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Iron-Catalyzed Hydrosilylation of Aldehydes and Ketones under Solvent-Free Conditions

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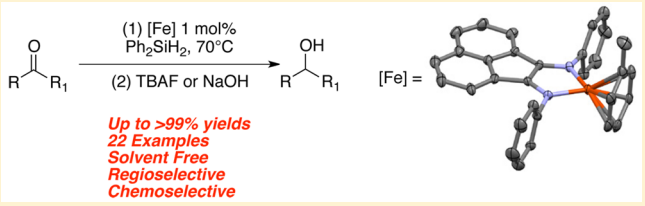
Supporting Information

ABSTRACT: Exposure of aldehyde or ketone to 1 mol % **BIAN-Fe(C_7H_8)** complex in the presence of diphenyl silane affords the corresponding protected alcohol in excellent yields, under mild reaction conditions. Aldehydes and ketones are reduced cleanly in the presence of a broad range of functional groups under solvent-free conditions.

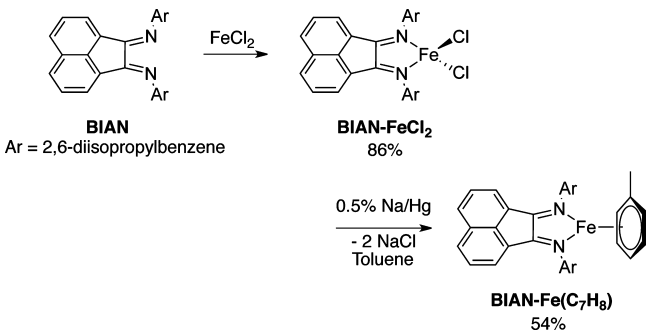


INTRODUCTION

Metal complexes of the robust framework of bis(arylimino)-acenaphthene (BIAN) involving the α-diimine fragment conjugated with the naphthalene ring have found widespread use in coordination chemistry and catalysis.[1] The corresponding iron complexes of BIAN are, however, limited to a relatively few reports,[2] and many of these are tridentate derivatives generated by incorporation of a pendant donor arm into the parent bidentate ligand.[3] The structural rigidity, stereoelectronic tunability based on the N-substitutents, and facile successive electron-accepting feature of the BIAN collectively make it an attractive ligand to design metal complexes suitable for electron transfer processes and catalytic application.

In view of these desirable properties, herein, we report the syntheses of two new iron complexes, **BIAN-$FeCl_2$** and **BIAN-Fe(C_7H_8)** (Scheme 1, BIAN = 1,2-((bis-2,6-diisopropyl-phenyl)imino)acenaphthene), and the application of the toluene complex in the chemoselective reduction of aldehydes and ketones under mild and solvent-free hydrosilylation conditions.

Scheme 1



Selective hydrosilylation of carbonyl compounds is an invaluable synthetic route to alcohols and silyl ether intermediates and has been widely employed in both academia and industry.[4] Complementary to carbonyl reduction protocols employing molecular hydrogen or hydride transfer reagents, hydrosilylation, followed by aqueous workup to cleave the Si–O bond, has emerged as a safe and relatively mild protocol for the synthesis of alcohols (Figure 1). Traditionally, protocols based on precious metal catalysts, particularly ruthenium, rhodium, and iridium, have seen the most widespread use.[5] However, the high cost, low abundance, and toxicity of these elements have prompted the development of alternative methods of carbonyl reduction based upon first-row transition metals such as iron and cobalt.[6] Iron, in particular, is a noteworthy substitute for this application since it is environmentally benign, abundant, inexpensive, and, more significantly, less toxic than the precious metals so often in use in pharmaceutical applications. Highly effective iron-based catalysts for carbonyl reduction have recently emerged based around multidentate ligand architectures featuring both P- and N-donor atoms.[7] Transfer hydrogenation and direct H_2 addition reactions have been reported by the Beller,[8] Casey,[9] and Morris[10] groups.

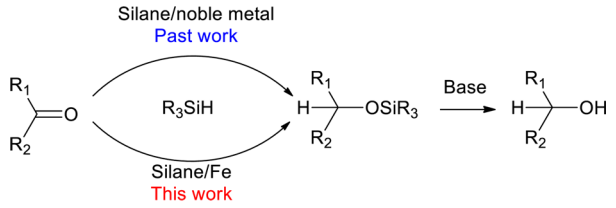


Figure 1. Strategies for catalytic hydrosilylation of carbonyl compounds.

Because of their widespread use, ease of synthesis from commercially available materials, and demonstrated success in

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industrial processes, we sought to explore the application of bidentate bis(imino) ligands in hydrosilylation reactions using base metals such as iron. Despite the diversity of recent contributions made toward the development of iron-catalyzed hydrosilylation of carbonyl compounds,[6] there is still a great demand for practical and chemoselective methodologies.

RESULTS AND DISCUSSION

Stirring 1 equiv of the BIAN ligand with $FeCl_2$ results in the formation of 14-electron, paramagnetic **BIAN-FeCl$_2$**, which, in the solid-state, displays a tetrahedral geometry at the iron center (Scheme 1). The solution magnetic moment was found to be 5.93 B.M. (Evans method)[11] in methylene chloride-*d*2 and is consistent with a tetrahedral, high-spin Fe(II) complex. The isolated dichloride is reduced with excess 0.5% sodium amalgam under an argon atmosphere to furnish the reduced Fe(0) center, which may be conveniently trapped with an aromatic solvent; shown in Scheme 1 is the 18-electron, diamagnetic toluene complex, **BIAN-Fe(C_7H_8)**. The molecular structures of both complexes are presented with the *i*Pr groups removed for clarity (Figure 2).

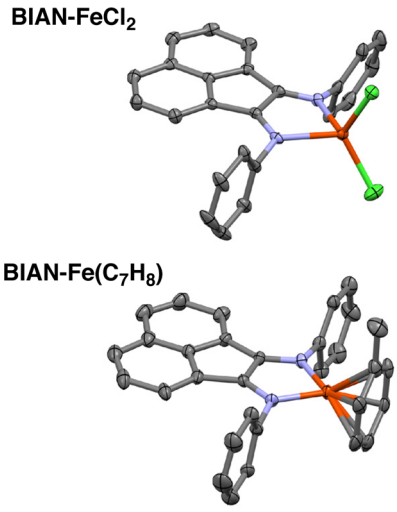


Figure 2. Solid-state structures of **BIAN-FeCl$_2$** and **BIAN-Fe(C_7H_8)** at 30% probability ellipsoids, H atoms and *i*-Pr groups removed for clarity.

Diimine chelates are well-known to behave in a redox noninnocent manner, and important electronic structural information can be gleaned via an inspection of chelate bond distances. Thus, **BIAN-FeCl$_2$** exhibits C−C and C−N distances of 1.506(6) and 1.283(6) Å, respectively. These values are typical of C−C single and C═N double bonds, indicating that no charge transfer has occurred. In contrast, the **BIAN-Fe(C_7H_8)** shows a significant shortening of the C−C bond distance 1.400(4) Å and concomitant lengthening of the C−N distance 1.343(3) Å. These values strongly suggest that a reduction of the ligand has taken place; studies by Cowley,[12a] Chirik,[12b] and Wieghardt[12c] in related systems do not allow an unambiguous assignment of the nature of this reduction (i.e., 0-, 1-, or 2-electrons) based solely on bond distances. To try to gain further insight, **BIAN-Fe(C_7H_8)** was analyzed using ^{57}Fe Mössbauer spectroscopy (Figure 3). At 80 K, the Mössbauer spectrum features a doublet with an isomer shift (δ) of 0.45 mm s^{-1} and a quadrupole splitting (ΔE_q) of 0.41 mm s^{-1}.[13] While such parameters have been widely applied in the study of

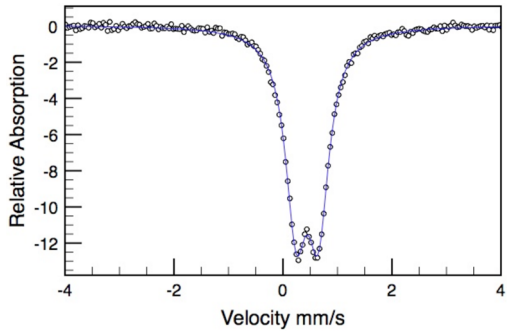
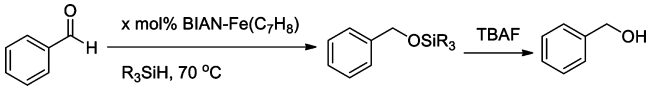


Figure 3. 80 K Mössbauer spectrum of **BIAN-Fe(C_7H_8)**.

redox noninnocent ligand systems, an excellent recent study by Neidig and Milstein has emphasized the importance of combining as many spectroscopic and computational methods as possible in properly assigning metal oxidation state.[14a] At this time, in the absence of further characterization studies employing SQUID magnetometry, EPR, variable-temperature Mössbauer spectroscopy, and computational (DFT) methods, we are hesitant to definitively assign an oxidation state to the metal center in **BIAN-Fe(C_7H_8)**.[14b] Some contribution from an "ene-diamide" form is, however, likely.[12b]

Several commercially available silanes were screened in the presence of the iron precatalyst for the hydrosilylation of benzaldehye (Table 1). Initially, the benzaldehyde is converted

Table 1. Screening of Silanes in the Hydrosilylation of Benzaldehyde[a]



entry	silane (equiv)	[Fe] cat (mol %)	time (h)	yield[b] (%)
1	Et_3SiH (3.0)	1.0	18	0
2	$(EtO)_3SiH$ (3.0)	1.0	18	>70
3	Ph_3SiH (2.0)	1.0	18	0
4	Ph_2SiH_2 (1.0)	1.0	1	>99[c]
5	Ph_2SiH_2 (3.0)	1.0	1	>99
6	Ph_2SiH_2 (1.0)	5.0	1	>99
7	$PhSiH_3$ (1.0)	3.0	1	>99
8	Ph_2SiH_2 (1.0)	none	18	0

[a]Reaction conditions: benzaldehyde (1.0 mmol), 70 °C. [b]Yields were determined by GC−MS analysis of crude reaction mixture using mesitylene as the internal standard. [c]$Ph_2Si(OCH_2Ph_2)_2$ was also observed when the reaction mixture was stirred overnight (ratio of 35:65).

into a siloxy intermediate, which affords benzyl alcohol upon workup. Among the silanes tested, triethoxysilane, diphenylsilane, and phenylsilane gave good yields of benzyl alcohol (Table 1, entries 2, 4−7). Neither triethylsilane nor triphenylsilane displayed any considerable reactivity (Table 1, entries 1 and 3). The observed differences in silane activity with the bis(arylimino)acenaphthene iron complex are consistent with earlier reports using bis(imino)pyridine iron complexes.[15] Thus, the relatively inexpensive diphenylsilane was selected for further investigation as it proved to be an ideal reductant, giving product in almost quantitative yield in less than 1 h at catalyst loadings as low as 1 mol % (Table 1, entry 4). Increased catalyst loading (Table 1, entry 6) or addition of excess silane (Table 1,

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entry 5) afforded no significant difference in overall yield of benzyl alcohol.

After optimizing the reaction conditions and selecting our silane reductant of choice, several aldehydes and ketones (Table 2) were reduced to demonstrate the generality of the catalytic hydrosilylation method under solvent-free conditions. Importantly, **BIAN-Fe(C_7H_8)** is an effective precatalyst without the need for an activator and with only 1 equiv of silane. In most cases, the reaction was complete within 1 h. The progress of the reaction was monitored by GC−MS or ^{1}H NMR spectroscopy by analysis of either the silyl ether or the corresponding alcohol after treatment with TBAF.

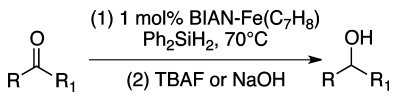
A broad functional group tolerance is observed: aromatic (Table 2, entries 1−8), aliphatic (Table 2, entries 9 and 10), and heterocyclic (Table 2, entries 11 and 12) aldehydes are all reduced in excellent yields. Similarly, aromatic (Table 2, entries 13−15), aliphatic (Table 2, entries 16−18), and heterocyclic ketones (Table 2, entries 19 and 20) are also reduced in good to excellent yields. The hydrosilylation of ketones is, in general, slower than the corresponding reaction for aldehydes. This could arise from an increased steric component; this is supported by entries 16−18 in Table 2. In each case, lower than expected yields are obtained for the sterically larger aliphatic ketones, and in the case of **1r** (Table 2, entry 18), an extended reaction time, 18 h, is required to obtain an isolated product yield of 85%.

To place these results into a proper context, it is worthwhile to compare these data with some leading examples of alternative first-row metal catalysts. For example, a recent report by Stradiotto and Turculet disclosed an Fe complex that displays TOFs of up to 393 min^{-1}.[7] In contrast, Tilley has reported the structurally simple [Fe{N(SiMe$_3$)$_2$}$_2$] to also effectively catalyze the hydrosilylation of aldehydes and ketones with TOFs of ∼10 min^{-1}.[16] It is also important to note that both the Stradiotto and Tilley catalysts are active between 23 and 25 °C. Thus, the activity of **BIAN-Fe(C_7H_8)**, TOF = 0.5 min^{-1} (acetophenone, Table 1, entry 13), is somewhat lower than that of comparable Fe-based analogues.

The iron-catalyzed hydrosilylation of α,β-unsaturated ketones was also examined (Figure 4). In contrast to the extended reaction times required of ketones (Table 2, entries 13−20), hydrosilylation of cyclohexenone (**3**) with Ph_2SiH_2 in the presence of 1 mol % of **BIAN-Fe(C_7H_8)** occurred smoothly in just 30 min at 70 °C. The corresponding alcohol (**4a**), with no evidence for alkene reduction, was obtained exclusively following workup with TBAF hydrolysis. However, if the reduction is allowed to proceed overnight, a 1:1 mixture of **4a** and cyclohexanone (**4b**) is obtained after workup. It is tempting to envision the possibility that **4b** arises from a competing alkene hydrosilylation pathway. However, given that we are aware of only one prior report of alkene hydrosilylation occurring preferentially in the presence of a carbonyl moiety,[17] we tend to discount this explanation. It is more likely that Fe-catalyzed isomerization of the allyl-silylether occurs[18] to generate a protected enol, which, upon workup, tautomerizes to form the ketone **4b** (Figure 4).

In a similar fashion, we carried out the hydrosilylation of the terpenoid citral (**5**; E:Z, 1:1.5, Scheme 2). Reduction occurred exclusively at the carbonyl and with no erosion in stereochemistry (the ratio of E:Z isomers remained 1:1.5; see the Supporting Information, S29).

Table 2. Iron-Catalyzed Hydrosilylation of Aldehydes and Ketones with BIAN-Fe(C_7H_8) and Ph_2SiH_2[a]



Entry	Substrate	Time (h)	Yield[b] (%)
1	**1a** 	0.5	92
2	**1b** 	0.5	95
3	**1c** 	0.5	98
4	**1d** 	0.5	86
5	**1e** 	0.5	92
6	**1f** 	0.5	98
7	**1g** 	1	96
8	**1h** 	1	90
9	**1i** 	0.5	78
10	**1j** 	0.5	98
11	**1k** 	0.5	87
12	**1l** 	0.5	89
13	**1m** 	3	87
14	**1n** 	3	95
15	**1o** 	3	98
16	**1p** 	3	85
17	**1q** 	3	85
18	**1r** 	18	85
19	**1s** 	3	91
20	**1t** 	3	88

[a]Reaction conditions: Substrate (1.0 mmol), **BIAN-Fe(C_7H_8)** (1.0 mol %), 70 °C. [b]Isolated yield of purified product after column chromatography.

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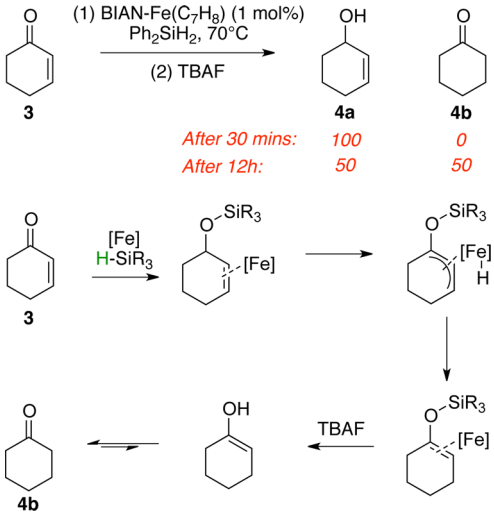
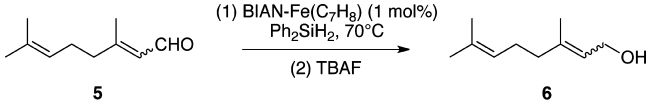


Figure 4. Hydrosilylation of cyclohexenone and potential isomerization mechanism with **BIAN-Fe(C_7H_8)**.

Scheme 2



CONCLUSIONS

In summary, readily accessed bis(imino)acenaphthene iron arene complex, **BIAN-Fe(C_7H_8)**, is an efficient precatalyst for the hydrosilylation of aldehydes and ketones using Ph_2SiH_2. This method exhibits broad functional group tolerance and high activities at 70 °C under solvent-free conditions. Further investigations into the scope, mechanism, and enantioselectivity of these reactions are a continuing area of investigation in our laboratory.

EXPERIMENTAL SECTION

General Synthetic Procedures. All reagents were purchased from commercial vendors and were used without further purification unless otherwise noted. CH_3CN was distilled from CaH_2. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique or in a glovebox. Flash column chromatography was performed using silica gel (230–400 mesh). Analytical thin-layer chromatography (TLC) was performed on 60 F254 (0.25 mm) plates, and visualization was accomplished with UV light (254 and 354 nm) and/or an aqueous alkaline $KMnO_4$ solution, followed by heating. Proton and carbon nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on a JEOL 400 MHz spectrometer with Me_4Si or solvent resonance as the internal standard (^{1}H NMR, Me_4Si at 0 ppm, $CHCl_3$ at 7.24 ppm; ^{13}C NMR, Me_4Si at 0 ppm, $CDCl_3$ at 77.0 ppm). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, br = broad, m = multiplet), coupling constants (Hz), and integration. Gas chromatography–mass spectrometry (GC–MS) and high-resolution mass spectrometry (HRMS) were performed on an electron ionization time-of-flight (EI-TOF) mass spectrometer. Melting points were recorded using a capillary melting point apparatus and are uncorrected.

X-ray Crystallography. Data for **BIAN-$FeCl_2$** and **BIAN-Fe(C_7H_8)** complexes were obtained on a Bruker Smart Apex II CCD diffractometer. All data were collected at room temperature using graphite-monochromated Mo–Kα radiation (λ = 0.71073 Å). Intensity data were collected using ω-steps accumulating area detector images spanning at least a hemisphere of reciprocal space. All the data were corrected for Lorentz polarization effects. A multiscan absorption correction was applied using SADABS[19] or CrystalClear.[20] Structures were solved by direct methods and refined by full-matrix least-squares against F^2 (SHELXTL[21]). All hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealized geometries. Crystallographic data for the two structures are given in the Supporting Information. CCDC-1044803 and CCDC-1044804 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

BIAN Ligand. BIAN ligand was synthesized by refluxing a suspension of acenaphthenequinone and 2,6-diisopropylaniline in the presence of acetic acid, according to a literature procedure.[22] Recrystallization of the crude ligand from hot toluene afforded air-stable orange crystals, 85% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 d, 8.2 Hz, 2H, (acenaphthene), 7.34 t, 7.8 Hz, 2 H, (acenaphthene), 7.27–7.22 (m, 6H, (Ar), 6.61, (d, 7.3 Hz, 2 H, (Aryl), 3.01 (sept, 6.9 Hz, 4 H(*i*Pr-Me) 1.22 (d, 6.9 Hz, 12 H(*i*Pr-Me), 0.95 (d, 6.9 Hz, 12 H(*i*Pr-Me).

BIAN-$FeCl_2$. To a 250 cm^3 round-bottom flask was added BIAN Ligand (4.222 g, 8.433 mmol), $FeCl_2$ (0.822 g, 6.49 mmol), and THF (150 cm^3). The resulting solution was allowed to stir at ambient temperature for 16 h, during which time the solution turned blue. The solution was filtered over a pad of Celite, and the volatiles were removed under vacuum to yield a solid residue. The solid was washed with pentane to afford a paramagnetic blue solid, 86% yield. ^{1}H NMR (400 MHz, C_6D_6): δ −16.75, −2.02, 0.46, 0.94 (d, 5.2 Hz), 1.20 (d, 5.2 Hz), 2.48, 3.04, 6.61, 7.44, 7.91, 12.03. Anal. Calcd for $C_{36}H_{40}Cl_2FeN_2$: C, 68.91, H, 6.43, N, 4.46. Found C, 69.84, H, 6.52, N, 3.87.

BIAN-Fe(C_7H_8). A 100 cm^3 round-bottom flask was charged with Hg (52.612 g, 262 mmol) and pentane (~10 cm^3). With vigorous stirring, Na (0.264 g, 11.4 mmol) was added, and the amalgam was stirred for 0.5 h. Subsequently, **BIAN-$FeCl_2$** (1.434 g, 2.285 mmol), pentane (10 cm^3), and toluene (10 cm^3) were added. The resulting solution was stirred for 48 h under ambient conditions to afford a red solution. The reaction mixture was decanted away from the amalgam and filtered through Celite. After solvent stripping from the filtrate, **BIAN-Fe(C_7H_8)** was isolated as a red solid, 54% yield. ^{1}H NMR (400 MHz, C_6D_6): δ 7.46 (t, 8 Hz, 2H), 7.39 (d, 8 Hz, 4H), 7.27, (d, 8 Hz, 2H), 6.81, (t, 7.4 Hz, 2H), 5.89, (t, 7.4 Hz, 1H, *p*-$C_6H_5CH_3$), 5.72 (d, 6.9 Hz, 2H), 4.96 (d, 6.0 Hz, 2H), 4.80 (t, 6.0 Hz, 2H), 3.86 (sept, 6.9 Hz, 4 H(*i*Pr-Me), 3.04 (s, *tol*, 3H) 1.59 (d, 6.9 Hz, 12 H(*i*Pr-Me), 0.78 (d, 6.9 Hz, 12 H(*i*Pr-Me). ^{13}C NMR (101 MHz, C_6D_6): δ 19.899, 24.50, 25.59, 28.43, 80.61, 80.98, 82.17, 97.67, 118.95, 123.99, 124.03, 126.63, 128.29, 130.71, 132.64, 141.68, 152.08, 152.87. Elem. Anal. Calcd for $C_{43}H_{48}FeN_2$: C, 79.61, H, 7.46, N, 4.32. Found C, 79.10, H, 7.48, N, 4.69.

Reduction of Aldehydes under "Solvent-Free" Conditions. In a glovebox, a 20 mL oven-dried scintillation vial containing a stir bar was charged with **BIAN-Fe(C_7H_8)** (1.0 mol %, 6.49 mg). Subsequently, substrate (1.0 mmol) and Ph_2SiH_2 (1.0 mmol, 184.3 mg) were added. The vial was sealed, and the reaction mixture was transferred to the Schlenk line and stirred at 70 °C for 30 min. A longer reaction time was required for aldehydes **1g** and **1h** (Table 2, entries 7 and 8).

Reduction of Ketones under "Solvent-Free" Conditions. In a glovebox, a 20 mL oven-dried scintillation vial containing a stir bar was charged with **BIAN-Fe(C_7H_8)** (1.0 mol %, 6.49 mg). Subsequently, substrate (1.0 mmol) and Ph_2SiH_2 (1.0 mmol, 184.3 mg) were added. The vial was sealed, and the reaction mixture was transferred to the Schlenk line and stirred at 70 °C for 3 h. A longer reaction time was required for the ketone **1r** (Table 2, entry 18).

Hydrolytic Workup and Purification of Alcohols. THF (2 mL) was added, and the reaction mixture was cooled to 0 °C. The reaction mixture was then quenched with TBAF, 1.0 M in THF (1 mL),

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allowed to warm up to room temperature, and stirred for 3 h. Solvent was evaporated, and the residue was dissolved in diethyl ether (30 mL) and washed with water (2 × 20 mL). The organic phase was separated, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Hydrolysis products with high boiling points were purified by a short silica gel column and washed with *n*-hexane/ethyl acetate (3:2) or dichloromethane/methanol (99:1). Triethylamine was added in the eluting solvent for heterocyclic substrates. Hydrolysis products with low boiling points (**1a**, **1d**, **1k**, **1l**, **1m**,**1n**, **1q**, **1s**, **1t**, and **3**) were purified by distillation.

Benzyl Alcohol (2a). A colorless oil (95 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31−7.36 (m, 5 H), 4.66 (s, 2 H), 2.42 (br s, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.94, 128.55, 7127.62, 127.02, 65.21.

4-Methoxybenzyl Alcohol (2b). A colorless oil (127 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, 2 H, 8.5 Hz), 6.86 (d, 2 H, 5.5 Hz), 4.53 (br s, 2 H), 3.78 (s, 3 H), 2.79 (br s, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.90, 133.06, 128.48, 113.73, 64.53, 55.12.

(4-*N*,*N*-Dimethylamino)benzyl Alcohol (2c). A colorless liquid (149.5 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, 8.7 Hz, 2 H), 6.62 (d, 8.7 Hz, 2 H), 4.53 (s, 2 H), 2.93 (s, 6 H), 1.96 (br s, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.24, 128.92, 128.52, 112.59, 65.13, 40.61.

(4-Trifluoromethyl)benzyl Alcohol (2d). A colorless oil (128.8 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59−7.61 (m, 2 H), 7.45−7.47 (m, 2 H), 4.76 (d, 4.0 Hz, 2 H), 1.94 (br s, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.69, 129.52 (q, $J_{C\text{-}F}$ = 32.0 Hz), 126.81, 125.44 (d, $J_{C\text{-}F}$ = 3.0 Hz), 122.81, 64.46. ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.39.

4-Nitrobenzyl Alcohol (2e). A colorless liquid (146.3 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17−8.19 (d, 2 H, 8.5 Hz), 7.49−7.51 (d, 2 H, 5.8 Hz), 4.80 (s, 2 H), 2.14 (br s, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.14, 134.27, 126.96, 123.700, 63.96.

Naphthalen-1-ylmethanol (2f). A colorless liquid (156.6 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08−8.06 (m, 1 H), 7.88−7.86 (m, 1 H), 7.80 (d, 8.2 Hz, 1H), 7.55−7.40 (m, 4 H), 5.07 (d, 5.5 Hz, 2 H), 2.18 (t, 6.0 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.17, 128.57, 128.54, 126.24, 125.78, 125.31, 125.21, 123.56, 63.44.

2,2-Diphenylethanol (2g). A colorless liquid (193.3 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.33 (m, 4 H), 7.30−7.23 (m, 6 H), 4.20−4.18 (m, 2 H), 4.15 (m, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.35, 134.29, 130.03, 128.62, 128.25, 128.66, 126.72, 66.01, 53.54.

2,6-Bis-methanol-bromobenzene (2h). A colorless solid (193.5 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.33 (m, 4 H), 7.30−7.23 (m, 6 H), 4.20−4.18 (m, 2 H), 4.15 (m, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.35, 134.29, 130.03, 128.62, 128.25, 128.66, 126.72, 66.01, 53.54.

3-Phenylpropan-1-ol (2i). A colorless liquid (106.2 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.33 (m, 4 H), 7.30−7.23 (m, 6 H), 4.20−4.18 (m, 2 H), 4.15 (m, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.35, 134.29, 130.03, 128.62, 128.25, 128.66, 126.72, 66.01, 53.54.

1-Octanol (2j). A colorless liquid (128 mg, 99%). ^{1}H NMR (400 MHz, CDCl3): δ 3.59 (t, 5.5 Hz, 2 H), 1.65 (br s, 1 H), 1.57 (m, 2 H), 1.30−1.19 (m, 10 H), 0.84 (t, J = 3 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 62.97, 32.74, 31.78, 29.37, 29.24, 25.71, 22.61, 14.04.

Thiophen-2-yl-methanol (2k). A colorless liquid (97 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27−7.25 (m, 1 H), 6.98−6.95 (m, 2 H), 4.77 (d, 5.5 Hz, 2 H), 2.27 (t, 6.0 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.04, 126.90, 125.57, 125.52, 59.68.

Pyridin-2-ylmethanol (2l). A colorless liquid (97.1 mg, 89%). ^{1}H NMR (400 MHz, CDCl3): δ 8.35 (d, 4.6 Hz, 1 H), 7.56 (dd, 7.8, 1.2 Hz, 1 H), 7.27 (d, 7.8 Hz, 1 H), 7.06 (dd, 5.5 Hz, 1.2 Hz, 1 H), 4.64 (s, 2 H). ^{13}C NMR (101 MHz, CDCl3): δ 159.90, 148.15, 136.77, 122.05, 120.67, 64.19.

1-Phenylethanol (2m). A colorless liquid (106.2 mg, 78%). ^{1}H NMR (400 MHz, CDCl3): δ 7.30−7.16 (m, 5 H), 3.66(t, 6.4 Hz, 2 H), 2.69 (q, 7.8 Hz, 2 H), 1.90−1.83 (m, 2 H), 1.50 (s, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.78, 134.32, 128.39, 125.83, 62.21, 34.17, 32.03.

2,4-Dimethylpentan-2-ol (2n). A colorless liquid (99 mg, 85%). ^{1}H NMR (400 MHz, CH_3OD): δ 2.96 (dt, 5.5 Hz, 1.3 Hz, 1 H), 1.70 (sept, 6.4 Hz, 2 H), 0.87(d, 6.4 Hz, 12H), ^{13}C NMR (101 MHz, $CDCl_3$): δ 81.76, 30.48, 19.75, 16.84.

1-((4-Trifluoromethyl)benzyl)ethanol (2o). A colorless oil (180.6 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, 8.5 Hz, 2 H), 7.41 (d, 5.8 Hz, 2 H), 4.86 (q, 3.6 Hz, 1 H), 1.43 (d, 1.4 Hz 3 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.63, 129.58 (q, $J_{C\text{-}F}$ = 32.0 Hz), 125.60, 125.32 (d, $J_{C\text{-}F}$, 3.8 Hz), 122.61, 120.01, 69.69. ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.36.

Diphenylmethanol (2p). A colorless solid, m.p, 68−70 °C (180.3 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40−7.30 (m, 8 H), 7.30−7.24 (m, 2 H), 5.80 (d, 5.5 Hz, 1 H), 2.47 (d, 5.5 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.73, 128.42, 128.49, 126.49, 76.13.

Cyclohexanol (2q). A colorless liquid (85 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.51 (s, 1 H), 2.37−2.35 (m, 1H), 1.82−1.79 (m, 2H), 1.67−1.62 (m, 2H), 1.49−1.45 (m, 1H), 1.22−1.18 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 70.25, 35.49, 25.41, 24.10.

Dicyclohexylmethanol (2r). A colorless solid, mp 62 °C (147.2 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.02 (dt, 5.5 Hz, 1.5 Hz, 1 H), 1.77−1.52 (m, 10H), 1.48−1.33 (m, 2H), 1.30−1.91 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 80.41, 39.84, 29.98, 27.31, 26.53, 26.48, 26.16.

1-(Thiophen-2-yl)ethanol (2s). A colorless liquid (116.6 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, 7.5 Hz, 1 H), 6.98 (t, 5.3 Hz, 2 H), 5.07 (m, 1 H), 1.60 (d, 4.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.82, 126.54, 124.28, 123.08, 66.06, 25.13.

1-(Pyridin-3-yl)ethanol (2t). A colorless liquid (96 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, 33 Hz 1 H), 7.69 (s, 1 H), 7.21−7.20 (m, 1H), 5.24−8.84 (br s, 1 H) 4.29 (br s, 1 H) ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.00,147.00, 141.67, 133.45, 123.49, 67.46, 25.11.

2-Cyclohexen-1-ol (4a). A colorless liquid (91.2 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.85−5.76 (m, 1 H), 5.73−5.74 (m, 1H), 4.16 (br s, 1 H), 3.43 (q, 4.7 Hz, 1 H), 2.25−1.75 (m, 4 H), 1.74−1.65 (m, 2H), 1.64−1.45 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 130.51, 129.80, 65.81, 65.44, 31.93, 24.99, 18.89, 15.20.

***trans*-2-Phenyl-2-propen-1-ol (6).** A colorless liquid (128.8 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39−7.41 (m, 2 H), 7.33−7.35 (m, 2 H), 7.25−7.27 (m, 1 H), 6.63 (d, 16.0 Hz, 1 H), 6.36 (dt, J = 15.9, 5.9 Hz, 1 H), 4.32 (dd, 4.6 Hz, 1.3 Hz, 2 H), 1.53 (t, 5.9 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.61, 134.31, 131.01, 128.53, 128.43, 127.62, 126.41, 63.58.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00630.

Complete experimental procedures and full characterization data for **BIAN-FeCl$_2$** and **BIAN-Fe(C$_7$H$_8$)** (PDF)

Crystallographic data for **BIAN-FeCl$_2$** (CIF)

Crystallographic data for **BIAN-Fe(C$_7$H$_8$)** (CIF)

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Notes

The authors declare no competing financial interest.

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