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1,1′-Ferrocenylene-Bridged Bis(N-Heterocyclic Olefin) Derivatives

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The 1,1′-ferrocenylene (fc)-bridged bis(N-heterocyclic olefin) compounds (IMes=CH)$_2$fc (**1**, IMes = 1,3-dimesitylimidazolin-2-ylidene) and (IPr=CH)$_2$fc (**2**, IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene) were synthesised from (ICH$_2$)$_2$fc (**3**) and the respective N-heterocyclic carbene IMes or IPr. Ligand substitution reactions of **1** and **2** with [BH$_3$(THF)] afforded the complexes [**1**(BH$_3$)$_2$] and [**2**(BH$_3$)$_2$] as mixtures of the *rac*- and *meso*-diastereomers. The new ferrocene derivatives **1**–**3** and the complexes *meso*-[**1**(BH$_3$)$_2$], *rac*-[**1**(BH$_3$)$_2$] and *rac*-[**2**(BH$_3$)$_2$] were structurally characterised by single-crystal X-ray diffraction. **1** and **2** represent a new class of ferrocene-based, and hence redox-active, bidentate ligands. The presence of three redox-active moieties, viz. the ferrocene unit and the two NHO units, is reflected by three consecutive oxidations according to an electrochemical investigation exemplarily performed with **2** by cyclic voltammetry.

Introduction

N-heterocyclic olefins (NHOs)[1] are alkylidene derivatives of N-heterocyclic carbenes (NHCs).[2] More specifically, the alkylidene moiety is appended to the $C_{carbene}$ atom, viz. NHC=CR$_2$. Their chemistry is currently showing a rapid development, reminiscent of that of the NHCs almost three decades ago. NHOs exhibit significantly higher stability under ambient conditions than NHCs and have therefore long been known. For example, the preparation of 2-benzylidene-1,3-dimethylimidazolidine was described by Böhme and Soldan already in 1961.[3] A comprehensive study addressing the synthesis, basicity and NMR spectroscopic features of imidazolidine-based NHOs was published in 1987 by Gruseck and Heuschmann.[4] In 1993, two years after Arduengo described the synthesis and crystal structure of the first stable NHC,[5] the first structurally characterised NHO, 1,3,4,5-tetramethyl-2-methyleneimidazoline, was reported by Kuhn,[6a] who also realised the potential of NHOs as σ-donor ligands in coordination chemistry.[6] NHOs may be regarded as highly ylidic olefins, since their characteristic C–C double bond is strongly polarised towards the exocyclic carbon atom.[6,7] In their coordination chemistry, NHOs are therefore prone to end-on binding to metal centres by forming dative σ-bonds.[1,2a] This is in contrast to ordinary alkenes, which coordinate in a side-on fashion, forming π-complexes. A comparison of the ligand properties of NHOs and NHCs reveals distinct differences in terms of sterics and electronics. NHOs are considered to have a lower coordination volume in comparison to their NHC counterparts due to the appended alkylidene moiety.[1c] Owing to the absence of any significant π-backbonding, NHOs tend to show weaker coordination to metal centres than NHCs.[8] Apart from their use as ligands in coordination chemistry, NHOs have recently been studied also in organocatalysis,[1b–d,9] polymer chemistry[1b,c,10] and small-molecule activation.[1b,11] Nucleophilicity and basicity are crucial factors in this context, whose systematic investigation, both computationally and experimentally, is presently making considerable progress.[12]

We recently reported the first ferrocene-based, and hence redox-functionalised, NHO, viz. fc(NCH$_2$*t*Bu)$_2$C=CH$_2$ (**A**, fc = 1,1′-ferrocenylene, Figure 1).[13] In view of the enormous importance of DPPF[14] and many other fc-bridged symmetric bidentate ligands,[15] we have extended this work now to bis(NHO) compounds of the type [NHC=CH]$_2$fc, exemplarily utilising the standard NHCs 1,3-dimesitylimidazolin-2-ylidene (IMes) and 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene (IPr). The new NHOs (IMes=CH)$_2$fc (**1**) and (IPr=CH)$_2$fc (**2**) of this study are shown in Figure 1. Note that bis(NHO) compounds are extremely scarce. We are aware of two examples only, which are also shown in Figure 1, viz. (IPr=CH)$_2$ph (**B**, ph = 1,2-phenylene) and (BIm=CH)$_2$ph (**C**, BIm = 1,3-diisopropylbenzimidazolin-2-ylidene).[16] Due to the isoelectronic relationship of a CH unit with an N atom, compounds **1** and **2** are akin to the fc-bridged bis(imidazolin-2-imine) [Im=N]$_2$fc (**D**, Im = 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidene) recently published by Tamm (Figure 1).[17]

Results and Discussion

Synthetic work

The synthesis of the new NHOs **1** and **2** (Scheme 1) was inspired by the method reported by Rivard for the preparation of

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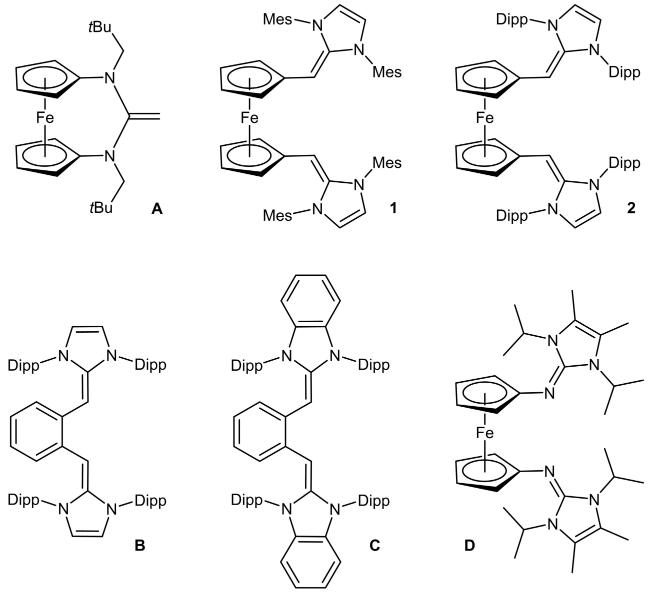
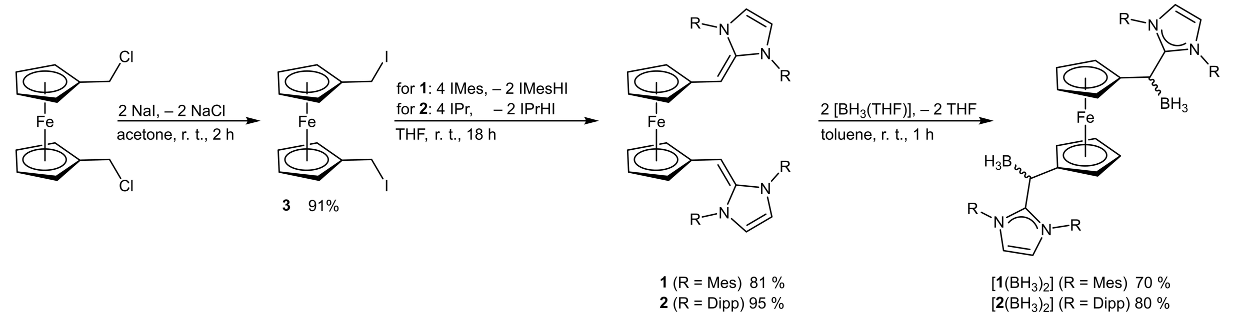


Figure 1. $\mathrm{fc(NCH_2{\it t}Bu)_2C{=}CH_2}$ (**A**), $\mathrm{(IMes{=}CH)_2fc}$ (**1**), $\mathrm{(IPr{=}CH)_2fc}$ (**2**), $\mathrm{(IPr{=}CH)_2ph}$ (**B**, ph = 1,2-phenylene), $\mathrm{(BIm{=}CH)_2ph}$ (**C**, BIm = 1,3-diisopropylbenzimidazolin-2-ylidene) and $\mathrm{[Im{=}N]_2fc}$ (**D**, Im = 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidene); Mes = mesityl, Dipp = 2,6-diisopropylphenyl.

$\mathrm{IPr{=}CH_2}$ from IPr (2 equivalents) and MeI.[18] Surprisingly, 1,1′-di(iodomethyl)ferrocene (**3**), which we utilised as starting material, had not been described before. This compound was easily obtained in excellent yield from the long known chloro homologue $\mathrm{(ClCH_2)_2fc}$[19] by a Finkelstein reaction. Its structure was determined by single-crystal X-ray diffraction (XRD, vide infra). IMes and IPr were generated in situ from the respective imidazolium chloride and KO*t*Bu in THF and subsequently reacted with $\mathrm{(ICH_2)_2fc}$ at ambient temperature. Compounds **1** and **2** were isolated in high yields (81 and 95 %, respectively) as orange solids and were structurally characterised by XRD (vide infra). According to Rivard, a drawback of his method mentioned above is the occurrence of variable amounts of residual NHC in the product.[8] In our case, this problem could be avoided by using slightly less than the stoichiometrically required 4 equivalents of the NHC. The ^{1}H NMR signal ($\mathrm{C_6D_6}$) due to the NHC=C*H* proton is observed at $\delta = 3.76$ and 3.40 ppm, respectively, for **1** (NHC=IMes) and **2** (NHC=IPr), which is close to the corresponding value of 3.97 ppm reported by Kinjo for $\mathrm{(IPr{=}C{\it H})_2ph}$.[16a] The NHC=CH ^{13}C NMR signal is located at $\delta = 61.9$ and 64.3 ppm, respectively, for **1** and **2**, similar to the chemical shift value of 69.2 ppm determined for $\mathrm{(IPr{=}CH)_2ph}$.[16a] For further comparison, the ^{1}H/^{13}C NMR chemical shift values of NHC=*CH*Ph are 4.36/68.5 ppm and 4.22/70.6 ppm for NHC = IMes and IPr, respectively.[16d,20] Due to the presence of two dissimilar bonding partners (H and cyclopentadienyl) at the NHC=*C* atoms of **1** and **2**, the NHC units exhibit two sets of signals for their backbone and respective N-substituents in the ^{1}H and ^{13}C NMR spectra.

The capability of **1** and **2** to act as bidentate ligands was exemplarily tested with $\mathrm{[BH_3(THF)]}$. The corresponding ligand substitution reactions with two equivalents of this reagent cleanly afforded the expected complexes [**1**$\mathrm{(BH_3)_2}$] and [**2**$\mathrm{(BH_3)_2}$] in good yields (70 and 80 %, respectively; Scheme 1). Their structures were determined by XRD (vide infra). The terminal C atom of the exocyclic double bond is tricoordinate in a free NHO, but becomes tetracoordinate upon complex formation with a Lewis acid (LA). For NHOs of the type NHC=CHR, complexation leads to the presence of four different substituents in a distorted pseudotetrahedral arrangement at this particular C atom, which thus constitutes a centre of chirality in [NHC–CHR–LA]. Two equivalent C atoms of this type are present in **1** and **2**, which gives rise to the formation of *rac*- and *meso*-diastereomers upon complexation. A ^{1}H NMR spectroscopic analysis of [**1**$\mathrm{(BH_3)_2}$] and [**2**$\mathrm{(BH_3)_2}$] reveals two distinct sets of signals in each case, indicating the formation of mixtures of both diastereomers. The *rac*/*meso* ratio thus determined for crude [**1**$\mathrm{(BH_3)_2}$] and [**2**$\mathrm{(BH_3)_2}$] is ca. 2/1 and 5/4, respectively. The diastereomers exhibit significantly different solubilities in both cases. Due to its higher solubility, the *meso*-diastereomer could be extracted from crude [**1**$\mathrm{(BH_3)_2}$] and [**2**$\mathrm{(BH_3)_2}$] with benzene and dichloromethane (DCM), respectively, which allowed the characterisation of this diastereomer in almost pure form by NMR spectroscopy in solution.



Scheme 1. Synthesis of the new NHOs **1** and **2** and their complexes [**1**$\mathrm{(BH_3)_2}$] and [**2**$\mathrm{(BH_3)_2}$] (obtained as mixtures of the *rac*- and *meso*-diastereomers; formal charges not shown).

Crystal structures

The molecular structure of (ICH$_2$)$_2$fc (**3**) is shown in Figure 2. Similar to (ClCH$_2$)$_2$fc,[21] the cyclopentadienyl rings of **3** exhibit an eclipsed anticlinal conformation. The C—I bond lengths are 2.216(8) and 2.198(8) Å, which is in the range typical for bonds involving C(sp^3) atoms. For example, C—I bond lengths in the narrow range from 2.187(2) to 2.1907(15) Å, and thus indistinguishable within experimental error, have been determined for o-, *m*- and *p*-$C_6H_4(CH_2I)_2$.[22] In view of the van der Waals radius of iodine (2.04 Å),[23] the I2—I2 distance of ca. 3.75 Å between pairs of neighbouring molecules is compatible with weak intermolecular I⋅⋅⋅I interactions, which can be classified as belonging to type I according to Desiraju and Parthasarathy, because both C—I—I angles are identical (155.8°).[24,25]

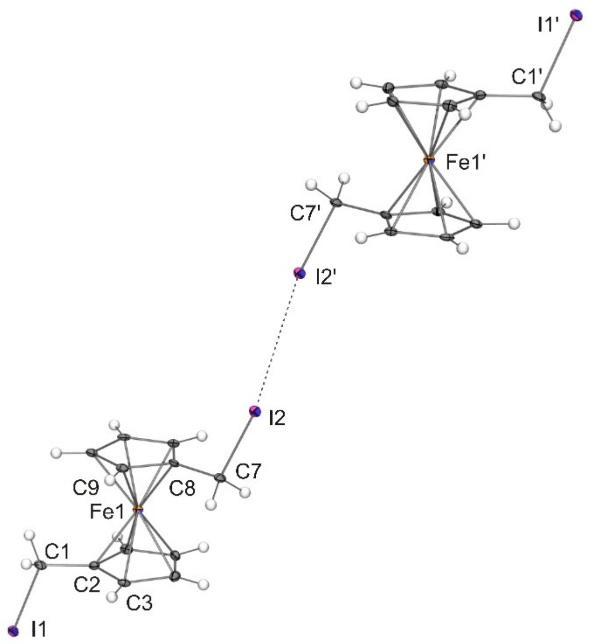


Figure 2. Molecular structure and aggregation (indicated by dotted line) of (ICH$_2$)$_2$fc (**3**) in the crystal (ORTEP with 30% probability ellipsoids).

The molecular structures of compounds **1** and **2** are shown in Figure 3 and Figure 4. Pertinent bond lengths and angles are collected in Table 1, which also contains corresponding data for the closely related benzylidene-containing NHOs IMes═CHPh,[20] ^{Me}IPr═CHPh (^{Me}IPr = 1,3-bis(2,6-diisopropylphenyl)-4,5-dimethylimidazolin-2-ylidene)[26] and ^{Me}IMe═CHPh (^{Me}IMe = 1,3,4,5-tetramethylimidazolin-2-ylidene).[27] Data for Kuhn's iconic methylidene-containing NHO ^{Me}IMe═CH$_2$[6a] and the closely related congeners IPr═CH$_2$[18] and SIPr═CH$_2$ (SIPr = 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene)[28] are also included for comparison.

The molecules of **1** and **2** are both centrosymmetric, showing an antiperiplanar staggered conformation of the cyclopentadienyl rings with diametrically opposed substituents. The lengths of their ylidic C—C double bonds are very similar, viz. 1.343(5) and 1.356(3) Å for **1** and **2**, respectively. These values lie in the middle of the range (1.32–1.38 Å) found for the previously reported NHOs in Table 1. The NHO π-systems of **1** and **2** are not coplanar with the cyclopentadienyl rings. The angles between the cyclopentadienyl ring plane and the plane formed by the cyclopentadienyl C$_{ipso}$ atom and the two C atoms of the ylidic unit attached to it are 41.1° and 37.9° for **1** and **2**, respectively. Comparable dihedral angles τ are formed by the best planes of the five-membered NHC ring and the corresponding cyclopentadienyl ring (Table 1). Similar deviations from coplanarity can be noted for the benzylidene-containing NHOs listed in Table 1. The N atoms are in an essentially trigonal planar bonding environment in all cases (sum of angles close to 360°). The largest, but still rather small, deviations from planarity are shown by the N atoms of one of the four independent molecules of SIPr═CH$_2$ (sum of angles 353.1° and

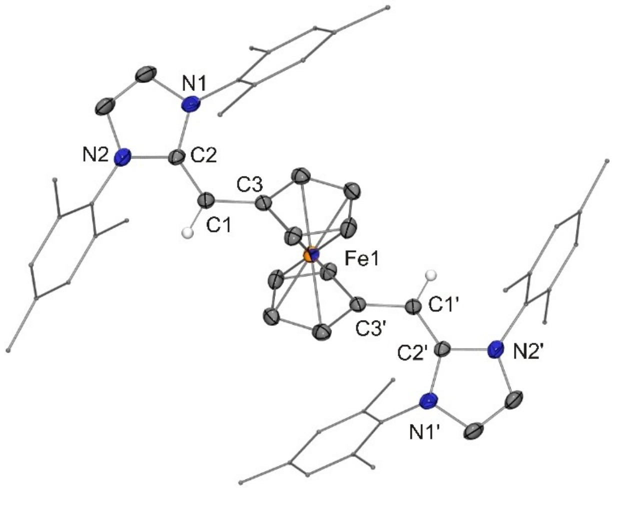


Figure 3. Molecular structure of **1** in the crystal (ORTEP with 30% probability ellipsoids, N-substituents drawn in wireframe representation and H atoms except IMesC*H* omitted for clarity).

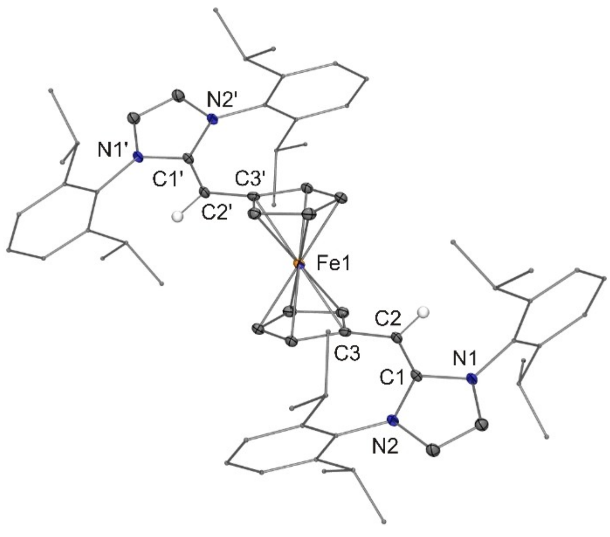


Figure 4. Molecular structure of **2** in the crystal (ORTEP with 30% probability ellipsoids, N-substituents drawn in wireframe representation and H atoms except IPrC*H* omitted for clarity).

Table 1. Pertinent metric parameters for the bis(NHO) compounds of this study. Data for closely related compounds are included for comparison.

	$N_2C–C$ [Å]	C–N (N_2C) [Å]	$N_2CC–B$ [Å]	τ[a] [°]	
$(IMes{=}CH)_2fc$ (**1**)	1.343(5)	1.399(4), 1.392(5)		43.4	this work
$(IPr{=}CH)_2fc$ (**2**)	1.356(3)	1.407(3), 1.398(3)		34.2	this work
IMes=CHPh	1.361(2)	1.398(2), 1.403(2)		37.5	ref. [20]
^{Me}IPr=CHPh[b]	1.371(4)	1.393(3), 1.399(3)		22.6	ref. [26]
	1.375(3)	1.393(3), 1.383(3)		25.8	
^{Me}IMe=CHPh	1.3833(15)	1.3750(14), 1.3830(14)		40.2	ref. [27]
$^{Me}IMe{=}CH_2$[b]	1.357(3)	1.382(3), 1.376(3)			ref. [6a]
	1.369(3)	1.373(3), 1.373(3)			
$IPr{=}CH_2$[c]	1.332(4)	1.391(3), 1.391(3)			ref. [18]
	1.322(4)	1.388(3), 1.395(3)			
	1.337(4)	1.391(3), 1.396(3)			
	1.334(4)	1.396(3), 1.385(3)			
$SIPr{=}CH_2$[c]	1.3346(19)	1.3921(16), 1.3935(17)			ref. [28]
	1.3388(18)	1.3847(17), 1.3824(17)			
	1.3356(19)	1.3826(17), 1.3892(17)			
	1.3365(19)	1.3871(16), 1.3846(16)			
rac-[**1**$(BH_3)_2$]	1.478(7)	1.352(7), 1.361(7)	1.672(9)	68.6	this work
meso-[**1**$(BH_3)_2$]	1.471(11)	1.359(8), 1.366(9)	1.683(12)	84.0	this work
rac-[**2**$(BH_3)_2$]	1.483(3)	1.355(3), 1.358(3)	1.695(4)	70.5	this work
$[SIPr–CH_2–BH_3]$	1.4522(17)	1.3361(16), 1.3376(16)	1.6767(19)		ref. [29]
$[IPr–CH_2–BH_2NMe_2BH_3]$	1.456(3)	1.348(2), 1.348(2)	1.660(3)		ref. [30]
$[^{Me}IMe–CH_2–B(C_6F_5)_3]$	1.4788(17)	1.3451(17), 1.3467(17)	1.6947(19)		ref. [27]
$[^{Me}IMe–CHPh–B(C_6F_5)_3]$	1.4997(19)	1.3499(18), 1.3515(18)	1.7084(19)		ref. [27]

[a] Dihedral angle between the best planes of a cyclopentadienyl or phenyl ring and the NHC ring connected to it. [b] Two independent molecules. [c] Four independent molecules.

354.1°) and by an N atom of ^{Me}IMe=CHPh (sum of angles 354.1°). In the latter case, the slight pyramidalisation of the N atom has been ascribed to steric repulsion between the phenyl and an *N*-methyl group.[27]

A structural investigation of [**1**$(BH_3)_2$] by XRD was possible for both diastereomers. Pertinent metric parameters are collected in Table 1. The molecular structure of *rac*-[**1**$(BH_3)_2$] (obtained as a racemic compound) is shown in Figure 5. Unfortunately, *meso*-[**1**$(BH_3)_2$] afforded crystals of poor quality, which affected the XRD result (see Figure S1 in the Supporting Information). The connectivities could be established unambiguously. However, a discussion of bond parameters is not meaningful. In the case of [**2**$(BH_3)_2$], crystals suitable for XRD were obtained for the *rac*-diastereomer only (Figure 6, Table 1). Although the first $NHO–BH_3$ complex was published already in 1993,[6a] only a single example has been structurally characterised so far, viz. $[SIPr–CH_2–BH_3]$.[29] Data for this compound as well as for the related complexes $[IPr–CH_2–BH_2NMe_2BH_3]$,[30] $[^{Me}IMe–CH_2–B(C_6F_5)_3]$ and $[^{Me}IMe–CHPh–B(C_6F_5)_3]$[27] are included in Table 1 for comparison. For the NHOs contained in Table 1 borane coordination induces an elongation of the exocyclic C–C bond of slightly more than 0.10 Å and a shortening of the bond lengths in the N_2C unit between ca. 0.03 and 0.05 Å, in line with a more pronounced ylidic character of the coordinated NHO.[1]

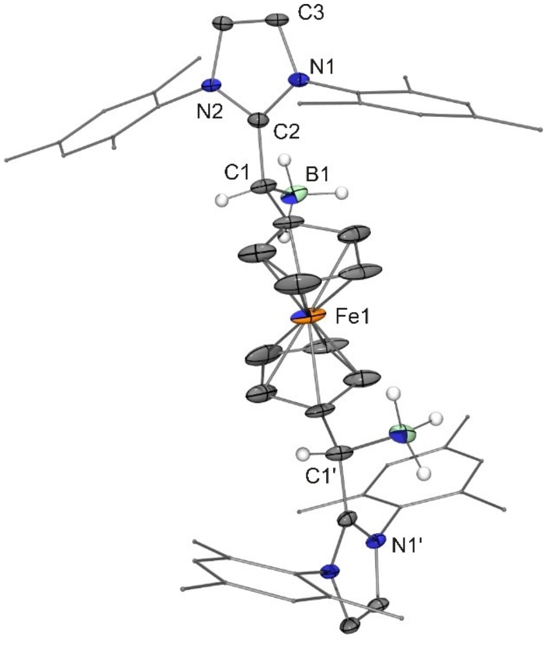


Figure 5. Molecular structure of *rac*-[**1**$(BH_3)_2$] in the crystal (ORTEP with 30% probability ellipsoids, N-substituents drawn in wireframe representation and C-bonded H atoms except IMesC*H* omitted for clarity). Only one enantiomer is shown.

Electrochemistry

The new bis(NHO) compounds **1** and **2** each contain three redox-active moieties, viz. the ferrocene unit and the two formally equivalent NHO units. Their redox behaviour was exemplarily studied for **2** by cyclic voltammetry in DCM (Figure 7) and THF solutions (see Figures S2–S4 in the Supporting Information). Potential data are collected in Table 2.

Compound **2** undergoes a first oxidation at a rather negative half-wave potential of −1.03 V vs. the ferrocenium/ferrocene couple (DCM, 0.1 м $nBu_4N[PF_6]$ supporting electro-

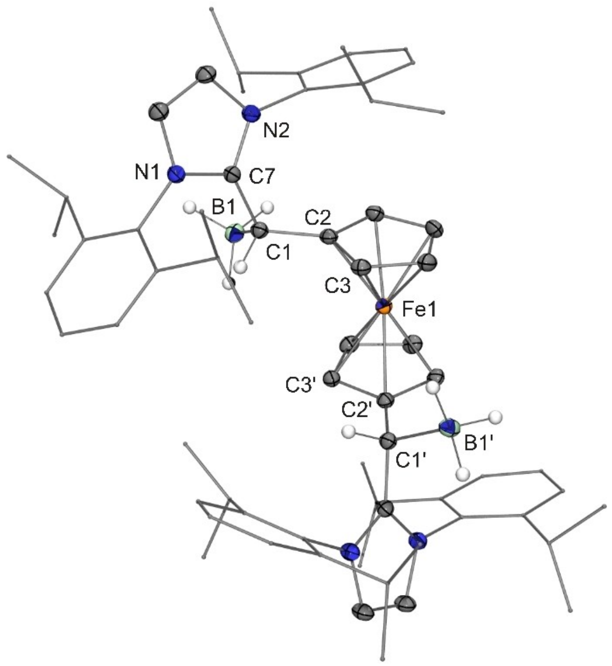


Figure 6. Molecular structure of *rac*-[**2**$(BH_3)_2$] in the crystal (ORTEP with 30% probability ellipsoids, N-substituents drawn in wireframe representation and C-bonded H atoms except IPrC*H* omitted for clarity). Only one enantiomer is shown.

lyte). The closely related compound $[Im{=}N]_2fc$ (**D**), which is one of the most electron-rich ferrocene derivatives known to date, shows a ferrocene-based quasi-reversible oxidation at a half-wave potential of −1.18 V, followed by an irreversible guanidine-centred second oxidation at considerably higher potential ($E_{p,ox} = -0.05$ V) under essentially the same conditions.[17a] Compound **2** exhibits a chemically reversible second oxidation at a half-wave potential of −0.44 V. This value may be compared with the anodic peak potential $E_{p,ox} \approx -0.1$ V vs. SCE (corresponding to ca. −0.6 V on the ferrocenium/ferrocene scale)[31] reported recently for the irreversible oxidation of the NHO 1-*tert*-butyl-3-methyl-2-methyleneimidazolidine in DMF solution.[32] A third, and irreversible, oxidation is observed for **2** at a peak potential $E_{p,ox} = 0.36$ V. We ascribe the chemically reversible first and second oxidation observed for **2** to a ferrocene-centred and an NHO-centred one-electron process, respectively. The second NHO moiety is plausibly involved in the irreversible third oxidation. A more detailed study will be performed to shed more light on this redox behaviour and the electronic structure of the cationic species $\mathbf{2}^{n+}$ ($n = 1$–3) involved.

Conclusion

The new bis(NHO) compounds $(IMes{=}CH)_2fc$ (**1**) and $(IPr{=}CH)_2fc$ (**2**), which are easily available from $(ICH_2)_2fc$ (**3**) and the corresponding NHC (IMes or IPr), represent a new class of ferrocene-based, and hence redox-active, bidentate ligands. The

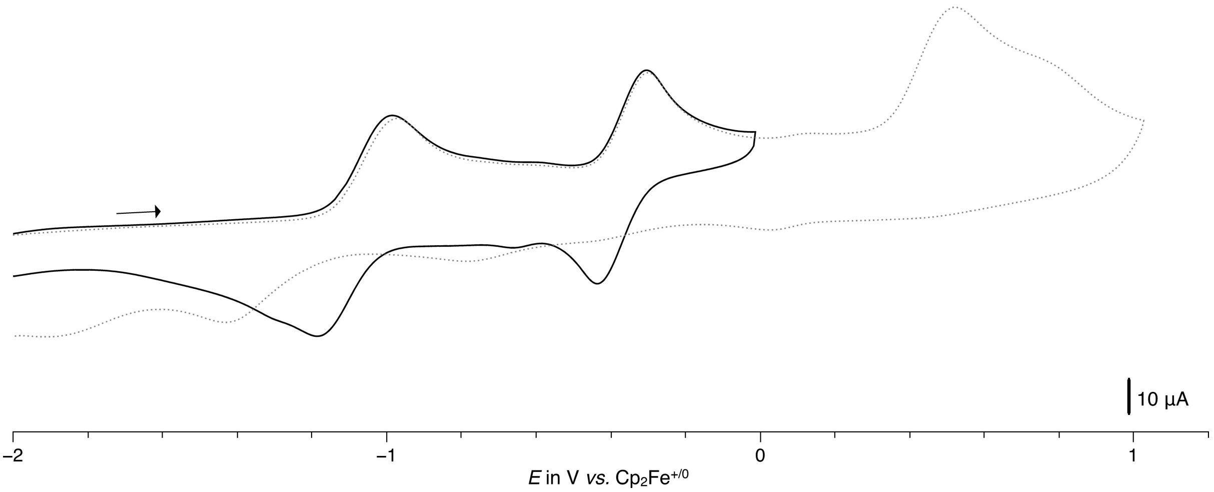


Figure 7. Cyclic voltammogram of **2** at $v = 0.25\ Vs^{-1}$ in DCM/0.1 м $nBu_4N[PF_6]$ at ambient temperature against the ferrocenium/ferrocene scale (solid black line: scan reversal after second oxidation, dotted grey line: scan reversal after third oxidation).

Table 2. Potential data in V vs. ferrocenium/ferrocene determined for **2**.[a]

	$E_{1/2}^{+/0}$	$E_{1/2}^{2+/+}$	$E_{p,ox}$ [b]
DCM	−1.03	−0.44	0.36
THF	−1.09	−0.22	0.52

[a] 0.1 м $nBu_4N[PF_6]$ supporting electrolyte, $v = 0.25\ Vs^{-1}$. [b] Irreversible third oxidation.

presence of three redox-active moieties, viz. the ferrocene unit and the two NHO units, is reflected by three consecutive oxidations according to an electrochemical investigation exemplarily performed with **2** by cyclic voltammetry. The electronic structure of the oxidised species (in particular that of the dication formed in the second oxidation step) will be addressed in future work. The capability of **1** and **2** for the coordination of Lewis acidic centres was demonstrated by ligand substitution reactions with [BH_3(THF)], which furnished the complexes [**1**(BH_3)$_2$] and [**2**(BH_3)$_2$]. A study addressing the ability of such bidentate C,C-ligands for chelate formation, analogous to DPPF and its many relatives, is presently underway. We will also investigate the deprotonation of (NHC=CH)$_2$fc to afford [(NHC=C)fc]$^{2-}$, because N-heterocyclic vinyl groups have started to emerge as powerful tools for the stabilisation of electron-deficient low-coordinate centres.[33]

Experimental Section

General considerations: All reactions involving air-sensitive compounds were performed in an inert atmosphere (argon or dinitrogen) by using standard Schlenk techniques or a conventional glovebox. Starting materials were procured from standard commercial sources and used as received. 1,1′-Di(hydroxymethyl)ferrocene,[34] 1,1′-di(chloromethyl)ferrocene[35] and the imidazolium chlorides IMesHCl and IPrHCl[36] were synthesised by adapted versions of the published procedures. NMR spectra were recorded at ambient temperature with Varian NMRS-500 and MR-400 spectrometers operating at 500 and 400 MHz, respectively, for ^{1}H. Elemental analyses were carried out with a HEKAtech Euro EA-CHNS elemental analyser at the Institute of Chemistry, University of Kassel, Germany. Cyclic voltammetry was performed using a three-electrode cell with a platinum working electrode, a silver counter electrode and a silver pseudo-reference electrode. All measurements were performed in a nitrogen-filled glovebox (MBraun/GB2202-C-VAC) in dried and degassed HPLC grade THF or DCM with 0.1 M *n*Bu$_4$N[PF$_6$] as supporting electrolyte and an analyte concentration of 1 mM. All potentials were referenced versus the ferrocenium/ferrocene couple. For this purpose ferrocene was added to the analyte solution after all data of interest had been acquired. The electrochemical cell was connected to a WaveDriver 20 Bipotentiostat (Pine Research) and the electrochemical data were recorded and processed with AfterMath (Ver. 1.5.9807, Pine Research). The data were subsequently exported and plotted with QtiPlot (Ver. 0.9.8.0).

Synthesis of 1,1′-Di(iodomethyl)ferrocene (3): Sodium iodide (1.06 g, 7.1 mmol) was added to a solution of 1,1′-di(chloromethyl)ferrocene (1.00 g, 3.5 mmol) in acetone (100 mL). The mixture was stirred for 2 h. Insoluble material was removed by filtration through a short pad of celite, which was subsequently washed with acetone (2×5 mL). The combined solutions were reduced to dryness under vacuum. The orange residue was extracted with hot *n*-hexane (100 mL). Insoluble components were removed from the extract by filtration through a short pad of celite, which was subsequently washed with hot *n*-hexane (3×10 mL). The solutions were combined. Volatile components were removed under vacuum, leaving the product as a bright orange microcrystalline solid. Further purification to obtain an analytical sample and crystals suitable for XRD was achieved by recrystallization from *n*-hexane or diethyl ether. Yield 1.49 g (91 %). $C_{12}H_{12}FeI_2$ (465.88): calcd. C 30.94, H 2.60 %; found C 30.76, H 2.98 %. ^{1}H NMR (400 MHz, acetone-d_6): $\delta = 4.53$ (s, 4 H, CH$_2$), 4.32, 4.29 ppm (2 m, 2×4 H, cyclopentadienyl CH). ^{13}C{^{1}H} NMR (101 MHz, acetone-d_6): $\delta = 87.7$ (C$_{ipso}$), 71.0, 70.8 (2×cyclopentadienyl CH), 5.8 ppm (CH$_2$).

Synthesis of (IMes=CH)$_2$fc (1): 1,1′-Di(iodomethyl)ferrocene (500 mg, 1.07 mmol) was added to a stirred solution of IMes, which had been freshly prepared from IMesHCl (1.409 g, 4.13 mmol) and KO*t*Bu (463 mg, 4.13 mmol) in THF (15 mL). The mixture was stirred for 18 h. Volatile components were removed under vacuum. The residue was extracted with a toluene (50 mL). Insoluble components were removed from the extract by filtration through a short pad of celite, which was subsequently washed with toluene (2× 15 mL). The solutions were combined. Volatile components were removed under vacuum, leaving the product as an orange microcrystalline solid, which was washed with diethyl ether (3×3 mL) and dried under vacuum. Further purification to obtain an analytical sample and crystals suitable for XRD was achieved by recrystallization from *n*-hexane. Yield 687 mg (81 %). $C_{54}H_{58}N_4Fe$ (818.91): calcd. C 79.20, H 7.14, N 6.84 %; found C 78.99, H 7.12, N 6.53 %. ^{1}H NMR (400 MHz, C$_6$D$_6$): $\delta = 6.82$, 6.63 (2 s, 2×4 H, C$_6$*H*$_2$Me$_3$), 5.65 (s, 4 H, NCHCHN), 3.76 (s, 2 H, IMesC*H*), 3.45, 3.30 (2 m, 2×4 H, cyclopentadienyl CH), 2.29, 2.25 (2 s, 2×12 H, *m*-Me), 2.14, 2.08 ppm (2 s, 2×6 H, *p*-Me). ^{13}C{^{1}H} NMR (101 MHz, C$_6$D$_6$): $\delta = 142.1$ (NCN), 137.9, 137.6, 136.7, 136.4, 136.3, 134.9 (6×Mes C$_{quat}$/C$_{ipso}$), 129.8, 129.1 (2× Mes CH), 115.0, 113.7 (2×NCHCHN), 86.1 (cyclopentadienyl C$_{ipso}$), 68.0, 67.7 (2×cyclopentadienyl CH), 61.9 (IMes*C*H), 21.2, 21.0 (2×*p*-Me), 18.8, 18.4 ppm (2×*m*-Me).

Synthesis of (IPr=CH)$_2$fc (2): 1,1′-Di(iodomethyl)ferrocene (500 mg, 1.07 mmol) was added to a stirred solution of IPr, which had been freshly prepared from IPrHCl (1.756 g, 4.13 mmol) and KO*t*Bu (463 mg, 4.13 mmol) in THF (15 mL). The mixture was stirred for 18 h. Volatile components were removed under vacuum. The residue was extracted with a toluene (30 mL). Insoluble components were removed from the extract by filtration through a short pad of celite, which was subsequently washed with toluene (2× 10 mL). The solutions were combined. Volatile components were removed under vacuum, leaving the product as an orange microcrystalline solid. Further purification to obtain an analytical sample and crystals suitable for XRD was achieved by recrystallization from *n*-hexane. Yield 964 mg (95 %). $C_{66}H_{82}N_4Fe$ (987.23): calcd. C 80.30, H 8.37, N 5.68 %; found C 80.06, H 8.56, N 5.05 %. ^{1}H NMR (400 MHz, C$_6$D$_6$): $\delta = 7.23$–7.20 (m, 2 H, C$_6$*H*$_3$*i*Pr$_2$), 7.15–7.11 (m, 6 H, C$_6$*H*$_3$*i*Pr$_2$), 6.96–6.95 (m, 4 H, C$_6$*H*$_3$*i*Pr$_2$), 5.71, 5.69 (2 m, 2×2 H, NCHCHN), 3.40 (s, 2 H, IPrC*H*), 3.39 (m, 4 H, cyclopentadienyl CH), 3.28–3.16 (m, 8 H, C*H*Me$_2$), 2.90 (m, 4 H, cyclopentadienyl CH), 1.30, 1.16, 1.13, 1.09 ppm (4 d, $^3J_{HH} = 6.9$ Hz, 4×12 H, CH*Me*). ^{13}C{^{1}H} NMR (101 MHz, C$_6$D$_6$): $\delta = 149.2$, 148.0 (2×Dipp C$_{quat}$), 144.3 (NCN), 137.5, 135.1 (2× Dipp C$_{ipso}$), 129.5, 129.0, 124.7, 123.9 (4×Dipp CH), 116.5, 114.9 (2× NCHCHN), 86.0 (cyclopentadienyl C$_{ipso}$), 68.1, 67.3 (2×cyclopentadienyl CH), 64.3 (IPr*C*H), 28.7 (two closely spaced signals, 2×*C*HMe$_2$), 24.3, 24.1 (2×CH*Me*$_2$), 23.1 ppm (two closely spaced signals, 2× CH*Me*$_2$).

Synthesis of [**1**(BH_3)$_2$]: A solution of [BH_3(THF)] (0.40 mL, 1.0 M in THF, 0.40 mmol) was added to a stirred solution of **1** (150 mg, 0.18 mmol) in toluene (10 mL). After 1 h the volume of the mixture was reduced under vacuum to ca. 1 mL. The product was precipitated by addition of diethyl ether (15 mL) as a fluffy yellow solid, which was filtered off, washed with diethyl ether (3×4 mL) and dried under vacuum. Yield 108 mg (70 %), *rac*/*meso* ratio ≈2 : 1 (see Figure S11 in the Supporting Information). The mixture of diastereomers was triturated with benzene (3×3 mL) to extract the *meso*-diasteromer and filtered. The filtrates were combined and volatile components removed under vacuum, affording essentially pure *meso*-[**1**(BH_3)$_2$]. Yield 37 mg. Single crystals of *meso*-[**1**(BH_3)$_2$] were obtained from a DCM solution which was layered which a small amount of *n*-hexane. Single crystals of *rac*-[**1**(BH_3)$_2$] were obtained by dissolving the residue from the extraction with DCM in benzene and subsequent slow evaporation of the solvent. NMR data given below refer to *meso*-[**1**(BH_3)$_2$]. $C_{54}H_{64}N_4B_2Fe$ (846.58): calcd. C 76.61, H 7.62, N 6.62 %; found C 76.23, H 7.77, N 5.86 %. ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 6.99$, 6.81 (2 br., 2×4 H, $C_6H_2Me_3$), 6.71 (br., 4 H, NCHCHN), 3.73, 3.69, 3.46, 3.38 (4 m, 4×2 H, cyclopentadienyl CH), 3.00 (br., 2 H, IMesC*H*), 2.33, 2.25, 1.89 (3 br., 3×12 H, Me), 0.99–0.35 ppm (br., 6 H, BH_3). ^{11}B NMR (160 Hz, CD_2Cl_2): $\delta = -26.4$ ppm (ill-resolved q, $^1J_{BH}$ 85 Hz). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): $\delta = 163.0$ (NCN), 140.1, 136.9, 136.8, 135.8 (br.), 132.9, 129.7 (br.), 129.5 (7×aryl C, one aryl C not detected), 120.9 (br., NCHCHN), 89.1 (cyclopentadienyl C_{ipso}), 72.6, 70.3, 69.5, 69.0 (4×cyclopentadienyl CH), 30.8 (br., CBH_3), 21.4, 21.4 (2×Me), 19.2, 19.0 ppm (br., 2×Me).

Synthesis of [**2**(BH_3)$_2$]: A solution of [BH_3(THF)] (0.33 mL, 1.0 м in THF, 0.33 mmol) was added to a stirred solution of **2** (150 mg, 0.15 mmol) in toluene (10 mL). After 1 h the volume of the mixture was reduced under vacuum to ca. 1 mL. The product was precipitated by addition of diethyl ether (15 mL) as a fluffy yellow solid, which was filtered off, washed with diethyl ether (3×4 mL) and dried under vacuum. Yield 122 mg (80 %), *rac*/*meso* ratio ≈5 : 4 (see Figure S15 in the Supporting Information). The mixture of diastereomers was triturated with DCM (3×3 mL) to extract the *meso*-diasteromer and filtered. The filtrates were combined and volatile components removed under vacuum, affording essentially pure *meso*-[**2**(BH_3)$_2$]. Yield 47 mg. Single crystals of *rac*-[**2**(BH_3)$_2$] were obtained by extracting the residue of the DCM extraction with benzene and subsequent slow evaporation of the solvent. NMR data given below refer to *meso*-[**2**(BH_3)$_2$]. $C_{66}H_{88}N_4B_2Fe$ (1014.90): calcd. C 78.11, H 8.74, N 5.52 %; found C 78.43, H 8.85, N 5.28 %. ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 7.60$–7.16 (br., 12 H, $C_6H_3i\mathrm{Pr}_2$), 6.73 (br., 4 H, NCHCHN), 3.68, 3.54, 3.34, 3.21 (4 m, 4×2 H, cyclopentadienyl CH), 3.18 (m, 2 H, IPrC*H*), 1.50–0.80 (br., *i*Pr, 56 H), 0.58 ppm (br., 6 H, BH_3). ^{11}B NMR (160 Hz, CD_2Cl_2): $\delta = -25.8$ ppm (br.). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): $\delta = 163.7$ (NCN), 147.3 (br.), 146.0 (br.), 133.2 (br.), 131.1 (br.), 130.8, 125.0 (br.), 124.6, 120.7 (br., 8×aryl C), 88.8 (cyclopentadienyl C_{ipso}), 72.5, 71.2, 70.2, 67.6 (4×cyclopentadienyl CH), 31.8 (br., *C*HMe$_2$), 29.3, 29.2 (2×CH*Me*$_2$), 26.6 (br., CBH_3), 26.1 (br., *C*HMe$_2$), 23.2 (br.), 22.6 ppm (2×CH*Me*$_2$).

X-ray Crystallography: For each data collection a single crystal was mounted on a micro-mount at 100(2) K and all geometric and intensity data were taken from this sample. Data collections were carried out using MoK_α radiation ($\lambda = 0.71073$ Å) on a Stoe IPDS2 diffractometer equipped with a 2-circle goniometer and an area detector in the case of **1** and **3**, whereas CuK_α radiation ($\lambda = 1.54186$ Å) and a Stoe StadiVari diffractometer equipped with a 4-circle goniometer and a DECTRIS Pilatus 200 K detector was used in all other cases. The data sets were corrected for absorption, Lorentz and polarisation effects. The structures were solved by direct methods (SHELXT) and refined using alternating cycles of least-squares refinements against F^2 (SHELXL2014/7).[37] C-bonded H atoms were included in the models in calculated positions, heteroatom-bonded H atoms have been found in the difference Fourier lists. All H atoms were treated with the 1.2 fold or 1.5 fold isotropic displacement parameter of their bonding partner. Experimental details for each diffraction experiment are given in Table S1 in the Supporting Information.

Deposition Numbers 2115936 (for **3**), 2115937 (for **1**), 2115938 (for **2**), 2115939 (for *rac*-[**1**(BH_3)$_2$]), 2115940 (for *meso*-[**1**(BH_3)$_2$]), and 2115941 (for *rac*-[**2**(BH_3)$_2$]) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Supporting Information (see footnote on the first page of this article): Crystallographic data, plots of cyclic voltammograms and NMR spectra.

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Conflict of Interest

The authors declare no conflict of interest.

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