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Synthesis, Characterization and Alkyne Trimerization Catalysis of a Heteroleptic Two-Coordinate Fe^{I} Complex

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ABSTRACT: The synthesis of the first heteroleptic, two-coordinate Fe^{I} complex IPr–Fe–N($SiMe_3$)DIPP (**1**) (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; DIPP = 2,6-$^{i}Pr_2$-C_6H_3) is reported. Protonation of the Fe^{II} bis(amido) complex Fe[N($SiMe_3$)DIPP]$_2$ followed by addition of IPr and reduction by potassium graphite in a one-pot reaction results in good yields of **1**. The redox activity of **1** and comparison between **1** and its reduction product by ^{57}Fe Mössbauer spectroscopy is discussed, and the reduction was found to be metal-based rather than ligand-based. The activity of **1** towards the catalytic cyclotrimerization of terminal and internal alkynes is described.

Introduction

Two-coordinate transition metal complexes have attracted considerable interest due to their novel structural and electronic properties.[1] In particular, previous investigations have focused on the structural consequences of two-coordination, and the potential of these complexes as single molecule magnets.[1,2] More recently, studies on the chemical reactivity of two-coordinate complexes have revealed a number of noteworthy transformations.[3] Because open-shell two-coordinate transition metal complexes are almost exclusively associated with earth-abundant first row metals, the potential of these compounds to serve as inexpensive, active catalysts for important reactions is of particular interest.[4] This possibility is supported by recent reports of two-coordinate complexes as catalysts for olefin hydrosilylation,[5] carbon-carbon cross-coupling[6] and dinitrogen reduction.[7] Progress in this area has inspired the development of new ligand frameworks and synthetic methods for two-coordinate complexes to widen the scope of available compounds and explore the effect of different ligands and oxidation states on chemical reactivity.[8,9,10]

With few exceptions, open-shell two-coordinate compounds have been limited to homoleptic complexes in either the M^{II} or, less commonly, the M^{0} oxidation state.[1] Complexes in the M^{I} or M^{III} oxidation states are very rare and are occasionally synthesized *via* reduction of M^{II} or oxidation of M^{0} complexes.[2a,3a,9] Recently, a general method for the preparation of two-coordinate Ni^{I} complexes was reported.[10] Since numerous two-coordinate Ni^{I} complexes are known, their properties and reactivity are the most thoroughly investigated for M^{I} complexes.[11] However, little is known about monovalent, two-coordinate complexes of other metals because general methods for their preparation have not been established.

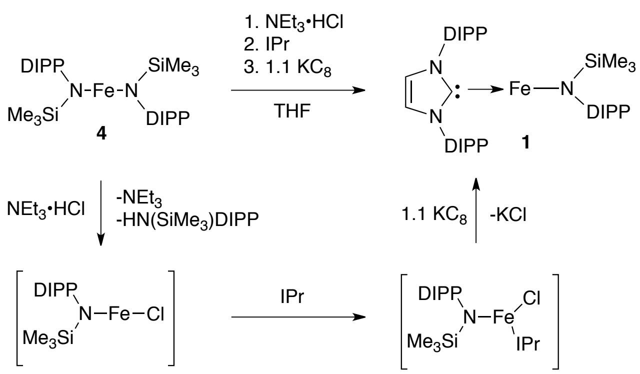
Though only a handful of two-coordinate complexes of Fe^{I} are known, they have attracted a great deal of attention.[2a,9b,12] Two-coordinate Fe^{I} complexes have been shown to possess exceptional magnetic blocking behavior[2a,13] and one such complex was recently reported to be catalytically active for N_2 reduction.[7] All known two-coordinate Fe^{I} complexes are homoleptic and have been derived from reduction of Fe^{II} complexes,[2a,9b,12c] resulting in $[FeX_2]^-$ complexes, or by oxidation of an Fe^{0} complex to a $[FeL_2]^+$ species.[12a,12b] No heteroleptic two-coordinate Fe^{I} complexes have been reported and the chemistry and catalytic activity of such compounds are unexplored. Given our success in preparing unsymmetrical two-coordinate Ni^{I} complexes of the L–Ni–X type, we sought to develop an analogous route to two-coordinate Fe^{I} complexes. Herein, we report the synthesis, physical properties and catalytic activity of the first heteroleptic, two-coordinate Fe^{I} complex IPr–Fe–N($SiMe_3$)DIPP (**1**; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; DIPP = 2,6-$^{i}Pr_2$-C_6H_3).

Results and Discussion

Synthesis of heteroleptic two-coordinate Fe^{I} complexes. Recently, this laboratory described a general synthetic method for the preparation of neutral two-coordinate Ni^{I} complexes of the type L–Ni–N($SiMe_3$)DIPP, from the easily prepared Ni^{I} bis(amido) complex K{Ni[N($SiMe_3$)DIPP]$_2$} (**2**).[10] Protonation of **2** with a weak acid in the presence of various bulky L-donors results in loss of HN($SiMe_3$)DIPP and trapping of the resulting Ni^{I} fragment by L to give a neutral, heteroleptic, two-coordinate Ni^{I} complex. This methodology seemed applicable to the synthesis of related Fe^{I} complexes, especially given Power's contemporaneous report of an anionic Fe^{I} bis(amido) complex analogous to **2**, [K(18-crown-6)]{Fe[N($SiMe_3$)DIPP]$_2$} (**3**).[9b] However, treatment of **3** with NEt_3•HCl in Et_2O at -30 °C in the presence of 1 equiv of IPr resulted only in formation of the Fe^{II} complex Fe[N($SiMe_3$)DIPP]$_2$ (**4**), which was observed by ^{1}H NMR spectroscopy (due to the paramagnetism of **4**, a yield could not be accurately determined). Thus, in this system protonation of the iron complex leads to oxidation of **3** to **4** and formation of H_2 (by ^{1}H NMR spectroscopy), rather than elimination of HN($SiMe_3$)DIPP. Development of a different synthetic route to neutral, two-coordinate Fe^{I} complexes was therefore required.

The successful strategy outlined in Scheme 1 is based on a one-pot reaction sequence involving protonation, ligand substitution, and then reduction, rather than the reduction, protonation, and ligand substitution order employed for nickel. Compound **4** was treated with 1 equiv of NEt_3•HCl at ambient temperature, followed by addition of a THF solution of IPr and then addition of 1.1 equiv of KC_8. Workup and recrystallization from toluene/hexamethyldisiloxane gave **1** in 77% overall yield as thin red plates, which desolvate under vacuum. Compound **1** is indefinitely stable in the solid state at ambient temperatures and shows no signs of decomposition after several months (by ^{1}H NMR spectroscopy).

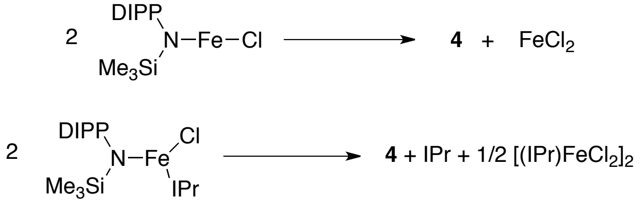
Scheme 1. Synthesis of compound 1.



Efforts to isolate the presumed intermediates in this reaction, ClFe[N($SiMe_3$)DIPP] (probably dimeric) and (IPr)ClFe[N($SiMe_3$)DIPP], led only to mixtures thought to contain these compounds. After addition of NEt_3•HCl to **4** in benzene-d_6, analysis of the reaction mixture by ^{1}H NMR spectroscopy indicated the complete consumption of **4**, and the presence of HN($SiMe_3$)DIPP as well as a new paramagnetic compound, presumed to be ClFe[N($SiMe_3$)DIPP] (see Supporting Information). After 22 h, a tan precipitate (presumably $FeCl_2$) was observed and the NMR spectrum revealed the regeneration of **4**, along with the previously observed HN($SiMe_3$)DIPP and the same new, paramagnetic product. Attempts to isolate ClFe[N($SiMe_3$)DIPP] resulted only in mixtures containing the new iron complex and **4**. These observations suggest that in solution, ClFe[N($SiMe_3$)DIPP] disproportionates to **4** and $FeCl_2$ (Scheme 2).

Attempts to isolate (IPr)ClFe[N($SiMe_3$)DIPP] were based on the reaction of **4** with NEt_3•HCl, followed by IPr in THF. Workup of the reaction mixture gave mixtures of **4**, the putative (IPr)ClFe[N($SiMe_3$)DIPP], free IPr, and [(IPr)$FeCl_2$]$_2$ (identified by its previously reported ^{1}H NMR spectrum).[14] From this reaction mixture, crystals of (IPr)ClFe[N($SiMe_3$)DIPP] were obtained from a toluene-pentane solvent mixture. This complex was characterized by single crystal X-ray diffraction (see Supporting Information). These observations suggest that (IPr)ClFe[N($SiMe_3$)DIPP] disproportionates in solution to the mixture of compounds shown in Scheme 2.

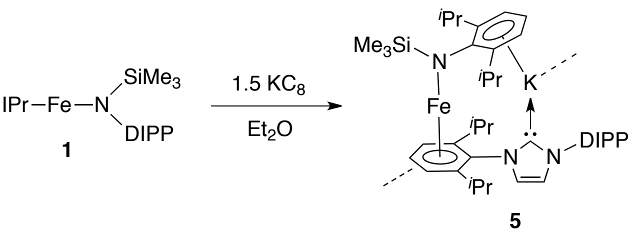
Scheme 2. Proposed disproportional decomposition pathways of synthetic intermediates for compound 1.



Reduction of 1 to an Fe(0) complex. Reports from this laboratory and others have shown that two-coordinate M^{II} bis(amido) complexes of Cr, Fe, Co and Ni are redox active, such that corresponding anionic (M^I) and cationic (M^{III}) analogues are accessible and isolable.[3a,9] Given the generality of this chemical property, over a variety of metals and *d*-electron counts, it was of interest to explore the redox properties of the two-coordinate, neutral Fe^I complex **1**.

Treatment of **1** with 1.5 equivs of potassium graphite in Et_2O gave dark red, needle-shaped crystals of paramagnetic K{(η^6-IPr)Fe-N($SiMe_3$)DIPP} (**5**) in 87% yield after subsequent workup and recrystallization (Scheme 3). Analysis of **5** by single crystal X-ray diffraction (*vide infra*) revealed that the complex results from an unexpected ligand rearrangement in which the IPr ligand is no longer bound *via* the carbenyl carbon. Instead, IPr serves as a π-bonded ligand *via* η^6-coordination of a DIPP substituent to the Fe center. This redox-induced ligand rearrangement, and the unusual structure of this complex, present interesting questions regarding the electronic structure and oxidation state of **5**. For this reason, compounds **1** and **5** were studied by ^{57}Fe Mössbauer spectroscopy.

Scheme 3. Reduction of 1 to 5. Dashed lines indicate intermolecular bonding in the solid state.



Mössbauer Spectroscopy of 1 and 5. The ^{57}Fe Mössbauer spectrum of compound **1** displays a sextet pattern, with an isomer shift of δ = 0.39 mm/s and quadrupole splitting of ΔE_q = -2.25 mm/s at 5 K (Figure 1). This spectrum closely resembles that of [K(crypt-222)]{Fe[C($SiMe_3$)$_3$]$_2$},[2a,13] which also displays a sextet spectrum with similar parameters (δ = 0.410 mm/s, ΔE_q = −2.557 mm/s). However, this spectrum differs substantially from that of [(CAAC)$_2$Fe][BAr^F_{24}],[12c] which displays a doublet at 5 K. This difference in Mössbauer spectra for the latter two complexes was attributed to the bond angles at iron, since the coordination geometry for [K(crypt-222)]{Fe[C($SiMe_3$)$_3$]$_2$} is essentially linear (bond angle of 179°)[2a] while [(CAAC)$_2$Fe][BAr^F_{24}], is bent with a C–Fe–C bond angle of approximately 165°.[12c] This is consistent with the observations for **1**, which possesses a C–Fe–N bond angle of 176.94(6)°.

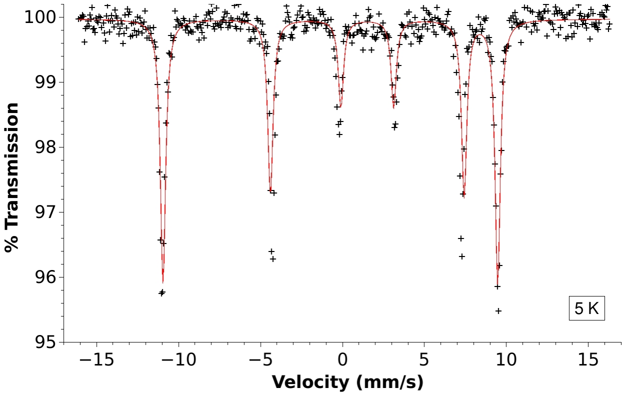


Figure 1. Zero-field ^{57}Fe Mössbauer spectrum of compound **1** acquired at 5 K. The red line corresponds to a least-square fit with an isomer shift of δ = 0.39 mm/s, and quadrupole splitting of ΔE_q = -2.25 mm/s.

Unlike **1**, compound **5** displays a Mössbauer spectrum that features a doublet at 5 K with a markedly increased isomer shift of δ = 0.81 mm/s, indicating substantially higher shielding of the 4s electrons by the 3d electrons in **5** compared to **1** (Figure 2). This suggests an increase in the d-electron count and a reduction at Fe rather than reduction of the ligand. This significant increase in the

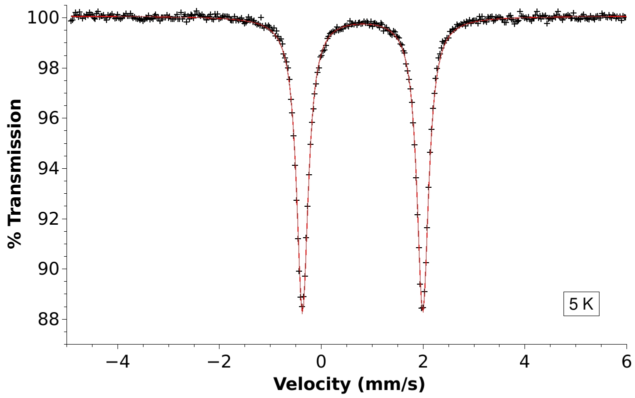


Figure 2. Zero-field ^{57}Fe Mössbauer spectrum of compound **5** acquired at at 5 K. The red line corresponds to a least-square fit with an isomer shift of $\delta = 0.81$ mm/s and a quadrupole splitting of $\Delta E_q = 2.36$ mm/s.

isomer shift parameter, relative to that for **1**, is consistent with an oxidation state of Fe(0) in **5**.

Solution Magnetic Properties of 1 and 5. The differences in Mössbauer parameters mentioned above, and their correlation with coordination geometry, is consistent with reported magnetic properties for two-coordinate Fe^I complexes. The bent complex $[(CAAC)_2Fe][BAr^F_{24}]$ has a magnetic moment of 4.3 μ_B, which is modestly higher than the spin-only value of 3.87 μ_B (by the Evans method[21]) expected for an $S = 3/2$ complex, reflecting some degree of magnetic anisotropy due to spin-orbit coupling. In comparison, the linear complexes $[K(crypt\text{-}222)]\{Fe[C(SiMe_3)_3]_2\}$ (179°) and $[K(18\text{-}crown\text{-}6)]\{Fe[N(SiMe_3)_2]_2\}$ (180°) exhibit magnetic moments of 5.2 and 5.12 μ_B, respectively, indicating stronger spin-orbit coupling interactions.[2a,12a]

Compound **1** follows the trend of linearity leading to higher anisotropy, with a magnetic moment of 5.0 μ_B. To help gauge the importance of a two-coordinate ligand field to the observed magnetic anisotropy, a simple, three-coordinate isocyanide adduct of **1**, IPr–Fe(XylNC)–N(SiMe$_3$)DIPP (**6**), was prepared (see Experimental Section). Analysis of **6** by Evans's method shows that the additional ligand diminishes the spin-orbit coupling, resulting in a markedly lower magnetic moment of 4.1 μ_B which is close to the spin-only value of 3.87 μ_B.

Analysis of **5** by Evans's method led to the observation of magnetic anisotropy in a non-two-coordinate compound, with an observed moment of 3.9 μ_B. This value is lower than that for **1**, which is consistent with additional pairing of electrons, but substantially higher than the spin-only value of 2.83 μ_B expected for an $S = 1$ ion. Since compound **5** is not two-coordinate, the origin of its increased magnetic moment is currently unclear.

Structural Properties. The X-ray crystal structures of compounds **1**, **5** and **6** are shown in Figures 3-5. Two-coordinate **1** possesses a linear geometry with a N–Fe–C_{NHC} bond angle of 176.94(6)°. The Fe–N and Fe–C_{NHC} bond lengths of 1.890(2) and 2.014(2) Å are unremarkable and similar to the values reported for related Fe^I compounds reported in the literature.[9b,12b,12c]

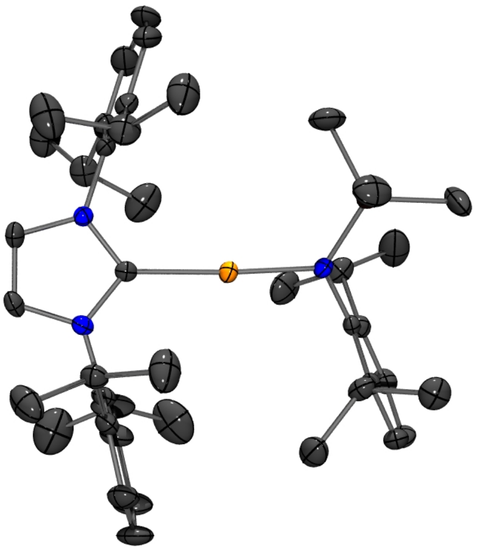


Figure 3. ORTEP diagram of **1**. Thermal ellipsoids shown at 50% probability. Carbon atoms are shown in dark grey, nitrogen in blue, iron in orange and silicon in red. Selected bond lengths (Å) and angles (deg): Fe–N, 1.890(2); Fe–C, 2.014(2); N–Fe–C, 176.94(6).

Reduction to Fe^0 results in lengthening of the Fe–N bond in **5** to 1.962(2) Å. The reorganization of the IPr ligand in **5** results in an interaction between the carbenyl carbon of IPr and the potassium ion, with a C–K distance of 2.877(3) Å. This is similar to the C–K bond lengths reported for the $[IPr–K–IPr]^+$ ion,[15] suggesting that there is a bonding interaction between the potassium ion and the carbenyl carbon. The new η^6-interaction between the Fe center and the DIPP moiety of the IPr ligand results in notable lengthening of the C–C bonds within the ring as compared to the unbound DIPP moiety (1.423 Å av. vs. 1.388 Å av., respectively). This degree of bond lengthening is on par with that observed in other examples of Fe^0–aryl complexes, and is attributable to π-back-bonding from the electron-rich Fe center to the aryl ring.[16]

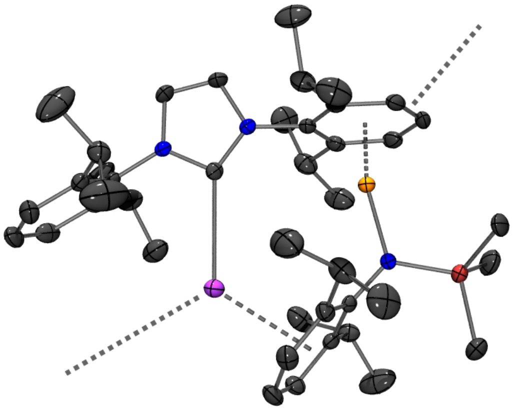


Figure 4. ORTEP diagram of **5**. Thermal ellipsoids shown at 50% probability. Carbon atoms are shown in dark grey, nitrogen in blue, iron in orange, potassium in purple and silicon in red. Selected bond lengths (Å): Fe–N, 1.962(2); C–K, 2.877(3).

Addition of the XylNC ligand to the coordination sphere of Fe results in an approximately trigonal planar geometry in **6**, accompanied by the expected lengthening of the Fe–N (1.933(2) Å) and

Fe–C_{NHC} (2.076(2) Å) bonds due to steric crowding. The C–N–C bond angle of the XylNC ligand is somewhat bent at nitrogen (160.8(2)°), with a slightly lengthened N-C triple bond of 1.192(2) Å (vs. 1.160 Å in the unbound molecule[17]), reflecting π-donation from the Fe center.

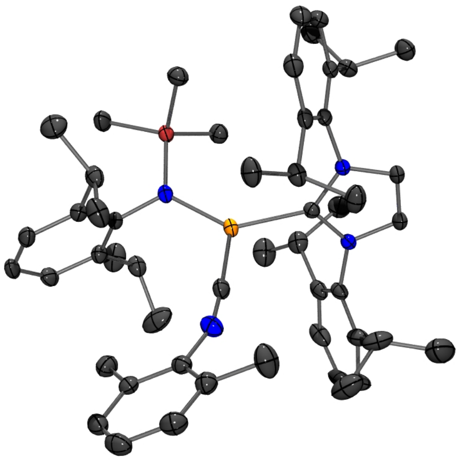
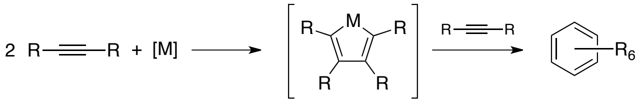


Figure 5. ORTEP diagram of **6**. Thermal ellipsoids shown at 50% probability. Carbon atoms are shown in dark grey, nitrogen in blue, iron in orange, and silicon in red. Selected bond lengths (Å) and angles (deg): Fe–N, 1.933(2); Fe–C_{NHC}, 2.076(2); Fe–C_{XylNC}, 1.856(2); XylN–C, 1.192(2); C_{Ar}–N–C, 160.8(2).

Catalytic Cyclotrimerization of Alkynes. Recent studies on the chemistry of two-coordinate, first-row metal complexes of Ni[3a] and Fe[12a] show that these compounds are capable of two-electron substrate activations mediated by a M^{I} to M^{III} oxidation state change. Such redox processes are generally thought to be difficult for first-row transition metal complexes, but are associated with key steps in many important catalytic cycles involving second- and third-row metals. Thus, an important goal for development of catalysts based on more abundant metals is to establish useful, two-electron reaction steps for these metals. For this reason, it was of interest to examine the efficacy of **1** as a catalyst for reactions in which formal two-electron redox processes are presumed to play a key role.

The cyclotrimerization of alkynes is an efficient and atom-economical method for the preparation of functionalized arenes. Such trimerization reactions are thought to proceed via a metalocyclopentadiene intermediate, the formation of which involves a formal two-electron oxidation of the metal center to form a new C-C bond (Scheme 4).[18] Similar reactions can also be used to produce unsymmetrical arenes, aromatic heterocycles and many other cyclic structures.[19] While known catalysts for this reaction are based on rhodium and cobalt, examples of catalysis by iron are rare.[20] The potential for two-coordinate compounds to mediate two-electron redox processes, and the dearth of examples of iron catalysts for this reaction type, prompted an examination of **1** as a catalyst for the cyclotrimerization of alkynes.

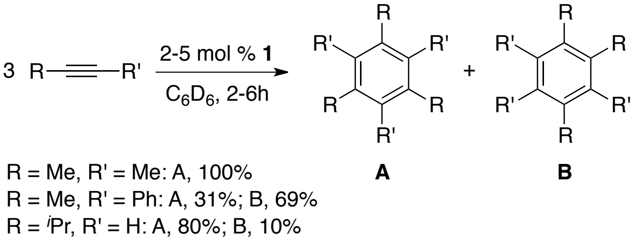
Scheme 4. Mechanism for alkyne cyclotrimerization.



Complex **1** is competent as a catalyst for cyclotrimerizations at fairly low loadings and under mild conditions (Scheme 5). Reaction of **1** with 50 equivs of 2-butyne in benzene-d_6 over 3 h at ambient temperature resulted in the quantitative formation of hexamethylbenzene (by ^{1}H NMR spectroscopy). The trimerization of 20 equivs of 1-phenyl-1-proyne resulted in complete conversion of the starting material over 6 h, and a mixture of the 1,3,5- and 1,2,4-substituted trimethyltriphenylbenzenes in 31 and 69% yields, respectively. Compound **1** was also found to catalyze the trimerization of a terminal alkyne, in the conversion of 50 equiv of 3-methyl-1-butyne to 1,3,5-triisopropylbenzene (80%) and 1,2,4-triisopropylbenzene (10%), over 2 h. Accompanying these trimerization products was a colorless, gummy precipitate that was found to be insoluble in benzene, THF and DMSO. Due to the insolubility of this substance, we tentatively suggest that it is derived from polymerization of 3-methyl-1-butyne. The activity and selectivity of **1** as a catalyst is comparable to that of the few reported Fe-based catalysts (turnover number of *ca.* 50),[20] but modest compared to that of state of the art Co and Rh catalysts, which can achieve TONs in the thousands.[21]

In an effort to further understand the role of **1** in the catalytic cycle, particularly as an on-cycle intermediate or a precatalyst, the post-catalytic reaction mixture was examined. At higher catalyst loadings in the trimerization of 2-butyne (10 mol %), by far the most prominent Fe-containing compound observed in the post catalytic mixture was **1**, with small quantities of other paramagnetic species also observed. Observation of the reaction mixture during catalysis indicates that all of **1** is initially consumed, and that the **1** observed in the post-catalytic reaction mixture is reformed from catalytically active intermediates. As the loading is lowered (5 mol % and 2 mol %), the amount of **1** observed in the post-catalytic mixture decreases and the amount of other paramagnetic species increases. This observation suggests that some degree of catalyst decomposition occurs. As the loading is lowered, a larger fraction of the catalyst decomposes over the course of the reaction. Under these conditions, each molecule of catalyst must perform more turnovers at lower loadings to complete the reaction. This decomposition is a greater factor in the catalysis of 1-phenyl-1-proyne and 3-methyl-1-butyne, where only small amounts of **1** are observed post-catalysis. Additionally, the qualitative rate of the reaction was found to be unaffected by the presence of mercury, supporting the involvement of a homogeneous catalyst (see Supporting Information).

Scheme 5. Catalytic cyclotrimerization of various alkynes by compound 1.



While trimerization reactions with simple alkyl- and aryl- substituted alkynes are efficient, substrates bearing bulky substituents or electron-withdrawing groups may be problematic. Thus, no reaction was observed between **1** and 50 equiv of bis(trimethylsilyl)acetylene in benzene-d_6 at 105 °C over 24 h. In addition, the reaction between **1** and 50 equiv of dimethylactylenedicarboxylate at ambient temperature over 24 h resulted solely in the formation of a gummy precipitate which was found to be insoluble in benzene, THF and DMSO, and is presumably polymeric.

Given the mechanism of previously studied alkyne trimerization catalysts, the arene-bound structure of compound **5** prompted exploration of the reduced species as a catalyst for the trimerization reaction. However, exposure of **5** to 50 equiv of 2-butyne in benzene-*d*$_6$ over 1 h at ambient temperature resulted in only 15% conversion to hexamethylbenzene, by which point all of the catalyst had decomposed. No additional conversion to product was observed.

Despite the limited scope of the trimerization catalysis reported here, the two-coordinate Fe^{I} framework of **1** offers numerous opportunities for catalyst modification *via* exchanges of the L- and X-type ligands that support the Fe center. The methodology for the preparation of **1** may in principle be extended to other L-type ligands with different steric profiles and donor properties. The amido ligand could then be used as a handle for the introduction of different X-type ligands, as in the case of an analogous series of Ni^{I} complexes.[10] Attempts to introduce different ligands in this manner and to fully explore reductive-coupling catalysis with **1** and its derivatives are currently underway.

Conclusions

The synthesis, spectroscopic properties, and catalytic activity of the rare two-coordinate Fe^{I} complex IPr–Fe–N(SiMe$_3$)DIPP (**1**) have been described. This complex is the first example of a heteroleptic two-coordinate Fe^{I} complex as well as the first neutral example of such a complex. Like other two-coordinate complexes, **1** was found to be redox active, in accepting an electron to form the Fe^{0} complex K{(η^6-IPr)Fe–N(SiMe$_3$)DIPP] (**5**). Compound **1** was also found to be a competent catalyst for the cyclotrimerization of both internal and terminal alkynes to form arenes at modest loadings under mild conditions. Exploration of the scope and mechanism of this reaction, as well as attempts to improve activity via ligand modification, are currently underway.

Experimental Section

General Considerations. Unless otherwise stated, all reactions and manipulations were carried out in an MBraun Lab Master DP glovebox or using standard Schlenk techniques under a nitrogen atmosphere. Pentane, toluene, and hexamethyldisiloxane were purchased from Sigma Aldrich. Diethyl ether was purchased from Honeywell and tetrahydrofuran was purchased from Macron Chemicals. Pentane, toluene, tetrahydrofuran and diethyl ether were dried and degassed using a JC Meyers Phoenix SDS solvent purification system. Hexamethyldisiloxane was dried by stirring over potassium metal for 2 days and degassed by four freeze-pump-thaw cycles. Benzene-*d*$_6$ was purchased from Cambridge Isotope Laboratories, dried over Na/K alloy and then degassed by four freeze-pump-thaw cycles. All NMR spectra were collected at ambient temperature (ca. 22°C) on Bruker AVB-400, AV-500, AV-600 or AVQ-400 NMR spectrometers, each equipped with a 5 mm BB probe, and referenced to the residual proteo solvent signals. Solution magnetic susceptibilities were determined by ^{1}H NMR spectroscopy using Evans's method.[22] Elemental analyses were performed by the UC Berkeley College of Chemistry Microanalytical facility. The abbreviation "DIPP" refers to a 2,6-diisopropylphenyl moiety. The abbreviation "IPr" refers to the N-heterocyclic carbene N,N'-1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene.

The abbreviation "HMDSO" refers to hexamethyldisiloxane. NEt$_3$•HCl was purchased from Sigma Aldrich and sublimed before use. Xylyl isocyanide was purchased from Sigma Aldrich and sublimed before use. FeCl$_2$ was purchased from Strem Chemical and used as received. Dimethylacetylenedicarboxylate was purchased from Sigma Aldrich and used as received. IPr,[23] LiN(SiMe$_3$)DIPP,[24] and potassium graphite[25] were prepared according to standard literature procedures. Fe[N(SiMe$_3$)DIPP]$_2$ was prepared using a modified procedure from the literature (detailed below).[26]

IPr–Fe–N(SiMe$_3$)DIPP (1). To a 20 mL scintillation vial was added Fe[N(SiMe$_3$)DIPP]$_2$ (**4**) (0.430 g, 0.78 mmol) and 4 mL of tetrahydrofuran (THF), to form a light yellow solution. To this stirred solution was added NEt$_3$•HCl (0.107 g, 0.78 mmol). Over the course of 10 min, the solution changed color from light yellow to tan and the NEt$_3$•HCl dissolved. To the stirred, tan solution was added a solution of IPr (0.30 g, 0.78 mmol) in 4 mL of THF, dropwise over the course of one minute, causing a color change from light tan to golden yellow. This yellow solution was stirred for an additional five minutes, then potassium graphite (0.116 g, 0.86 mmol, 1.1 equiv) was added, causing an immediate color change to dark red along with the formation of black graphite. The resulting mixture was stirred for 15 min, and then stirring was ceased and the mixture was allowed to settle. The mixture was then filtered through a pipette fitted with a glass fiber filter into a 20 mL scintillation vial, the red filtrate was placed under vacuum, and the volatile components of the mixture were removed under vacuum. The resulting red residue was washed with two portions of 2 mL of HMDSO and dried under vacuum. This residue was then dissolved in 8 mL of toluene and layered with 12 mL of HMDSO and placed in a -30 °C freezer for 12 h to yield 0.37 g (68%) of **1** as long, narrow, red plates which were isolated by decantation and dried under vacuum until fully desolvated, requiring approximately 2 hours to reach constant mass. The supernatant was dried under vacuum and the residue was recrystallized and isolated in an identical fashion using 1.5 mL of toluene and 7 mL of HMDSO, yielding an additional 0.048 g of **1**, bringing the total yield to 0.414 (77%). Where possible, ^{1}H NMR shifts are assigned to specific protons by integration. ^{1}H NMR (500 MHz, C$_6$D$_6$, 20 °C) δ 89.01 (2H), 59.17 (2H), 46.48 (4H), 34.38 (2H), 29.77 (6H, amido-NAr-CH(C*H*$_3$)), 13.94 (1H, amido-N-*para*-Ar-*H*), 8.65 (12H, NHC-NAr-CH(C*H*$_3$)), -6.53 (9H, -Si(C*H*$_3$)$_3$), -14.73 (2H), -19.27 (4H), -75.37 (12H, NHC-NAr-CH(C*H*$_3$), overlapping with adjacent signal), -76.27 (6H, amido-NAr-CH(C*H*$_3$), overlapping with adjacent signal). μ_{eff} = 5.0 μ_B (C$_6$D$_6$, 20°C, Evans's method). Anal. Calcd. for $C_{42}H_{62}FeN_3Si$: C, 72.80%; H, 9.02%; N, 6.06%. Found: C, 72.55%; H, 8.78%; N, 6.16%. Crystals suitable for single crystal X-ray diffraction studies were obtained from the workup described above.

Fe[N(SiMe$_3$)DIPP]$_2$ (4). Modified synthetic procedure:[26] to a 20 mL scintillation vial was added FeCl$_2$ (0.526 g, 4.15 mmol) and 4 mL of Et$_2$O to produce a suspension. To the stirred suspension at ambient temperature was added a solution of LiN(SiMe$_3$)DIPP (2.00 g, 7.86 mmol, 1.9 equiv) in 10 mL of Et$_2$O, causing the mixture to turn dark brown. The mixture was stirred for 16 h, and then the volatile components were removed under vacuum. Once visibly dry, the residue was dried under vacuum for 2 additional hours, during which time the color of the residue changed from brown/tan to orange (note: this extra drying is essential for consistently preparing pure product). To the resulting residue was added 8 mL of pentane and the mixture was stirred for 15 min, allowed to settle, and was then filtered through a pipette equipped with a glass fiber filter into a 20 mL scintillation vial. The filtrate was placed in the -30 °C freezer for 12 h, yielding 1.44 g of **4** (66%) as red/orange crystals, which were isolated by decantation and dried under vacuum. The supernatant was dried under vacuum and the residue was recrystallized in an identical fashion using 2 mL of pentane to yield an additional 0.42 g of **4**, bringing the total yield to 1.86 g (85%). ^{1}H NMR (400 MHz, C_6D_6, 20 °C) δ 64.15, 51.33, 36.43, -54.92.

K[(η^6-IPr)Fe–N($SiMe_3$)DIPP] (5). To a 20 mL scintillation vial was added **1** (0.200 g, 0.289 mmol) and 6 mL of Et_2O, to give a red solution. To the stirred solution was added potassium graphite (0.058 g, 0.43 mmol, 1.5 equiv), causing an immediate color change from red to dark red/orange along with the formation of black graphite. The mixture was stirred for 30 min, then stirring was ceased and the mixture was allowed to settle. The mixture was then filtered through a pipette fitted with a glass fiber filter into a 20 mL scintillation vial and the volatile components were removed under vacuum. The resulting residue was dissolved in 5 mL of toluene and the solution was layered with 15 mL of pentane and placed in a -30 °C freezer for 12 h, yielding 0.142 g of **5** (68%) as long, dark red needle-shaped crystals which were isolated by decantation and dried under vacuum. The supernatant was dried under vacuum, and recrystallized and isolated in an identical fashion using 2 mL of toluene and 10 mL of pentane, yielding an additional 0.041 g of **5**, bringing the total yield to 0.183 g (87%). Note: compound **5** dissolves rather slowly in toluene, so several minutes of agitation are required to dissolve the residue for recrystallization. The ^{1}H NMR spectrum of **5** in benzene-d_6 varies greatly with concentration, which we attribute to the presence of various oligomers capped by benzene (see X-ray crystal structure for polymeric structure of **5**). μ_{eff} = 3.9 μ_B (C_6D_6, 20°C, Evans's method). Anal. Calcd. for $C_{42}H_{62}FeKN_3Si$: C, 68.91%; H, 8.54%; N, 5.74%. Found: C, 69.24%; H, 8.45%; N, 6.12%. Crystals suitable for single crystal X-ray diffraction studies were obtained from the workup described above.

IPr–Fe(CNXyl)–N($SiMe_3$)DIPP (6). To a 20 mL scintillation vial was added **1** (0.108 g, 0.156 mmol) and 2 mL of Et_2O, to form a red solution. To this solution was added a solution of xylyl isocyanide (0.0205 g, 0.156 mmol) in 2 mL of Et_2O causing an immediate color change from red to very dark orange. The volatile components of the mixture were immediately removed under vacuum and the resulting residue was dissolved in 2 mL of Et_2O and layered with 8 mL of HMDSO. This mixture was placed in the -30 °C freezer for 12 h, yielding 0.104 g of **6** (81%) as dark orange crystals which were isolated by decantation and dried under vacuum. The ^{1}H NMR spectrum of **6** contains numerous broad and overlapping peaks from 4-7.25 ppm, so assigning shifts to individual peaks and integration of these peaks is not possible. All clearly visible characteristic peaks of **6**: ^{1}H NMR (500 MHz, C_6D_6, 20 °C) δ 63.57, 48.62, 28.07, 12.97, 8.54, 4.55, 3.05, -8.50, -24.05, -54.11. μ_{eff} = 4.1 μ_B (C_6D_6, 20°C, Evans's method). Anal. Calcd. for $C_{51}H_{71}FeN_4Si$: C, 74.33%; H, 8.68%; N, 6.80%. Found: C, 74.01%; H, 8.88%; N, 6.85%. Crystals suitable for single crystal X-ray diffraction studies were obtained from the workup described above.

ASSOCIATED CONTENT

Additional experimental procedures, crystallographic data, and spectral characterization are available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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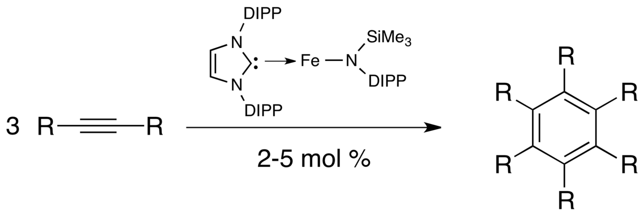

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