Reactions of $[\text{FeL}_2(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ ($\text{L} = N$ -pyrimid-2-ylimidazolylidene) with N-, P-, O-, and S-donors and its catalytic activity

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Reactions of $[\text{FeL}_2(\text{CH}_3\text{CN})_2]^{2+}$ ($\text{L} = N$ -pyrimid-2-ylimidazolylidene) with various N-, P-, O-, and S-donors were investigated. By replacing the labile acetonitrile, various iron-NHC complexes containing additional N-, P-, O-, and S-ligands were prepared. All the iron-NHC complexes were fully characterized by NMR spectroscopy and X-ray crystallography. $[\text{FeL}_2(\text{CH}_3\text{CN})_2]^{2+}$ could efficiently catalyze the coupling reactions of various Grignard reagents with heteroaryl bromides or chlorides.

iron, *N*-heterocyclic carbene, C–C coupling, X-ray diffraction

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Because iron is cheap, nontoxic, and environmentally friendly, iron complexes are important catalysts. Interest in the catalytic applications of iron in organic synthesis has increased in recent years [1–6]. In earlier studies, we found that functionalized *N*-heterocyclic carbenes (NHCs) were good ligands in homogeneous catalysis because of strong donating abilities [7–11]. Fe-NHCs could be used as catalysts to develop cheap and green catalytic organic transformations for industrial applications. Some Fe-NHC complexes have been used in polymerization of olefins and C–C and C-heteroatom bond formation reactions. Grubbs and coworkers [11] reported the catalytic activity of well-defined $[(\text{NHC})_2\text{FeX}_2]$ complexes in atom transfer radical polymerization. Iron(II) complexes of functionalized NHC were found to catalyze ring-opening polymerization of γ -caprolactone [12]. Iron-SIPr (saturated 1,3-bis(2,6-diisopropylphenyl) imidazolylidene) fluoride could catalyze selective biaryl coupling [13]. A half-sandwich iron-NHC complex was reported as an efficient catalyst for C–H bond activation/borylation of furans and thiophenes [14,15], hydrogen transfer reactions [16], and hydrosilylation of carbonyl derivatives [17]. Several iron complexes, including

mononuclear complexes containing monodentate [18–20] or polydentate NHC ligands [21–25], iron clusters [26–28], and polymeric iron complexes [29], have been recently reported. However, compared to noble metal-NHC complexes [30,31], the organometallic chemistry of iron-NHC complexes has not been well explored.

We [32] recently reported that iron-NHC complexes can be prepared from iron powder with imidazolium salts or an Ag-NHC complex in air. Alternatively, iron-NHC complexes can be electrochemically prepared using an imidazolium salt as the supporting electrolyte [33]. These synthetic procedures allow for scaling the preparation of iron-NHC complexes, and thus offer more opportunity for careful investigation of the reactivity and application of iron-NHC complexes. In this paper, we report the reactions of $[\text{FeL}_2(\text{CH}_3\text{CN})_2]^{2+}$ ($\text{L} = N$ -pyrimid-2-ylimidazolylidene) with N-, P-, O-, and S-donors and the structural characterization of resulting iron(II)-NHC complexes.

1 Experimental

1.1 General remarks

All the chemicals were obtained from commercial suppliers

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and used without further purification. $[\text{FeL}_2(\text{CH}_3\text{CN})_2]^{2+}$ (**1**, $\text{L}=\text{N}$ -pyrimid-2-ylimidazolyldiene) was prepared according to an established procedure [32]. Elemental analyses were performed on a Flash EA1112 instrument (Thermo Fisher Scientific, Waltham, MA, USA). ^1H , ^{13}C and ^{31}P NMR spectra were recorded on Bruker (Billerica, MA, USA) Avance-400 (400 MHz) spectrometer. Chemical shifts (δ) are expressed in ppm downfield to tetramethylsilane at $\delta = 0$, and coupling constants (J) are expressed in Hz.

1.2 Synthesis of $[\text{FeL}_2(\text{Ph}_3\text{PO})_2](\text{PF}_6)_2$ (**2**)

A yellowish-red solution of **1** (38 mg, 0.05 mmol) in 4 mL of acetonitrile and triphenylphosphine (26 mg, 0.1 mmol) was stirred at 60°C for 10 h in air. Most of **1** was recovered. However, further crystallization of the filtrate gave a few dark red single crystals suitable for X-ray diffraction. Spectroscopic characterization was not performed.

1.3 Synthesis of $[\text{FeL}_2(\text{dppe})](\text{PF}_6)_2$ (**3** and **3'**)

A yellowish-red solution of **1** (38 mg, 0.05 mmol) in 4 mL of acetonitrile and 1,2-bis(diphenylphosphino)ethane (20 mg, 0.05 mmol) was stirred at 40°C for 12 h in air. After concentrating to approximately 2 mL, addition of 20 mL of diethyl ether afforded a red solid which was collected, washed with diethyl ether, and dried in vacuo. Yield: 44 mg (83%). Recrystallization from CH_3CN -diethyl ether gave **3** and **3'** as dark red and red crystalline solids which were separated by hand. For **3**: ^1H NMR (400 MHz, acetone- d_6): δ 9.00 (dd, $J = 4.8, 1.6$ Hz, pyrimidyl, 1H), 8.64 (dd, $J = 4.8, 1.6$ Hz, pyrimidyl, 1H), 8.55 (d, $J = 6.0$ Hz, pyrimidyl, 1H), 8.28, 8.26 (both d, $J = 2.2$ Hz, imidazolyldiene, each 1H), 7.75 (d, $J = 6.0$ Hz, pyrimidyl, 1H), 7.72 (d, $J = 2.4$ Hz, imidazolyldiene, 1H), 7.68–7.64 (m, Ph, 2H), 7.53–7.39 (m, pyrimidyl and Ph, 9H), 7.31–7.24 (m, Ph, 3H), 7.15–7.00 (m, pyrimidyl, imidazolyldiene and Ph, 7H), 6.76 (t, $J = 8.8$ Hz, Ph, 2H), 4.33 (dtd, $J = 41.6, 15.0$, and 4.4 Hz, CH_2 , 1H), 4.10 (dtd, $J = 41.6, 15.0$, and 4.4 Hz, CH_2 , 1H), 3.47 (s, CH_3 , 3H), 3.43–3.38 (m, CH_2 , 1H), 3.35–3.29 (m, CH_2 , 1H), 2.58 (s, CH_3 , 3H). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, DMSO- d_6): δ 74.0, 57.4 (both d, $J_{\text{PP}} = 39$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, acetone- d_6): δ 198.6 (dd, $J_{\text{C-P}} = 23.6, 21.2$ Hz, Fe–C), 196.3 (dd, $J_{\text{C-P}} = 16.4, 12.3$ Hz, Fe–C), 163.9, 163.8, 161.2, 160.3, 159.8, 158.9, 158.0, 135.7–128.7 (Ph), 120.2, 119.9, 119.0, 118.9, 116.7, 37.5, 36.2, 26.7 (dd, $J_{\text{C-P}} = 25.8, 12.6$ Hz), 24.4 (dd, $J_{\text{C-P}} = 26.4, 11.8$ Hz). Anal. Calcd. (%) for $\text{C}_{42}\text{H}_{40}\text{F}_{12}\text{FeN}_8\text{P} \cdot \text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$: C, 47.03; H, 4.04; N, 11.22. Found (%): C, 46.75; H, 3.81; N, 11.27. For **3'**: ^1H NMR (400 MHz, acetone- d_6): δ 8.96 (dd, $J = 5.0, 1.4$ Hz, pyrimidyl, 2H), 8.34 (dd, $J = 5.0, 1.4$ Hz, pyrimidyl, 2H), 8.19 (d, $J = 1.8$ Hz, imidazolyldiene, 2H), 7.49, (t, $J = 5.0$, pyrimidyl, 2H), 7.46–7.40 (m, Ph, 2H), 7.36–7.35 (m, Ph, 2H), 7.39–7.32 (m, Ph, 8H), 7.25–7.22 (m, Ph, 4H), 7.20 (d, $J = 1.8$ Hz, imidazolyldiene, 2H), 7.00–6.96 (m, Ph, 4H), 4.03

(dd, $J = 26.8, 9.6$ Hz, CH_2 , 2H), 3.15 (d, $J = 8.4$ Hz, CH_2 , 2H), 3.1 (s, CH_3 , 6H). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, acetone- d_6): δ 63.9 (d, $J_{\text{PP}} = 26.7$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, acetone- d_6): δ 200.1 (t, $J_{\text{CP}} = 19.1$ Hz, Fe–C), 166.4, 161.8, 160.2, 132.4, 131.7, 130.2–130.0 (Ph), 129.4, 129.3, 129.2, 121.5, 120.2, 39.8, 27.5 (t, $J_{\text{CP}} = 19.8$ Hz). Anal. Calcd. (%) for $\text{C}_{42}\text{H}_{40}\text{F}_{12}\text{FeN}_8\text{P}_4$: C, 47.39; H, 3.79; N, 10.53. Found (%): C, 47.31; H, 3.86; N, 10.44.

1.4 Synthesis of $[\text{FeL}_2(\text{en})](\text{PF}_6)_2$ (**4**)

Compound **4** was prepared from **1** (38 mg, 0.05 mmol) and ethane-1,2-diamine (10 μL , 0.05 mmol) in 4 mL of acetonitrile in a similar manner to **3**. Yield: 33 mg (91%). Recrystallization from $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ -diethyl ether gave dark red crystals. ^1H NMR (400 MHz, DMSO- d_6): δ 8.84 (dd, $J = 5.2, 1.6$ Hz, pyrimidyl, 2H), 8.77 (dd, $J = 5.2, 1.6$ Hz, pyrimidyl, 2H), 8.27, 7.48 (both d, $J = 2.0$ Hz, imidazolyldiene, each 2H), 7.46 (d, $J = 5.2$ Hz, pyrimidyl, 2H), 4.88 (d, $J = 10.8$ Hz, NH_2 , 2H), 4.18 (d, $J = 4.8$ Hz, NH_2 , 2H), 2.90, 2.35 (both br, CH_2 , each 2H), 2.72 (s, CH_3 , 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6): δ 205.3 (Fe–C), 164.2, 160.7, 157.7, 128.7, 118.1, 117.5, 43.2, 35.9. Anal. Calcd. (%) for $\text{C}_{18}\text{H}_{24}\text{F}_{12}\text{FeN}_{10}\text{P}_2 \cdot 0.5\text{CH}_3\text{CN} \cdot 0.5\text{CH}_2\text{Cl}_2$: C, 29.68; H, 3.38; N, 18.63. Found (%): C, 30.08; H, 3.30; N, 18.60.

1.5 Synthesis of $[\text{FeL}_2(\text{pda})](\text{PF}_6)_2$ (**5**)

Compound **5** was prepared from **1** (76 mg, 0.1 mmol) and propane-1,3-diamine (50 μL) in a similar manner to **3**. Yield: 69 mg (93%). Recrystallization from $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ -diethyl ether gave dark red crystals. ^1H NMR (400 MHz, DMSO- d_6): δ 8.97 (d, $J = 5.6$ Hz, pyrimidyl, 2H), 8.86 (d, $J = 5.6$ Hz, pyrimidyl, 2H), 8.23, 7.41 (both d, $J = 2.2$ Hz, imidazolyldiene, each 2H), 7.50 (t, $J = 5.6$ Hz, pyrimidyl, 2H), 4.54, 3.92 (both t, $J = 6.5$ Hz, NH_2 , each 2H), 2.87, 2.68, 1.58 (all unresolved m, CH_2 , each 2H), 2.67 (s, CH_3 , 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, acetone- d_6): δ 203.1 (Fe–C), 165.0, 158.0, 128.3, 118.6, 118.4, 117.5, 40.1, 39.8, 35.0, 27.1. Anal. Calcd. (%) for $\text{C}_{19}\text{H}_{26}\text{F}_{12}\text{FeN}_{10}\text{P}_2 \cdot 1.5\text{CH}_3\text{CN} \cdot 0.5\text{CH}_2\text{Cl}_2$: C, 32.01; H, 3.76; N, 19.08. Found (%): C, 32.47; H, 3.65; N, 18.78.

1.6 Synthesis of $[\text{FeL}_2(\text{phen})](\text{PF}_6)_2$ (**6** and **6'**)

Compounds **6** and **6'** were prepared from **1** (38 mg, 0.05 mmol) and 1,10-phenanthroline (9 mg, 0.05 mmol) in a similar manner to **3**. Yield: 24 mg (57%). Recrystallization from CH_3CN -diethyl ether gave two isomers of crystals that were red and dark red, respectively. For **6**: ^1H NMR (400 MHz, DMSO- d_6): δ 8.92 (d, $J = 4.8$ Hz, pyrimidyl, 2H), 8.68 (d, $J = 7.6$ Hz, phenanthroline, 2H), 8.53 (s, phenanthroline, 2H), 8.28, 7.70 (both s, imidazolyldiene, each 2H), 8.13 (d, $J = 4.8$ Hz, pyrimidyl, 2H), 7.73–7.67 (m, phenanthroline, 4H), 7.40 (t, $J = 4.8$ Hz, pyrimidyl, 2H), 2.64 (s,

CH₃, 6H). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆): δ 203.5 (Fe–C), 167.8, 159.7, 154.6, 148.4, 136.0, 129.9, 129.5, 128.0, 125.7, 120.7, 118.8, 35.3. Anal. Calcd. (%) for C₂₈H₂₄F₁₂FeN₁₀P₂·0.5Et₂O·H₂O: C, 40.38; H, 3.39; N, 15.70. Found (%): C, 39.95; H, 2.90; N, 15.63. For **6'**: ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.4 (t, *J* = 6.8 Hz, pyrimidyl, 3H), 8.62 (d, *J* = 8.4 Hz, pyrimidyl, 1H), 8.59, 8.41, 7.84, 7.49 (all s, imidazolylidene, each 1H), 8.38 (d, *J* = 9.2 Hz, pyrimidyl, 1H), 8.27 (d, *J* = 8.8 Hz, pyrimidyl, 1H), 8.03–7.98 (m, phenanthroline, 3H), 7.80 (d, *J* = 6.0 Hz, phenanthroline, 1H), 7.63 (t, *J* = 6.8 Hz, phenanthroline, 1H), 7.37 (d, *J* = 5.6 Hz, phenanthroline, 1H), 7.32 (t, *J* = 5.8 Hz, phenanthroline, 1H), 7.28 (t, *J* = 10.8 Hz, phenanthroline, 1H), 3.26, 2.47 (all s, CH₃, each 3H). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆): δ 204.6 (Fe–C), 203.1 (Fe–C), 163.6, 161.5, 160.1, 159.7, 159.5, 159.0, 158.5, 153.5, 148.5, 147.5, 137.6, 136.8, 130.5, 130.0, 129.9, 129.5, 128.1, 126.9, 126.2, 120.7, 119.8, 119.5, 118.5, 118.4, 36.1, 35.1. Anal. Calcd. (%) for C₂₈H₂₄F₁₂FeN₁₀P₂·0.5CH₃CN: C, 40.18; H, 2.97; N, 16.97. Found (%): C, 40.58; H, 3.08; N, 16.42.

1.7 Synthesis of [FeL₂(acac)](PF₆) (**7**)

A solution of **1** (38 mg, 0.05 mmol) in 4 mL of acetonitrile was added to acetylacetonate (6 μ L, 0.06 mmol) and K₂CO₃ (8.3 mg, 0.06 mmol) at 40°C. After stirring for 5 h, the solution was concentrated to approximately 2 mL. Addition of diethyl ether (20 mL) afforded a dark red solid which was collected, washed with water and diethyl ether, and dried in vacuo. Yield: 24 mg (77%). Recrystallization from CH₃CN-diethyl ether gave dark red crystals suitable for X-ray diffraction. ¹H NMR (400 MHz, acetone-*d*₆): δ 8.86 (dd, *J* = 5.0, 2.4 Hz, pyrimidyl, 2H), 8.87 (dd, *J* = 5.0, 2.4 Hz, pyrimidyl, 2H), 8.25, 7.37 (d, *J* = 2.0 Hz, imidazolylidene, each 2H), 7.47 (t, *J* = 5.0 Hz, pyrimidyl, 2H), 5.45 (s, CH, 1H), 2.96 (s, CH₃, 6H), 1.86 (s, CH₃, 6H). ¹³C{¹H} NMR (100 MHz, acetone-*d*₆): δ 207.5 (Fe–C), 189.2, 163.6, 160.4, 157.4, 127.8, 118.0, 117.7, 98.6, 35.6, 27.9. Anal. Calcd. (%) for C₂₁H₂₃F₆FeN₈O₂P: C, 40.53; H, 4.05; N, 18.01. Found (%): C, 40.42; H, 3.69; N, 17.79.

1.8 Synthesis of [FeL₂(pyridine-2-thiolate)](PF₆) (**8**)

Compound **8** was prepared from **1** (36 mg, 0.05 mmol), pyridine-2-thiol (5.5 mg, 0.05 mmol), and K₂CO₃ (8.3 mg, 0.06 mmol) in 4 mL of acetonitrile using the same procedure as for **7**. Yield: 15 mg (48%). Recrystallization from CH₃CN-diethyl ether gave dark red crystals suitable for X-ray diffraction. ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.80 (dd, *J* = 5.6, 2.2 Hz, pyrimidyl, 1H), 9.04 (dd, *J* = 5.0, 2.2 Hz, pyrimidyl, 1H), 8.61 (dd, *J* = 5.0 Hz, 2.2 Hz, pyrimidyl, 1H), 8.47, 8.41, 7.70, 7.62 (all d, *J* = 2.4 Hz, imidazolylidene, each 1H), 7.83 (dd, *J* = 5.6, 2.2 Hz, pyrimidyl, 1H), 7.75 (t, *J* = 5.6 Hz, pyrimidyl 1H), 7.21 (dt, *J* = 6.8, 1.6 Hz,

pyridyl, 1H), 7.01 (t, *J* = 5.0 Hz, pyrimidyl, 1H), 6.64 (d, *J* = 4.8 Hz, pyridyl, 1H), 6.54 (d, *J* = 8.4 Hz, pyridyl, 1H), 6.45 (ddd, *J* = 7.2, 5.2, 1.6 Hz, pyridyl, 1H), 3.19, 3.09 (both s, CH₃, each 3H). ¹³C{¹H} NMR (100 MHz, acetone-*d*₆): δ 211.6 (Fe–C), 210.0 (Fe–C), 176.6, 164.8, 163.3, 162.3, 158.0, 155.8, 154.0, 152.7, 134.0, 128.2, 128.1, 124.6, 119.2, 118.2, 117.1, 117.0, 35.4, 35.0. Anal. Calcd. (%) for C₂₁H₂₀F₆FeN₉PSO·0.5H₂O: C, 39.39; H, 3.31; N, 19.69. Found (%): C, 39.78; H, 3.03; N, 19.19.

1.9 General procedure for Kumada reactions

A Schlenk tube was charged with **1** (1.9 mg, 0.002 mmol), anhydrous THF (2 mL), and heteroaryl halide (1.0 mmol) under a N₂ atmosphere. A solution of Grignard reagent (2.0 mL, 1.0 mol/L in THF) at room temperature was added to the solution of **1** in one portion with stirring. After 12 h, a saturated aqueous solution of NH₄Cl was added to quench the reaction. The mixture was extracted with CH₂Cl₂ (3 $\times$ 10 mL), and the combined organic layer was dried over MgSO₄. After removal of solvent, the crude product was purified by column chromatography on silica gel to afford the desired product.

1.10 X-ray crystallography

Single-crystal X-ray diffraction data from **2** were collected on a Siemens (Munich, Germany) Smart/CCD area-detector diffractometer, and from **3**, **3'**, **4**, **6**, **7**, and **8** on an Oxford Diffraction Gemini Ultra A diffractometer (Agilent Technologies, Santa Clara, CA, USA) with Mo K α radiation (λ = 0.71073 Å) and in ω -2 θ scan mode. Data from **5** were collected with Cu K α radiation (λ = 1.54184 Å). Unit-cell dimensions were obtained with least-squares refinement. Data collection and reduction were performed using SMART and SAINT software for **2** and using the Oxford Diffraction CrysAlisPro software for **3–8** [34,35]. The structures were solved by direct methods, and the non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on *F*² using the SHELXTXL package [36]. Hydrogen atom positions for all of the structures were calculated and allowed to ride on their respective C atoms with C–H distances of 0.93–0.97 Å and *U*_{iso}(H) = 1.2–1.5 *U*_{eq}(C). Disordered solvent could not be modeled successfully and was removed from the reflection data of **5** with SQUEEZE (solvent accessible void volume 459.0 Å³) [37]. Details are given in Table 1.

2 Results and discussion

[FeL₂(CH₃CN)₂]²⁺ (**1**) was prepared by reacting Ag-*N*-pyrimid-2-ylimidazolylidene complex with iron powder [32,33]. Reactions of **1** with various donors were performed at 40°C, and the results are summarized in Scheme 1.

Table 1 Summary of X-ray crystallographic data for complexes **2–4** and **6–8**

	2	3	3'	4	6	7	8
Formula	C ₅₂ H ₄₆ F ₁₂ FeN ₈ O ₄ P ₄	C ₄₈ H ₄₉ F ₁₂ FeN ₁₁ P ₄	C ₄₂ H ₄₀ F ₁₂ FeN ₈ P ₄	C ₁₈ H ₂₆ F ₁₂ FeN ₁₀ P ₂	C ₃₀ H ₂₇ F ₁₂ FeN ₁₁ P ₂	C ₂₀ H ₂₃ F ₆ FeN ₉ O ₂ P	C ₂₁ H ₂₀ F ₆ FeN ₉ PS
Fw	1254.70	1187.71	1064.55	728.28	887.42	620.29	631.35
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	orthorhombic	Monoclinic	Monoclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>C</i> 2/ <i>c</i>	<i>Pbcn</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	11.0030(10)	11.5997(6)	11.1540(18)	19.5256(6)	12.7587(5)	20.8286(7)	10.3598(3)
<i>b</i> (Å)	11.7000(12)	13.0303(6)	13.4789(15)	9.1837(3)	25.3697(10)	14.3051(4)	13.9602(3)
<i>c</i> (Å)	12.1080(15)	20.3431(11)	14.945(3)	15.3852(5)	22.2437(6)	18.9004(7)	18.7153(5)
α (°)	71.4670(10)	86.845(4)	85.090(13)	90	90	90	90
β (°)	79.479(2)	79.105(4)	87.87(2)	97.314(3)	90	101.892(4)	101.777(3)
γ (°)	76.325(2)	65.347(5)	82.584(16)	90	90	90	90
<i>V</i> (Å ³)	1426.2(3)	2743.2(2)	2219.1(6)	2736.39(15)	7200.0(4)	5510.6(3)	2649.72(12)
<i>Z</i>	1	2	2	4	8	8	4
<i>D</i> _{calc} (Mg/m ³)	1.461	1.438	1.593	1.768	1.638	1.495	1.583
<i>M</i> (mm ⁻¹)	0.467	0.477	0.578	0.782	0.612	0.688	6.536
<i>F</i> (000)	640	1216	1138	1464	3586	2278	1216
θ range	1.79–25.01	3.18–25.01	2.71–27.56	3.53–25.09	3.28–25.01	2.96–25.01	3.98–67.06
Reflections collected	7503	9644	24155	5939	23133	4846	17954
Reflections unique (<i>R</i> _{int})	4969 (0.0260)	9644 (0.0000)	10155 (0.0602)	2427 (0.0259)	6333 (0.0485)	4846 (0.0000)	4725 (0.0536)
Goodness-of-fit on <i>F</i> ²	1.023	0.939	1.073	1.075	0.936	1.108	1.062
<i>R</i> [<i>I</i> > 2 σ <i>I</i>]	0.0590, 0.1397	0.0747, 0.2037	0.0978, 0.2303	0.0493, 0.1403	0.0650, 0.1873	0.0482, 0.1372	0.0866, 0.2475
<i>R</i> (all data)	0.1039, 0.1758	0.1296, 0.2202	0.1527, 0.2750	0.0631, 0.1473	0.1120, 0.2034	0.0605, 0.1454	0.1064, 0.2722
Largest diff. peak and hole (e Å ⁻³)	0.616, −0.458	0.955, −0.558	0.906, −0.558	0.738, −0.454	2.855, −0.482	0.823, −0.503	1.117, −0.738

Scheme 1 Syntheses for **2–6**, **7**, and **8**. (i) PPh₃, CH₃CN, 60°C; (ii) dppe, acetone, 40°C; (iii) ethane-1,2-diamine, CH₃CN, 40°C; (iv) propane-1,3-diamine, acetone, 40°C; (v) 1,10-phenanthroline, CH₃CN, 40°C; (vi) acetylacetone, K₂CO₃, 40°C; (vii) pyridine-2-thiol, K₂CO₃, CH₃CN, 40°C.

2.1 Reactions of $[\text{FeL}_2(\text{CH}_3\text{CN})_2]^{2+}$ with phosphines

Treatment of $[\text{FeL}_2(\text{CH}_3\text{CN})_2]^{2+}$ with two equivalents of PPh_3 in acetonitrile did not give the expected $[\text{FeL}_2(\text{PPh}_3)_2]^{2+}$, and the starting complex was recovered in up to 80% yield. A few single crystals of $[\text{Fe}(\text{LO})_2(\text{Ph}_3\text{PO})_2]^{2+}$ (**2**) were obtained from some reactions. However, **2** was not obtained in all experiments. The structure of **2** is shown in Figure 1. The asymmetric unit consists of a half molecule with an inversion center at the Fe(II) ion. The two imidazolylidene and PPh_3 were oxidized to imidazolone and PPh_3O , respectively. The oxidation of coordinated imidazolylidene to imidazolone in air has been observed in some cases [33]. Such reactions might imply that the complex could activate molecular oxygen in air [38]. Each pair of the same donors was arranged in a *trans* fashion. Two Ph_3PO molecules occupied the axial positions. The Fe–O bond distances between iron and Ph_3PO or imidazolone were essentially the same. The ligand 1-methyl-3-(pyrimidin-2-yl)-1*H*-imidazol-2(3*H*)-one was twisted forming a six-membered ring with Fe(II) ion in a boat conformation.

Unlike PPh_3 , dppe reacted readily with **1** affording a mixture of **3** and **3'** in a ratio of approximately 1/4. The two isomers could be easily separated by recrystallization from acetonitrile and diethyl ether. The ^{31}P NMR spectrum of **3** showed two doublets at δ 74.0 and 57.4 with $J_{\text{PP}} = 39$ Hz, and that of **3'** showed a doublet with a coupling constant of 26.7 Hz. In the ^{13}C NMR spectrum of **3**, two double doublets were observed at δ 198.6 ($J_{\text{C-P}} = 23.6$ and 21.2 Hz) and δ 196.3 ($J_{\text{C-P}} = 16.4$ and 12.3 Hz) because of coupling of the carbenic carbon with *cis*- and *trans*-arranged phosphines. By comparison, **3'** showed only one triplet at δ 200.1 with $J_{\text{C-P}} = 19.1$ Hz because of its coupling with two phosphines. The structures of **3** and **3'** are given in Figure 2.

Figure 1 ORTEP drawing of the cationic section of **2**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been removed for clarity. Selected bond distances (Å): Fe(1)–O(1) 2.054(3), Fe(1)–O(2) 2.063(3), and Fe(1)–N(3) 2.102(4). Symmetry code: A $-x+2$, $-y+1$, $-z+1$.

Figure 2 ORTEP drawing of the cationic sections of **3** (a) and **3'** (b). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been removed for clarity. Selected bond distances (Å) for **3**: Fe(1)–C(2) 1.954(5), Fe(1)–C(10) 1.949(5), Fe(1)–N(8) 2.027(4), Fe(1)–N(4) 2.044(4), Fe(1)–P(1) 2.270(2), and Fe(1)–P(2) 2.302(2). For **3'**: Fe(1)–C(1) 1.990(5), Fe(1)–C(9) 1.969(5), Fe(1)–N(3) 2.036(5), Fe(1)–N(7) 2.020(5), Fe(1)–P(1) 2.284(2), and Fe(1)–P(2) 2.277(2).

The two P-donors of dppe were crystallographically inequivalent and *trans* to one NHC and one pyrimidine group, respectively. In **3'**, the two imidazolylidenes were arranged *trans* to each other, and two phosphorous atoms were located *trans* to the two pyrimidines. The two planar 1-methyl-3-(pyrimidin-2-yl)imidazolylidenes were perpendicular to each other. The Fe–C and Fe–P bond distances were normal and consistent with those of known iron(II) complexes [39,40].

2.2 Reactions of $[\text{FeL}_2(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ with N-donors

As described in Scheme 1, reaction of ethane-1,2-diamine with **1** readily led to the replacement of two coordinated acetonitriles, and produced $[\text{FeL}_2(\text{en})](\text{PF}_6)_2$ (**4**) as a dark red crystalline solid. $[\text{FeL}_2(\text{pda})](\text{PF}_6)_2$ (**5**) was obtained in a similar manner. The carbene carbon signals of **4** and **5** in their ^{13}C NMR spectra showed only one singlet at δ 205.3 and 203.1, respectively. This illustrates that the two NHC moieties are magnetically equivalent. The structure of **4** is given in Figure 3. The iron was surrounded by two 1-methyl-3-(pyrimidin-2-yl)imidazolyli-dene ligands and one 1,2-ethylenediamine molecule. The two nitrogen atoms of ethylenediamine were *trans* to the NHC groups, and the two pyrimidines were *trans* to each other. The Fe–C and Fe–N bond distances were essentially the same as those in **1** [33].

Substitution of two acetonitriles of **1** by phenanthroline also gave a mixture of two isomers (**6** and **6'**) of $[\text{FeL}_2(\text{phen})](\text{PF}_6)_2$ as red and dark-red crystalline solids. The ^1H NMR spectrum of **6** showed only one set of resonance signals from 1-methyl-3-(pyrimidin-2-yl)imidazolyli-dene, and its carbene carbon showed only one singlet at δ 203.5 in the ^{13}C spectrum. In the ^1H and ^{13}C spectra of **6'**, each aromatic proton and carbon showed independent resonance peaks. The ^{13}C resonance peaks of the two carbenic carbons were observed at δ 204.6 and 203.1 for **6'**. The structure of **6** is given in Figure 4. The replacement of two acetonitriles resulted in a rearrangement of the coordination environment, and the two nitrogen atoms of phenanthroline

Figure 3 ORTEP drawing of the cationic section of **4**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been removed for clarity. Selected bond distances (Å): Fe(1)–C(1) 1.922(3), Fe(1)–N(3) 1.996(3), and Fe(1)–N(5) 2.061(3). Symmetry code: A $-x+1, y, -z+1/2$.

Figure 4 ORTEP drawing of the cationic section of **6**. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å): Fe(1)–C(1) 1.975(5), Fe(1)–C(9) 1.966(5), Fe(1)–N(3) 2.000(4), Fe(1)–N(7) 2.011(4), Fe(1)–N(9) 1.954(4), Fe(1)–N(10) 1.970(4).

were both *trans* to two pyrimidines. The two NHC groups were also arranged in a *trans* fashion. Two 1-methyl-3-(pyrimidin-2-yl)imidazolyli-dene and one phenanthroline were arranged perpendicular to each other. The Fe–C bond distances were slightly longer than those in **3** and **4** because of a large *trans* effect from the C-donors.

2.3 Reactions of $[\text{FeL}_2(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ with O-donors

Treatment of **1** with acetylacetone in the presence of K_2CO_3 afforded $[\text{FeL}_2(\text{acac})](\text{PF}_6)$ (**7**), which was isolated as a dark red crystalline solid. The ^1H NMR spectrum of the crystals in acetone- d_6 showed that two isomers existed in solution in a 2/3 ratio. However, only **7** could be crystallized from the solution. The structure of **7** is given in Figure 5. The compound can be viewed as a substitution product of **1**, in which two acetonitrile molecules are replaced by an acetylacetonate. The Fe–O bond distances and the O–Fe–O angle are not unusual [41].

2.4 Reactions of $[\text{FeL}_2(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ with O-donors

Treatment of **1** with pyridine-2-thiol and K_2CO_3 gave $[\text{FeL}_2(\text{pyridine-2-thiolate})](\text{PF}_6)$ (**8**) as a dark red solid. In its ^1H NMR spectrum, each proton of the aromatic rings showed an independent resonance peaks. The ^{13}C NMR spectrum of **8** shows two peaks ascribed to two imidazolyli-dene carbons at δ 211.6 and 210.0. The structure of **8** is depicted in Figure 6. In the coordination sphere, two imidazolyli-dene groups were arranged *trans* to a pyrimidine and the sulfur atom. The Fe–S distance of 2.421(2) Å is relatively longer than those found in other iron(II) complexes with pyridine-2-thiolate. This could be because of a large *trans* effect for the NHC ligand [42,43]. PyS^- forms a

Figure 5 ORTEP drawing of the cationic section of **7**. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å): Fe(1)–C(10) 1.905(3), Fe(1)–C(2) 1.912(3), Fe(1)–N(1) 1.967(3), Fe(1)–N(5) 1.980(3), Fe(1)–O(2) 1.983(2), and Fe(1)–O(1) 1.987(2).

Figure 6 ORTEP drawing of the cationic section of **8**. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å): Fe(1)–C(2) 1.908(6), Fe(1)–C(10) 1.905(7), Fe(1)–N(9) 1.955(5), Fe(1)–N(7) 1.987(6), Fe(1)–N(3) 2.033(5), and Fe(1)–S(1) 2.421(2).

four-membered chelate ring through coordination of S(1) and N(9).

3 Catalytic Kumada coupling reactions

The catalytic efficiencies of iron salts in Kumada cross coupling reactions of Grignard reagents with aryl or alkyl halides have been demonstrated previously [13,44–47]. However, investigations of Kumada coupling catalyzed by a well-defined iron-NHC complex are rare. We initially examined

the coupling reactions of various Grignard reagents with aryl bromides or chlorides using an amount-of-substance fraction of 2.5% of **1**. Unfortunately, the yields of desired biphenyls were poor and homocoupling products were the major products. Further studies showed that heteroaryl bromides could be smoothly coupled with ArMgBr in moderate yields at room temperature (Table 2). Decreasing the catalyst amount-of-substance fraction to 0.2% did not influence the yields significantly. Further decreases in the catalyst amount-of-substance fraction to 0.1% considerably decreased the yield. 2,6-Dibromopyridine could be doubly arylated, giving 2,6-diphenylpyridine in 52% yield. Under the same reaction conditions, 2-chloropyridine and 2-chloropyrimidine were much less efficient.

Table 2 Kumada couplings of Ar²MgBr and heteroaryl halide Ar¹X at room temperature ^{a)}

Entry	Ar ¹ X	Ar ² MgBr	Cat. loadings (mol%)	Yield (%) ^{b)}
1			2.5	67
2	1a	2a	1.0	65
3	1a	2a	0.5	65
4	1a	2a	0.2	63
5	1a	2a	0.1	50
6	1a		0.2	71
7	1a		0.2	63
8	1a		0.2	56
9	1a		0.5	64 ^{c)}
10	1a		0.2	21
11		2a	0.2	52
12		2a	0.2	38
13		2a	0.2	32

a) Reaction condition: heteroaryl chloride 1.0 mmol, Grignard reagent 2.0 mmol, THF 4 mL, 12 h, under N₂. b) Isolated yield. c) 90°C, 24 h. The reaction was carried out in toluene.

4 Conclusion

In summary, $[\text{FeL}_2(\text{CH}_3\text{CN})_2]^{2+}$ ($\text{L} = N$ -pyrimid-2-ylimidazolyliene) reacted with various N-, P-, O-, and S-donors to produce a number of iron-NHC complexes with ancillary heteroatom ligands. The structural characterization of these iron-NHC complexes provides new information for further design of new iron catalysts. $[\text{FeL}_2(\text{CH}_3\text{CN})_2]^{2+}$ can efficiently catalyze the coupling reaction of various Grignard reagents with heteroaryl bromides or chlorides. Improvement of the catalytic behavior and application in other transformations of the iron-NHC complexes could be expected by tuning the NHC ligands.

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