3-dioxan-2-ylethyl)₂ (1^{IMes}) and (SIPr)Fe(1,3-dioxan-2-ylethyl)₂ (4^{SIPr}) were prepared according to literature procedure.⁴¹

In Situ Reactivity.

Fe(OAc)₂ (0.010 mmol) was combined with SIMes·HCl or IPr·HCl (0.021 mmol) in THF at 55 °C in 2 mL of THF, and alkyl Grignard reagent was added quickly (0.122 mmol, 12 equiv to iron) to form the precatalyst. The reaction was cooled to 23 °C after 20 min, and 1-iodo-3-phenylpropane was added (0.400 mmol). (2-(1,3-Dioxan-2-yl)ethyl)magnesium bromide in THF (0.500 mmol, 0.5 M) was added via syringe pump at a rate of 0.16 mL/h for 6.25 h.^{32,41} Dodecane was added to the reaction to match the molarity of electrophile after it was cooled to room temperature. Reactions were quenched using 0.1 mM HCl in THF and filtered through a Florisil pad. Cross-coupled product yields were determined using quantitative GC analysis.

Preparation of (S^{IMes})Fe(1,3-dioxan-2-ylethyl) (2^{S^{IMes}}).

To a scintillation vial were added Fe(OAc)₂ (50 mg, 0.29 mmol) and 1,3-dimesitylimidazolium chloride (98.6 mg, 0.29 mmol) along with a stir bar. To the solid mass was added (2-(1,3-dioxan-2-yl)ethyl)magnesium bromide in THF (2.3 mL, 0.5 M, 1.16 mmol) in one portion at room temperature. The reaction mixture was stirred at room temperature for 10 min, followed by cooling to −78 °C. The yellow slurry was then warmed on a room temperature stir plate for 5 min while stirring, after which room temperature pentane (ca. 14 mL) was added to the mixture and the vial cooled back to −78 °C. The resulting solution was filtered through Celite (precooled to −78 °C), and the yellow filtrate was stored at −80 °C for 1 week, rendering yellow crystals. Evans method analysis of crystalline 2^{S^{IMes}} redissolved in THF-*d*⁸ indicates $\mu_{\text{eff}} = 4.9(0.2) \mu_{\text{B}}$. Elemental Anal. Calcd: C, 66.89; H, 8.16; N, 4.73. Found: C, 65.827; H, 8.187; N, 4.321.

Preparation of (IPr)Fe(1,3-dioxan-2-ylethyl)₂ (3^{IPr}).

To a scintillation vial were added Fe(OAc)₂ (43.4 mg, 0.25 mmol) and 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (100 mg, 0.25 mmol) along with a stir bar. To the solid mass was added (2-(1,3-dioxan-2-yl)ethyl)magnesium bromide in THF (3.0 mL, 0.5 M, 1.5 mmol) in one portion at room temperature. The reaction mixture was stirred at room temperature for 10 min, followed by cooling to −78 °C. The yellow slurry was then warmed on a room temperature stir plate for 5 min while stirring, after which room temperature pentane (ca. 10 mL) was added to the mixture and the vial cooled back to −78 °C. The resulting solution was filtered through Celite (precooled to −78 °C), and the yellow filtrate was stored at −80 °C for 1 week, rendering yellow crystals. Evans method analysis of crystalline 3^{IPr} redissolved in THF-*d*⁸ indicates $\mu_{\text{eff}} = 4.4 \mu_{\text{B}}$ due to the presence of excess MgBr_n(THF)_m salts which could not be experimentally separated from the isolated material. Elemental Anal. Calcd for 4:1, (IPr)Fe(1,3-dioxan-2-ylethyl)₂:MgBr₂: C, 64.99; H, 8.11; N, 3.89. Found: C, 64.966; H, 8.421; N, 3.049.

Preparation of Solid ⁵⁷Fe Mössbauer Samples.

Scintillation vials containing crystalline material were transported quickly into a glovebox in a liquid nitrogen precooled aluminum pie block. The vials were then placed in a cold well at −78 °C, and the mother liquor was decanted and discarded. The residual crystalline material was washed with cold pentane (−78 °C, 2 mL) and decanted. The washing and decanting process was repeated five times. A mortar and pestle were placed on top of an aluminum pie block submerged in liquid nitrogen for cooling. A liquid nitrogen chilled metal spatula was used to collect crystalline material from the vial, and the frozen crystalline solids were chipped off onto the mortar. The crystalline solids were finely ground with a cold pestle. A Delrin Mössbauer sample cup was placed on the cold aluminum pie block surface, and a cold spatula was used to transfer the frozen mull material into the cup. The cup was then sealed with an inner cup lined with silicon grease and stored in liquid nitrogen.

⁵⁷Fe Mössbauer Spectroscopy.

Solid samples for ⁵⁷Fe Mössbauer spectroscopy were made with isolated complexes based on natural abundance of ⁵⁷Fe or from ⁵⁷Fe-enriched samples of isolated complexes. Frozen

solution samples for ^{57}Fe Mössbauer spectroscopy were prepared from $^{57}\text{Fe}(\text{OAc})_2$ or isolated ^{57}Fe -enriched complexes. All samples were prepared in an inert atmosphere glovebox with a liquid nitrogen fill port to freeze each sample at 77 K within the glovebox. Each sample was loaded into a Delrin Mössbauer sample cup for measurements and loaded under liquid nitrogen. Low temperature ^{57}Fe Mössbauer measurements were performed using a SEE Co. MS4 Mössbauer spectrometer integrated with a Janis SVT-400T He/N₂ cryostat for measurements at 5 K. Isomer shifts were determined relative to α -Fe at 298 K. All Mössbauer spectra were fit using the program WMoss (SEE Co).

Preparation of Solid MCD Samples.

Scintillation vials containing crystalline material were transported quickly into a glovebox in a liquid nitrogen precooled aluminum pie block. The vials were then placed in a cold well at $-78\text{ }^{\circ}\text{C}$, and the mother liquor was decanted and discarded. The residual crystalline material was washed with cold pentane ($-78\text{ }^{\circ}\text{C}$) and decanted. The washing and decanting process was repeated five times. A mortar and pestle were placed on top of an aluminum pie block submerged in liquid nitrogen for cooling. A liquid nitrogen chilled metal spatula was used to collect crystalline material from the vial, and the frozen crystalline solids were chipped off onto the mortar. A few drops of cold isopentane ($-80\text{ }^{\circ}\text{C}$) were added to the mortar. The mortar was lifted from the aluminum pie block long enough to allow the mixture to thaw, and the solids were promptly ground with the cold pestle and refrozen. The process was repeated until a fine mull was obtained. A quartz disc was placed on the cold aluminum pie block surface, and a cold spatula was used to transfer the frozen mull material onto the disc. The quartz disc was lifted from the aluminum pie block long enough to allow for the material to thaw and spread thinly over the disc. A second precooled quartz disc was quickly set on top of the first disc and the material refrozen. All components of the MCD cell were assembled while submerged in liquid nitrogen.

Magnetic Circular Dichroism (MCD) Spectroscopy.

NIR MCD experiments were conducted using a Jasco J-730 spectropolarimeter and a liquid nitrogen cooled In-Sb detector. The spectral range accessible was 2000–600 nm. The instrument utilizes a modified sample compartment incorporating focusing optics and an Oxford Instruments SM4000–7T superconducting magnet/cryostat allowing measurements from 1.6 to 290 K with magnetic fields up to 7 T. A calibrated Cernox sensor inserted directly in the copper sample holder was used to measure the temperature of the sample $\pm 0.001\text{ K}$. All MCD spectra were baseline corrected using zero-field scans.

Electronic Structure Calculations.

Spin unrestricted density functional theory (DFT) calculations were performed with the Gaussian 09 package.⁴⁸ All geometry optimization calculations were performed with the B3LYP functional with the def2-TZVP basis set on all atoms in the gas phase.⁴⁹ The dispersion correction of Grimme (GD2) was used in geometry optimizations of all complexes.⁵⁰ The geometries of all complexes were fully optimized starting from X-ray crystal structures. All optimized geometries had frequencies found to be positive. Energies are given in the Supporting Information and include zero-point and thermal corrections. Further calculations of molecular orbitals (MOs) and TD-DFT used the B3LYP

functional^{51–54} with the def2-TZVP⁴⁹ basis set on all atoms. The analyses of MO compositions and Mayer bond orders were performed using the AOMix program.^{55,56} Orbitals from the Gaussian calculations were plotted with the ChemCraft program.⁵⁷

Samb Vca. 2.0 Calculations.

All values were computed using Samb Vca. 2.0 - A Web Application for the Buried Volume and Steric Maps Calculation.⁴⁴ The percent buried volume (% V_{bur})^{43,58} of the first coordination sphere around iron (3.5 Å radius) occupied by the NHC ligands was computed for the B3LYP/def2-TZVP optimized structures of 1–4. Bondi radii and sphere radius were set to standard values of 1.17 and 3.5 Å, respectively. H atoms were included in the steric calculations due to the unique combination effect of backbone saturation and side arm *N*-substituent groups on the structure. Steric maps⁴⁴ indicate 0.00 Å on their axes as the sphere radius of 3.5 Å from the metal center. Positive values (red) represent areas of high steric hindrance (into the sphere), and negative values (blue) represent distance away from the sphere radius.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

X-ray crystal structures of NHC iron-alkyl complexes (A) (IMes)Fe(1,3-dioxan-2-ylethyl)⁴¹ (**1^{IMes}**), (B) (SIMes)Fe(1,3-dioxan-2-ylethyl)₂ (**2^{SIMes}**), (C) (IPr)Fe(1,3-dioxan-2-ylethyl)₂ (**3^{IPr}**), and (D) (SIPr)Fe(1,3-dioxan-2-ylethyl)⁴¹ (**4^{SIPr}**). Hydrogen atoms omitted for clarity except for the NHC backbones and thermal ellipsoids are shown at the 50% probability level. (E) Corresponding steric maps for the iron-alkyl complexes representing NHC proximity to the iron center. % *V*_{bur} was calculated using alkyl ligands as the pseudo *xy* plane, a radius of 3.5 Å from the iron center, and included H atoms; axes labels are in Å.

Figure 2. Skeletal overlay of (A) IPr (blue) and SIPr (red) and (B) IMes (yellow) and SIMes (green) ligands extracted from crystallo-graphic structures of **1^{IMes}**, **2^{SIMes}**, **3^{IPr}**, and **4^{SIPr}** showing distortion in one of the SIPr side arm groups. NHC backbone hydrogens are represented translucent spheres of the same color as the NHC.

Figure 3. 5 K, 7 T NIR MCD spectra of (NHC)Fe(1,3-dioxan-2-ylethyl) compounds. (**1^{IMes}**) (IMes)Fe(1,3-dioxan-2-ylethyl)₂, (**2^{SIMes}**) (SIMes)Fe(1,3-dioxan-2-ylethyl)₂, (**3^{IPr}**) (IPr)Fe(1,3-dioxan-2-ylethyl)₂, and (**4^{SIPr}**) (SIPr)Fe(1,3-dioxan-2-ylethyl)₂. All spectra were collected on solid state mull samples of crystalline material.

Figure 4. Calculated frontier molecular orbital diagrams for NHC-iron-alkyl complexes and representative molecular orbitals from **3**^{IPr}.

Scheme 1.

Examples of Cross-Coupling Reactions with Iron-NHCs and the Results of IPr vs SIPr on Product Yields^{18,27,32}

Table 1.

Reactivity of NHC Variations in Alkyl–Alkyl Cross-Coupling with Iron

NHC	A (%)	B (%)	C (%)
IMes·HCl	78	15	7
SIMes·HCl	77	15	8
IPr·HCl	69	23	8
SIPr·HCl	23	56	21

Table 2.

Quantified Canted Angles of Dioxane Rings Chelated to Iron in 1–4 Relative to the RMS Plane of the Dioxane Rings and the Plane Normal to the Fe-C13 Line

complex	dioxane ring O1–O2/C3–C6	dioxane ring O3–O4/C9–C12
1 ^{IMes}	29.2°	28.5°
2 ^{SiMes}	39.7°	11.3°
3 ^{IPr}	29.0°	74.1°
4 ^{SiPr}	38.6°	n.a.

Table 3.Summary of ^{57}Fe Mössbauer and MCD Parameters for $(\text{NHC})\text{Fe}(\text{1,3-dioxan-2-ylethyl})_2$ Compounds

complex	Mössbauer		NIR MCD
	δ (mm/s)	E_Q (mm/s)	LF bands (cm^{-1})
1 ^{IMes}	0.57	2.42	5310, 7600
2 ^{SIMes}	0.54	2.56	5400, 7630
3 ^{IPr}	0.58	2.36	<5000, 8060
4 ^{SIPr}	0.44	2.91	5800, 8480

Table 4.

Calculated Mayer Bond Order and Charge Donation Analysis for NHC-Iron-Alkyl Complexes

complex	Mayer bond order		charge donation analysis ($\alpha + \beta$)	
	Fe–NHC	Fe–C _{alkyl}	Fe–O	net donation to Fe–NHC fragment
1 ^{IMes}	0.627	0.691	0.117	1.154 e [−]
		0.692	0.122	
2 ^{SIMes}	0.682	0.727	0.109	1.160 e [−]
		0.690	0.122	
3 ^{IPr}	0.624	0.726	0.091	1.223 e [−]
		0.662	0.133	
4 ^{SIPr}	0.771	0.769	0.138	1.267 e [−]
		0.662		