Synthesis and Catalysis of Redox-active Bis(imino)acenaphthene (BIAN) Iron Complexes

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Dedicated to Prof. Jürgen Heck on the occasion of his 66th birthday.

Abstract: Reactions of various substituted bis(imino)acenaphthenes (R-BIAN) with $FeCl_2(thf)_{1.5}$ afforded the tetrahedral complexes (R-BIAN)$FeCl_2$ (**2**) from bulky α-diimines and the octahedral complexes [Fe(R-BIAN)$_3$][$FeCl_4$]$_2$ (**3**) from less bulky ligands. The driving force of the formation of complexes **3** is the high ligand-field stabilization of the low-spin Fe(II). The two sets of complexes exhibit distinct CT band intensities and redox activities. (R-BIAN)$FeCl_2$ complexes showed reversible ligand-centered reductions at –0.9 V (vs. FcH/FcH$^+$); further reduction led to decomposition. Irreversible oxidations were observed at 0.2 and 0.4 V associated with a reduction at –0.4 V as well as a ligand-centered redox event at 1.0 V. First applications of the Fe(BIAN) complexes to hydrogenations of alkenes documented good catalytic activity under mild conditions.

Introduction

The past years have witnessed an increasing interest in the synthesis of well-defined iron complexes and catalysts.[1] These developments have mainly been driven by sustainability criteria (low price, low toxicity) and a lack of available complexes and mechanistic insight.[2] Besides iron nanoparticles and various precursors forming such particles under the reaction conditions,[3] a broad range of well-defined iron complexes have been applied in various catalytic transformations. Very recently, non-innocent, redox-active ligands have complemented the earlier examples of phosphine[4] and *N*-heterocyclic carbene complexes[5] and have tremendously enriched the landscape of coordination chemistry and catalytic applications.[6] One of the most prominent classes of redox-active ligands are diimines of which several classes of complexes and catalysts have been reported. α-Diimine iron complexes with the simplest ligands of this class, 1,4-diazabutadiene (DAB), have been studied since the 1970s.[7] Bis(imino)pyridine (PDI) ligands were successfully applied by Brookhart et al. and Gibson et al. to olefin polymerizations.[8] The key characteristic of PDI ligands is their ability to reversibly exchange electrons with the coordinated metal. Elementary steps within the catalytic cycle involving the transfer of electrons between the metal complex and the substrate are facilitated by such ligand participation as uncommon oxidation states at the metal atom can be avoided. Although bis(imino)acenaphthenes (BIANs) have been known for more than 50 years, they have received much less attention as redox-active ligands in coordination chemistry and catalysis.[9],[10]

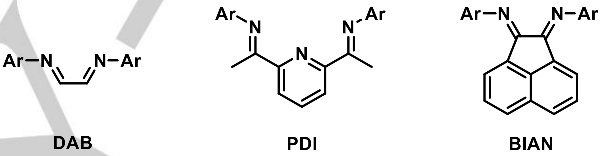

Figure 1. Generic structures of important diimine ligands: bis(imino)pyridine (PDI), 1,4-diazabutadiene (DAB), bis(imino)acenaphthene (BIAN).

The rigidity of the acenaphthene backbone forces these molecules to adopt an *s-cis* conformation which facilitates the formation of stable metal complexes. The stereoelectronic properties of BIANs can easily be tuned by the incorporation of substituted primary amines during imine formation. Such ligands have been reported to efficiently coordinate almost all main-group elements[10] and transition metals.[11] BIANs have been extensively studied in olefin polymerizations[12] and have been shown to be active in many other catalytic transformations.[13] Surprisingly, only very few examples of iron complexes with BIAN ligands have been published.[14] Most of these reports involve modification of the general ligand structure by a pendant donor arm with the aim of mimicking the PDI behavior.[15] Recently, Fe complexes with sterically hindered dipp$_2$BIAN (dipp=Ar=2,6-diisopropylphenyl, see Figure 1) and mes$_2$BIAN (mes=Ar=mesityl, see Figure 1) have been successfully applied as precatalysts to hydrosilylations of carbonyl compounds[16] and olefins.[17] These studies documented only moderate activity of the complexes and involved no full electrochemical characterization of the complexes despite the strongly reducing reaction conditions and the postulation of an active catalyst species in lower oxidation states.
In an effort to enhance the knowledge of well-defined Fe complexes of the BIAN ligand family (**1**), we herein report the synthesis of several high-spin ((R-BIAN)$FeCl_2$, **2**) and low-spin complexes ([Fe(R-BIAN)$_3$][$FeCl_4$]$_2$, **3**, and [Fe(R-BIAN)$_3$][BF_4]$_2$, **4**) and document their structural, optoelectronic, and electrochemical properties.

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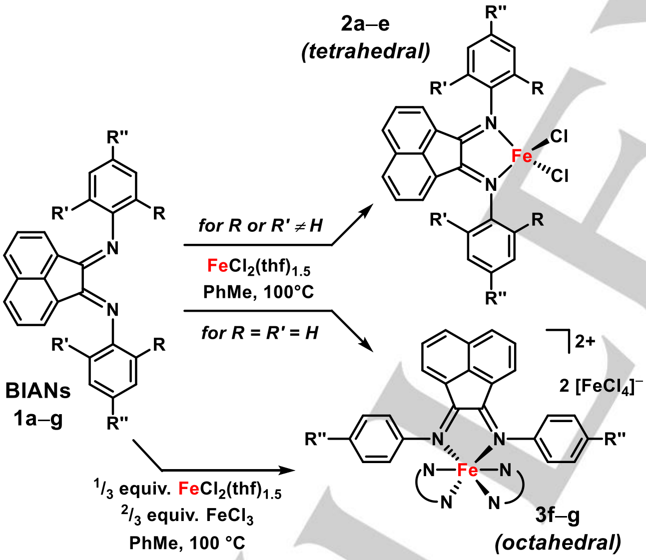
Results and Discussion

Synthesis. The reaction of equimolar amounts of $FeCl_2(thf)_{1.5}$ with bis(imino)acenaphthenes (**1a**–**g**) in toluene at 100 °C resulted in the formation of isolable iron complexes for all cases studied. However, the nature of the *N*-aryl substituents of the BIANs had a crucial role on the composition of resultant Fe(BIAN) complexes. BIANs containing at least one *ortho*-substituent in the *N*-aryl groups gave tetrahedral 1:1 complexes **2**; the less bulky phenyl- and 4-tolyl-BIAN derivatives gave the octahedral 1:3 complexes **3** (Scheme 1). Both series of complexes could clearly be distinguished by mass spectrometry (**2**: $[M]^+$; **3**: $[M]^{2+}$) and UV/Vis spectroscopy (*vide infra*). Complexes **2** and **3** were green solids forming green solutions in acetonitrile. They are soluble in polar organic solvents, such as tetrahydrofuran or dichloromethane, and to a lesser extent in toluene, but are insoluble in hydrocarbons. In general, the 1:3 complexes exhibited higher solubility. The tetrahedral iron complexes **2** were sensitive toward oxidation[18] and hydrolysis. The addition of water to an acetonitrile solution of **2a** (Ar = dipp) instantly caused a color change from green to yellow consistent with the formation of the free BIAN ligand **1a**. In contrast, the octahedral complexes **3** were less sensitive: exposure of solutions thereof to aerobic conditions did not result in visible changes of the appearances over a couple of hours.



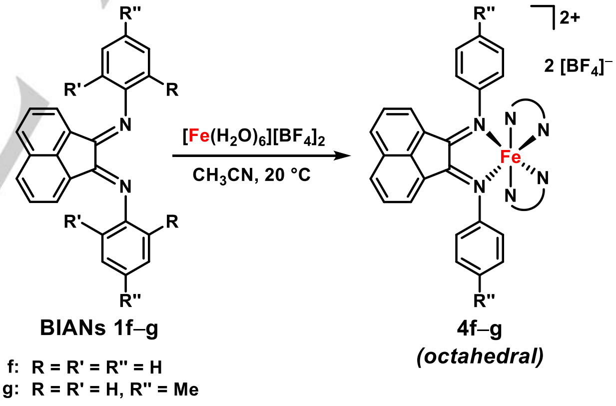
a: R = R' = *i*-Pr, R'' = H
b: R = R' = R'' = Me
c: R = R' = Et, R'' = H
d: R = R' = Me, R'' = H
e: R = *i*-Pr, R' = R'' = H
f: R = R' = R'' = H
g: R = R' = H, R'' = Me

Scheme 1. Ligands **1a**–**g** and synthesis of Fe(BIAN) complexes **2a**–**e**, **3f**–**g**.

The conclusion whether tetrahedral (**2**) or octahedral (**3**) complexes were formed could also be drawn from the presence of unreacted BIAN or by-products thereof in the crude reaction mixture. Purification of the crude mixtures by washing with toluene gave slightly green filtrates for complexes **2** and orange-to-red filtrates for **3**. The synthesis of the $[Fe(R\text{-}BIAN)_3][FeCl_4]_2$ complexes **3** from $FeCl_2(thf)_{1.5}$ is stoichiometrically unbalanced regarding chloride anions and electrons. Assuming strict exclusion of air during the preparation, the oxidation of Fe(II) to Fe(III) must be accompanied by reduction of BIAN which is also documented by the color of the toluene filtrates of **3**. The synthesis of derivative **3f** was also performed from $FeCl_2(thf)_{1.5}$, $FeCl_3$ and **1f** in a 1:2:3 ratio, which increased the yield of the Fe complex from 75% to 87 % and gave a more accurate elemental analysis.

The number of transition metal complexes in which the metal is coordinated by three BIAN ligands is quite limited[14c],[19] and most of these examples are best described with at least one ligand being reduced to a radical anion. To our knowledge, $[Cr((3,5\text{-}Xyl)_2BIAN)_3][PF_6]_3$ [19d] and $[Fe(H_2BIAN)_3][FeBr_3(thf)]_2$ [14c] are the only exclusions. The latter example shows obviously some similarities to compounds **3**; in both cases equimolar amounts of an Fe(II) salt and a BIAN were reacted. However, the ferrate anions in **3** contain Fe(III), which might be caused by the use of iron dichloride instead of iron dibromide, the application of toluene instead of THF or the different electrochemical behavior of **1f** and **1g** and H_2BIAN.

The presence of the paramagnetic and redox-active counterion $[FeCl_4]^-$ in complexes **3f**–**g** resulted in difficult characterizations by NMR and cyclic voltammetry (CV). Therefore, complexes **4f**-**g** were prepared from $[Fe(H_2O)_6][BF_4]_2$ in acetonitrile (Scheme 2).



f: R = R' = R'' = H
g: R = R' = H, R'' = Me

Scheme 2. Synthesis of Fe(BIAN) complexes **4f** and **4g**.

Characterizations. For comparison of spectroscopic data of the ligand-derived complexes, selected Zn complexes (**5a**,**f**,**g**) were synthesized by reaction of $[Zn(H_2O)_6][BF_4]_2$ with **1f**,**g** in acetonitrile and, according to a literature procedure, by reaction of $ZnCl_2$ with **1a** in glacial acetic acid.[20]

UV/Vis spectra of the Fe and Zn complexes and the free ligands were recorded in acetonitrile solution at room temperature. The free R-BIANs **1a**–**g** exhibited intense absorptions in the UV region and a broad absorption at around 400 nm which are commonly assigned to π-π* transitions of the aryl substituents and the acenaphthene backbone and to an intra-ligand charge transfer, respectively.[21] These bands are slightly shifted in the Fe and Zn complexes (Figure 2, Table S1). Additionally, all Fe complexes exhibited charge transfer (CT) absorptions in the range of 550 and 800 nm. The intensity of these absorptions strongly depends on the coordination geometry and serves as an excellent probe to distinguish tetrahedral (molar absorptivity 150–500 M^{-1}·cm^{-1}) and octahedral (6200–14100 M^{-1}·cm^{-1}) Fe(BIAN) complexes. Complex **2a** exhibited two weak absorptions (ligand field bands) in the near infrared at 1435 and 1830 nm with extinction coefficients of 8 and 16 M^{-1}·cm^{-1}, respectively, which is in good agreement with other tetrahedral Fe(II)N$_2$Cl$_2$ complexes (Figure S6).[22]

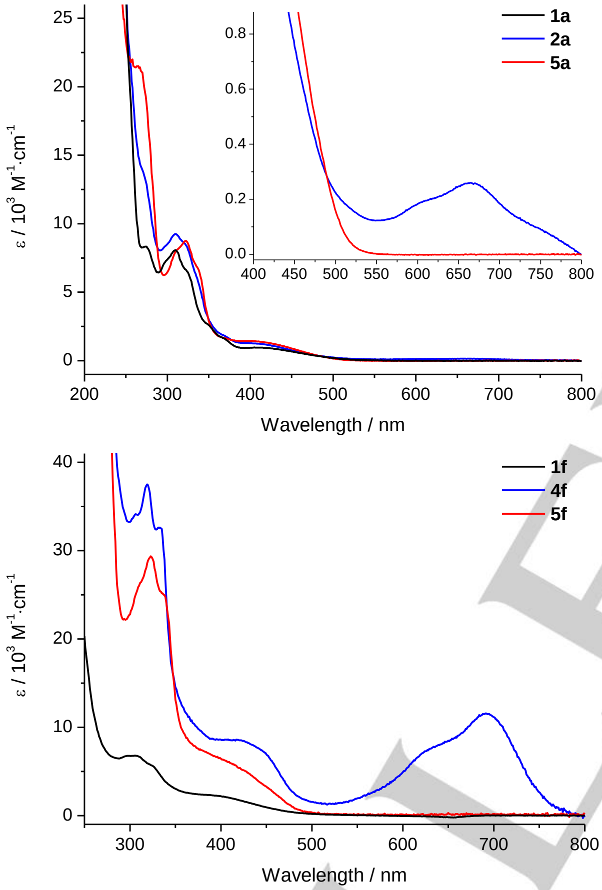


Figure 2. Top: UV/Vis spectra of **1a** (black), **2a** (Fe, blue), and **5a** (Zn, red) in acetonitrile at 10^{-4} M (inset: **2a** and **5a** at 10^{-3} M). Bottom: UV/Vis spectra of **1f** (black), **4f** (Fe, blue), and **5f** (Zn, red) in acetonitrile at 10^{-5}–10^{-4} M.

Selected Fe and Zn complexes were analyzed by single crystal X-ray diffraction. The molecular structures and important bond lengths (Å) and bond angles (°) are given in Figures 3–4 (**2b**,**c**) and S10,11,13–15 (**3f**,**g** **4g**, **5a**,**f**). The crystal and structure refinement data are summarized in Tables S3,4. The asymmetric units of **2b** and **5f** contain only half of the molecule as the Fe compound and the Zn cation lie at a site of crystallographic C_2 symmetry. Contrary, for **3g** and **5a** two independent molecules were found in the asymmetric units. The metal ions are coordinated in a distorted tetrahedral N$_2$Cl$_2$ or distorted octahedral N$_6$ geometry. The distortion is caused by the rigidity of the planar BIAN ligands which results in N–M–N′ bond angles (N, N′ of the same BIAN moiety) between 77 and 82 ° depending on the M–N distance. For the Zn and the tetrahedral Fe complexes, M–N bond lengths between 2.11 and 2.18 Å were found. These separations are 1.99–2.00 Å in the octahedral complexes **3f**,**g** and **4g** which clearly indicates the low-spin state of Fe(II). The Fe–Cl separation in the counterions of **3f** and **3g** is typical for [FeCl$_4$]$^-$.[23] The acenaphthene backbone is essentially planar; the *N*-aryl substituents are orthogonal to this plane. The bond lengths of the N=C–C=N moiety are indicative of a C–C single bond and two C=N double bonds, which is in full agreement with the formulation of a neutral 1,2-diimine ligand.[24],[25] It is noteworthy that the octahedral Fe complexes **3** and **4** contain slightly shortened C–C bonds whereas the C=N bonds are slightly longer. This deviation does not necessarily indicate a partial reduction of the BIAN ligands but could be a consequence of an increased metal-to-ligand backbonding. Comparison of Zn complex **5a** with the corresponding Fe(II) complex[16] and Co(II) complex[26] shows that they form an isomorphous family. The complexes **2b**,**c** and **3g** exhibit in the solid-state parallel displaced π···π interactions between the *N*-aryl substituents, the acenaphthene backbone and co-crystallized toluene molecules. Graphical representations along with geometrical data can be found in the ESI.

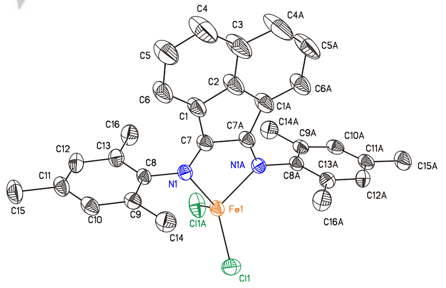


Figure 3. ORTEP diagram (50% probability level) of the molecular structure of **2b** with the atom-numbering scheme. All H atoms and one molecule *n*-pentane are omitted for clarity. Symmetry code: A: –x, y, –z+0.5. Selected bond lengths (Å), angles (°): C7–C7A 1.521(5), C7–N1 1.274(3), C8–N1 1.444(3), Fe1–Cl1 2.2217(7), Fe1–N1 2.1368(19); C7–N1–C8 119.09(19), C7–N1–Fe1 112.92(16), C8–N1–Fe1 112.92(16), N1–Fe1–Cl1 113.65(6), N1–Fe1–Cl1A 113.86(5), N1–Fe1–N1A 78.64(10), Cl1–Fe1–Cl1A 117.24(5).

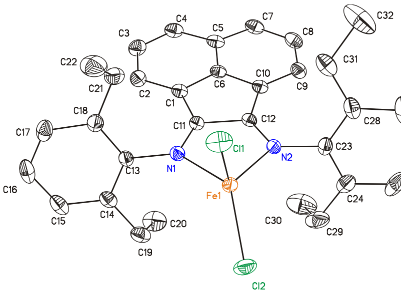


Figure 4. ORTEP diagram (50% probability level) of the molecular structure of **2c** with the atom-numbering scheme. All H atoms and one molecule toluene are omitted for clarity. Selected bond lengths (Å), angles (°): C11–C12 1.510(2), C11–N1 1.284(2), C12–N2 1.281(2), C13–N1 1.4350(19), C23–N2 1.4378(19), Fe1–Cl1 2.2283(5), Fe1–Cl2 2.2182(5), Fe1–N1 2.1422(13), Fe1–N2 2.1251(12); C11–N1–C13 119.69(13), C11–N1–Fe1 111.83(10), C13–N1–Fe1 127.60(9), C12–N2–C23 120.82(13), C12–N2–Fe1 112.78(10), C23–N2–Fe1 125.92(10), N1–Fe1–N2 78.41(5), N1–Fe1–Cl1 104.18(4), N1–Fe1–Cl2 122.51(4), N2–Fe1–Cl1 112.62(4), N2–Fe1–Cl2 113.81(4), Cl1–Fe1–Cl2 118.635(18).

The presence of the octahedral Fe complexes in a low-spin state explains the different reactivity of $FeCl_2$ and $ZnCl_2$ toward BIANs bearing only H atoms in the 2- and 6-positions of the *N*-aryl substituents. The thermodynamic driving force of the formation of $Fe(BIAN)_3$ complexes is most likely due to a significant gain in ligand field stabilization. Consequently, the reaction of $ZnCl_2$ with **1g** gave the tetrahedral 1:1 complex.[21c]

^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded of the octahedral Fe and Zn complexes **4f**,**g** and **5f**,**g**. Unlike in the free BIAN ligands **1f**,**g**, two sets of resonances were observed for the *ortho*/*ortho′* and *meta*/*meta′* positions of the aryl substituents, which are also significantly broader than the remaining resonances of the acenapthene backbone. This clearly indicates that free rotation of the *N*-aryl substituents is hindered in Fe and Zn complexes. The longer M–N distances of **5f**,**g** indicate a smaller rotation barrier and thus give broader ^{1}H resonances of the *ortho* and *meta* protons in comparison with the respective Fe complexes. The $^{13}C\{^{1}H\}$ NMR spectra confirmed the presence of (up to) 13 different carbon atoms in the aromatic region. The magnetic moments of **2a**–**e** in thf-d_8 solutions were between 4.9 and 5.3 μ_B (Evans NMR method), which indicates the presence of high-spin Fe(II) centers.

The redox chemistry of bis(imino)acenaphthenes has extensively been studied in the past. The cyclic voltammograms (CVs) are strongly dependent on the electronic nature of the *N*-aryl substituents; however, the common features are two separate reductions to the monoanionic and dianionic forms and oxidation of the terminal *N*-aryl substituents.[21b],[25] A $4e^{-}$-reduction of **1a** was achieved by Fedushkin et al. by reaction with sodium metal in diethyl ether. The solid-state structures showed that the first two electrons reduce the acenaphthene diimine to the acenaphthylene diamine, and the following two reductions occurred at the naphthalene moiety.[27] CVs were recorded for the tetrahedral complexes **2a**,**c** and **5a** and the octahedral complexes **4f**,**g** and **5f**,**g** in acetonitrile using $[N(n\text{-}Bu)_4][PF_6]$ as electrolyte (Tables 1, S2 and Figures 5, S16–25). The electrochemical features of compounds **2** were very similar and will therefore be discussed on the example of **2a** (Table 1). Fe complex **2a** showed a reversible reduction at –0.91 V which is also present in the Zn complex **5a** at slightly more negative potential (Figure 5). This corresponds to the reduction of the neutral BIAN to the radical anion state. Upon further decrease of potential, additional cathodic waves were observed (e.g. BIAN reduction to dianion, reduction of Fe(II)). However, the following redox events gave complex CVs which were indicative of rapid decomposition of the analyte. An increased potential range to +1.5 V afforded irreversible oxidations at 0.20, 0.42 and 0.99 V and an irreversible reduction at –0.36 V. The reduction event also occurred when the potential was raised to +0.7 V (Figure 5, bottom, dashed line). A comparison with the respective Zn compound showed that solely the oxidation at 0.99 V is ligand-centered (Figure 5, bottom).

Table 1. Cyclic voltammetry data of **2a**,**c**,**d** and **5a**.

	$E_1^{\text{o}\prime}$ (ΔE_p) / mV	E_{pa1} / mV	E_{pa2} / mV	E_{pa3} / mV	E_{pc} / mV
2a	–910 (87)	195	420	990	–360
2c	–920 (78)	185	410	1015	–385
2d	–925 (76)	160	380	n.d.	–355
5a	–995 (88)	–	–	1010	–

n.d.: not determined. E_{pa}: anodic peak potential. E_{pc}: cathodic peak potential.

The difference between $E_1^{\text{o}\prime}$ of **2a**,**c**,**d** and **5a** of 70–85 mV documented that the BIAN ligand in the Fe complexes is slightly less electron-rich than in the Zn complex. A more pronounced metal-to-ligand back bonding in the Zn complex or a stronger π-donation of the BIAN ligands toward Fe would in principle be in agreement with the observation. Though, the inspection of the C–C and C=N bond lengths of the N=C–C=N moiety, which are affected by both interactions, showed no significant differences (*vide supra*). It is instructive to note that Krüger and co-workers recorded a CV of the octahedral Fe(II) complex of **1f** with *N*,*N′*-dimethyl-2,11-diaza[3.3](2,6)pyridinophane that showed reversible BIAN reduction to the radical anion (–1.01 V) and dianion (–1.52 V) and reversible Fe(II)→Fe(III) oxidation (+0.73 V vs. FcH/FcH^{+}).[14d] The striking difference to the behavior of the tetrahedral complexes may result from the degree of anion coordination to the metal. The reduction of the BIAN ligands facilitates the cleavage of coordinated chloride anions forming highly reactive tri- or di-coordinated metal species in solution. Due to the relatively low concentration of the analyte, a stabilization of these species by dimerization is rather unlikely [28] and consequently, rapid decomposition of the reduced metal complexes is to be expected. This may explain why for singly reduced **2a**,**c**,**d** and **5a** an irreversible electrochemical behavior is observed upon further decrease of the applied potential. However, it should not be concealed that free bis(imino)acenaphthenes very often do not show reversible redox events in CVs.[21b],[25]

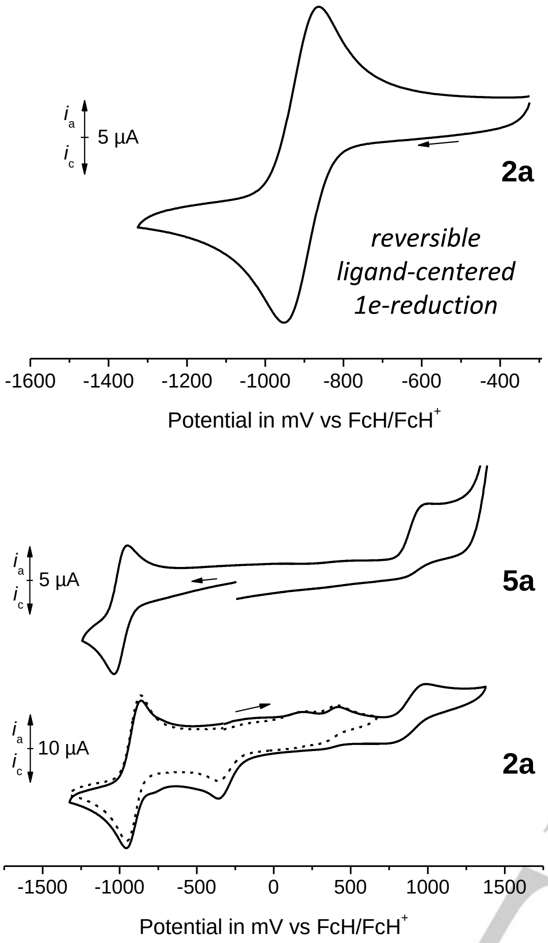
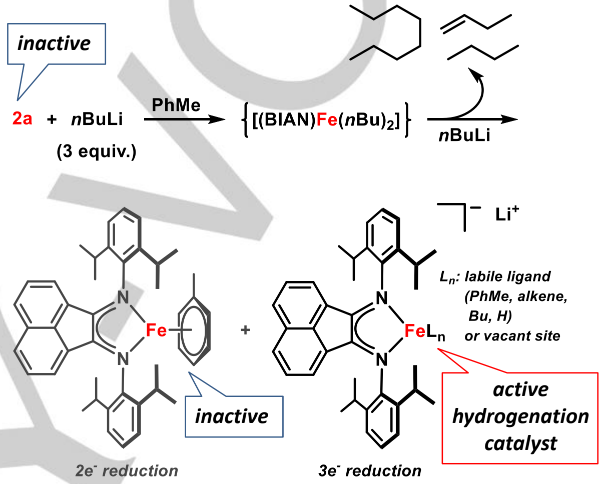
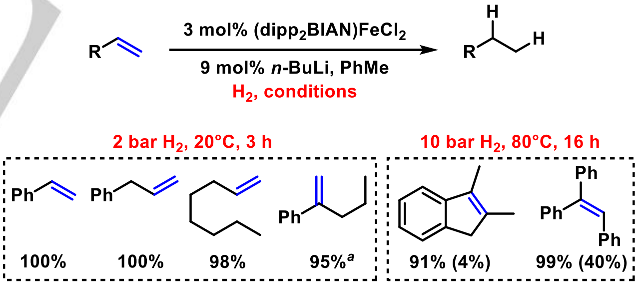


Figure 5. Cyclic voltammograms (scan rate 200 mV·s^{-1}) of **2a** (10^{-3} M (solid line: –1.3 to 1.4 V, dashed line: –1.3 to 0.7 V)) and **5a** ($0.5\cdot10^{-3}$ M).

Catalytic studies. We have then applied the tetrahedral complexes of type **2** to the hydrogenation of alkenes.[29],[30] Good catalytic activities were only observed when the complexes were activated by addition of a strong reductant. Treatment of **2a** with 3 equiv. *n*-butyllithium (*n*-BuLi) afforded the active hydrogenation catalyst.[31] The observation of octane (70%), octenes (18%), and hexadecane (12%) formation from the reaction of **2a** with 3 equiv. *n*-octyllithium in toluene correspond to a reduction of the metal complex by two or more electrons. However, the reduction of **2a** with *n*-BuLi on a preparative scale (150 mg **2a**) afforded a mixture of species. The major component (~70 %) could be separated by extraction of the dried residue with hexane and was identified as (dipp$_2$BIAN)Fe(η^6-C_7H_8), which had previously been prepared by Findlater and co-workers.[16] This formal two-electron reduction species was inactive in the hydrogenation of α-methylstyrene (1.9 bar H_2, 20 °C, 3 h). In contrast, the minor component of the reduction of **2a** with *n*-BuLi which was obtained from extraction with toluene and washing with hexane showed identical catalytic activity to the in-situ generated catalyst mixture ((dipp$_2$BIAN)FeCl$_2$, n-BuLi). In accordance with recent literature, we postulate a three-electron reduction of the (BIAN)FeCl$_2$ complex to a low-valent (BIAN)Fe species which possibly contains the BIAN ligand in the radical anion or dianion state (Scheme 3).[16],[17],[32] Attempts to disclose the chemical identity of this fraction have not yet been successful. Application of the **2a**/BuLi catalyst solution to the hydrogenation of various alkenes resulted in excellent yields of the corresponding alkane products (Scheme 4). Similar reactions with catalytic FeCl$_2$(thf)$_{1.5}$ (and no ligand) gave much lower yields.[33] It is important to note that clean hydrogenations of tri- and tetra-substituted alkenes were achieved at elevated H_2 pressure and temperature.



Scheme 3. Reductive activation of pre-catalyst **2a**.



Scheme 4. Catalytic hydrogenations of alkenes (yield of reactions with 3 mol% FeCl$_2$(thf)$_{1.5}$ in parentheses); ^{a} traces of isomerized product.

Conclusion

A series of Fe complexes of the general composition (R-BIAN)FeCl$_2$ (**2**) and [Fe(R-BIAN)$_3$][FeCl$_4$]$_2$ (**3**) was prepared by reaction of FeCl$_2$(thf)$_{1.5}$ with various bis(imino)acenaphthenes (BIANs). The presence of *N*-aryl substituents in 2- or 6-position governs the formation of tetrahedral or octahedral complexes. The low-spin configuration of Fe(II) in the octahedral complexes **3** suggests that a gain in ligand-field stabilization is the thermodynamic driving force of this pathway. UV/Vis spectroscopy allowed the unambiguous distinction between complexes of type **2** and **3** as the latter exhibited much stronger CT absorptions in the visible region. This interpretation is in full accordance with the results obtained from mass spectrometry and X-ray diffraction. The electrochemical properties of complexes **2** and $[Fe(BIAN)_3][BF_4]_2$ (**4**) were determined by cyclic voltammetry. All compounds showed reversible BIAN-centered 1e$^-$-reductions in the potential range of –0.7 to –1.2 V vs FcH/FcH$^+$, whereby the BIAN ligand in **2** is reduced to a radical anion. A further decrease of the potential leads to irreversible reductions. For $(BIAN)FeCl_2$, a ligand-related irreversible oxidation at 1.0 V was identified along with two Fe-centered irreversible oxidations at 0.2 and 0.4 V associated with a reduction at –0.4 V.

(*i*) The facile synthetic access to iron BIAN complexes, (*ii*) their stereoelectronic modulation by variation of the *N*-aryl substituents, stoichiometry, and counterion, and (*iii*) the non-innocent character of the BIAN ligands are a prime motivation to apply such complexes as catalysts to redox reactions. Initial catalytic studies in hydrogenations of olefins documented the excellent activity of $(dipp_2BIAN)FeCl_2$ (**2a**). Our group is currently investigating further avenues toward new iron-catalyzed reduction, hydrofunctionalization and dehydrogenation protocols with these complexes.

Experimental Section

General procedure for the synthesis $(Ar_2BIAN)FeCl_2$ (2): A Schlenk flask was charged with $FeCl_2(thf)_{1.5}$ (1.0 mmol) and the BIAN ligand (1.1 mmol, 1.1 equiv.) in toluene (20 mL). The mixture was heated to 100 °C and stirred for 16 h during which a precipitate formed. After cooling to r.t., the suspension was concentrated in vacuo and filtered. The solid residue was washed with toluene (3×5 mL) and dried.

$[Fe(Ph_2BIAN)_3][FeCl_4]_2$ (3f): A Schlenk flask was charged with $FeCl_2(thf)_{1.5}$ (0.2 mmol), $FeCl_3$ (0.4 mmol, 2 equiv.) and Ph_2BIAN (0.6 mmol, 3 equiv.) in toluene (12 mL). The mixture was heated to 100 °C and stirred for 16 h during which a green precipitate formed. After cooling to r.t., the suspension was concentrated in vacuo and filtered. The solid residue was washed with toluene (3×5 mL) and dried to afford the **3f** as a green complex in 87% yield (251 mg).

General procedure for the synthesis $[Fe(Ar_2BIAN)_3][BF_4]_2$ (4): A Schlenk flask was charged with $[Fe(H_2O)_6][BF_4]_2$ (1.0 mmol) and BIAN (3.3 mmol, 3.3 equiv.) in acetonitrile (40 mL). After stirring for 20 h at r.t., the green solution was filtered. The filtrate was evaporated to dryness and the solid residue was washed with thf/toluene (1:1, 4×10 mL) and toluene (3×5 mL) and then dried.

General procedure for catalytic hydrogenations of alkenes: A 4 mL vial was charged with a freshly prepared solution of **2a** in toluene (2.50 mL, 0.003 M) and a solution of *n*-BuLi in toluene (45 µL, 0.5 M) under argon. The alkene (0.25 mmol) was added and the vial transferred to a high-pressure reactor. The reactor was purged with H_2 (1 min), sealed, and the internal temperature and pressure adjusted. After the desired reaction time, the autoclave was purged and the vial retrieved. The reaction was quenched with saturated aqueous $NaHCO_3$ (0.5 mL) and extracted with ethyl acetate (1 mL). The organic phases were filtered through a plug of silica (ethyl acetate) and analyzed by quantitative GC-FID analysis vs. internal *n*-pentadecane.

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Keywords: iron • imines • redox-active ligands • electrochemistry • hydrogenations

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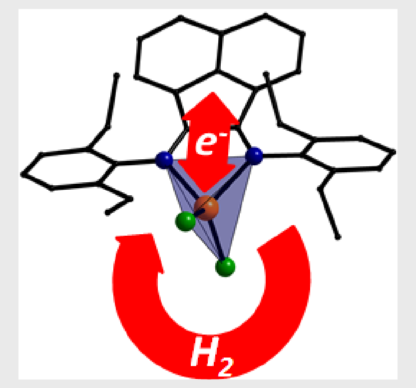
FULL PAPER

A set of redox-active tetrahedral and octahedral bis(imino)acenaphthene iron(II) complexes were prepared and fully characterized. The complexes showed reversible BIAN-centered 1e$^-$-reductions and could be applied to catalytic hydrogenations of bulky alkenes upon reductive activation.



M. Villa, D. Miesel, A. Hildebrandt, F. Ragaini, D. Schaarschmidt, and A. Jacobi von Wangelin**

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Synthesis and Catalysis of Redox-active Bis(imino)acenaphthene (BIAN) Iron Complexes