

CHAPTER 5

METALLOMACROCYCLES AS LIGANDS: SYNTHESIS AND CHARACTERIZATION OF
ALUMINIUM-BRIDGED BISGLYOXIMATO COMPLEXES OF IRON

The text for this chapter was taken in part from:

Kelley, P.; Radlauer, M. R.; Yanez, A. J.; Day, M. W.; Agapie, T. *Dalton Trans.* **2012**,
41, 8086-8092.

ABSTRACT

Dialuminiummacrocycles based on bisglyoximato moieties were prepared and their coordination chemistry with FeII was investigated. The nature of the ancillary ligands bound to aluminum affect the overall geometry of the metallomacrocycles. Additionally, remote substituents on aluminium-bound ligands affect the binding mode, electrochemistry, and electronic properties of the central iron.

INTRODUCTION:

Metallomacrocycles have been studied for a variety of applications including the synthesis of extended solids, catalysis, selective binding of ions and sensing.¹⁻¹⁸ Rational selection of metal precursors and ligands has afforded metallomacrocycles with diverse shape and size. Incorporation of binding sites for additional metals into the metallomacrocycles typically relies on the ability of coordinating atoms to bridge between the macrocycle metals and the incoming metals. Such systems, known as metallocrowns, have been extensively studied.^{2, 3, 19} An alternative approach to coordinating additional metals involves orthogonal metal-binding atoms on the organic units of the macrocycles. Systems with monodentate phosphines, phenanthroline, phenols or diimines donors capable of binding diverse transition metals are known.²⁰⁻²⁴

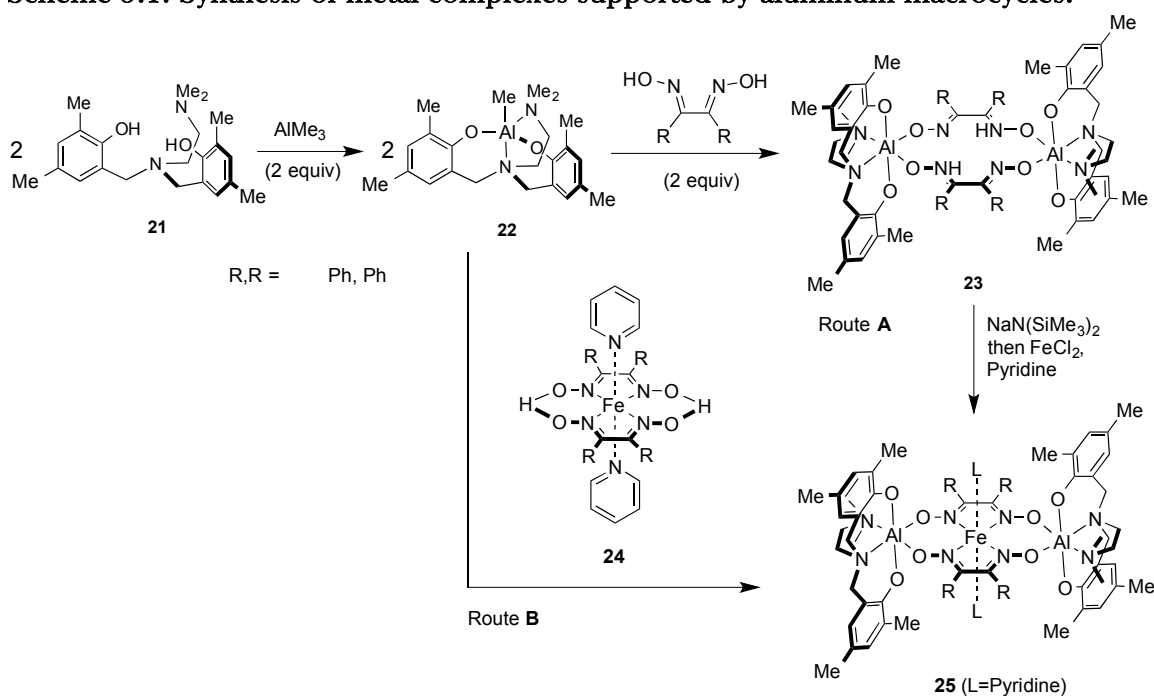
Transition metal complexes supported by bisglyoximato moieties exhibit the interesting ability to bind metal centres in a coordination environment similar to biologically relevant macrocycles. Iron bisglyoximato complexes have chemistry reminiscent of heme species.^{25, 26} The reactivity of cobalt bisglyoximato complexes was investigated in the context of vitamin B12 chemistry^{27, 28} and, recently, in the context of catalytic proton reduction to dihydrogen.²⁹⁻³⁴ The large majority of these species display proton or boron bridges between the oxygen atoms. Boron-bridged variants are generally constructed from the preformed, proton-bridged, metal-bisglyoximate species.³⁵⁻³⁸ Metallomacrocycles consisting of two glyoximato ligands and bridges other than hydrogen or boron are rare, but examples are known with aluminium, gallium, indium or copper moieties.^{39, 40} Additionally there are several examples of cryptands consisting of tris-glyoximato moieties with the oxygen donors bound to antimony, tin,

iron, manganese, and chromium.⁴¹⁻⁴⁷ We report herein on the synthesis of metallomacrocycles based on aluminium bridged bisglyoximato frameworks and their coordination chemistry with iron.

RESULTS & DISCUSSION:

In order to assemble metallomacrocycles capable of chelating a variety of metals, a strategy to link two dioximato ligands was employed. Aluminium precursors supported by tetradentate ligands capable of affording two open *cis*-coordination sites were selected. Diphenoxide diamines have been used as ancillary ligands for olefin polymerization precisely due to the availability of two *cis* coordination sites.⁴⁸⁻⁵⁰ Furthermore, the synthesis of these ligands is modular and allows for steric and electronic variation as well as changes in the linkages between the donor atoms. Methylaluminium species were prepared *in situ* by a modification of literature procedures and used as precursors for protonolysis reactions with glyoximes (Scheme 5.1).^{51,52}

Scheme 5.1: Synthesis of metal complexes supported by aluminum macrocycles.



Treatment of diphenylglyoxime (Scheme 5.1), which is sparingly soluble in THF, with **21** led to a homogeneous mixture indicating that a reaction occurred. The

^1H NMR spectrum in C_6D_6 contains signals corresponding to both the phenoxide ligand and the dioximato backbone. Additionally, a peak slightly downfield of 14 ppm indicated protonation of two of the nitrogen atoms of the glyoximato moiety. To investigate the binding mode of the aluminiummacrocycle to metal centres that can access six-coordinate geometry, Fe(II) complexes were synthesized. Via synthetic route B, previously reported iron diglyoximato complex (**24**),^{26,53} was treated with methylaluminium species **3a** in THF. Precursor **24** is sparingly soluble in THF, but slowly dissolved as the reaction proceeded to generate a bright purple solution. Purification by fractional precipitation afforded the isolation of a red-purple solid. Using route A, treatment of **23** with base followed by FeCl_2 and pyridine allows the isolation of a red-purple solid with spectroscopic properties identical to the product obtained from route B. The ^1H NMR spectrum of the red-purple residue in C_6D_6 shows a single major peak for each of the three types of methyl groups, NMe_2 , para- CH_3 and ortho- CH_3 . Additionally, two coordinated pyridines are present (by integration of ^1H NMR peaks). Similar to previously synthesized palladium complexes in the group, these spectroscopic data suggest a C_{2v} structure (or fast exchange) with two pyridines bound along the C_2 axis. ESI-MS data shows a peak at $m/z = 1452.7$ that is consistent with assignment of the product as **25**.

Attempts of growing X-ray quality single crystals of **25** resulted in yellow crystals from a red-purple solution in THF layered with hexanes. An XRD study of this material revealed an unexpected binding for the macrocycle (**26**, Figure 5.1 and Scheme 5.2). The iron centre is six-coordinate, with a trigonal prismatic geometry. The iron ligands are two phenoxide oxygens bridging between iron and aluminium and the four oxime moieties. The conformation of the metallomacrocycle bound to iron

has the two dioximato planes departing from coplanarity with a dihedral angle of 63° . Compound **26** was prepared free of pyridine by trituration of **25** with toluene several times. **26** shows a paramagnetic ^1H NMR spectrum with broad peaks between 1 and 14 ppm. Further studies were performed to elucidate the behaviour of **25** and **26** in solution. An NMR sample of **25** in CD_2Cl_2 displayed the diamagnetic peaks as described above, but also some paramagnetic peaks consistent with the presence of **26**. Addition of excess pyridine led to an increase of the diamagnetic peaks assigned to **25**.

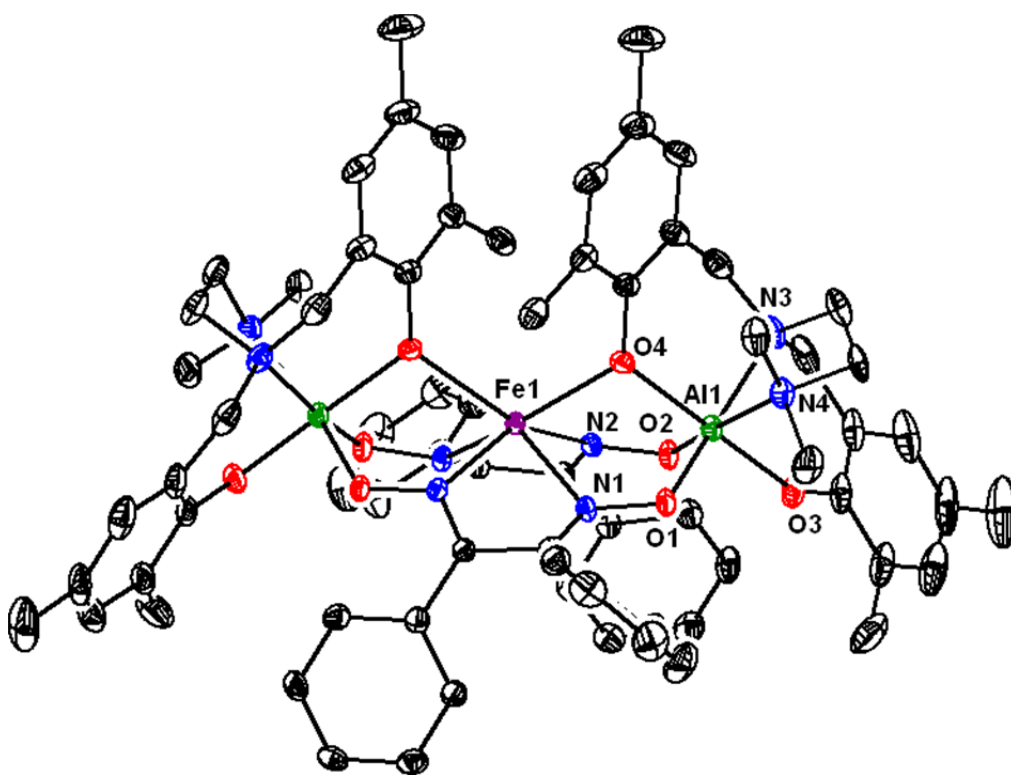
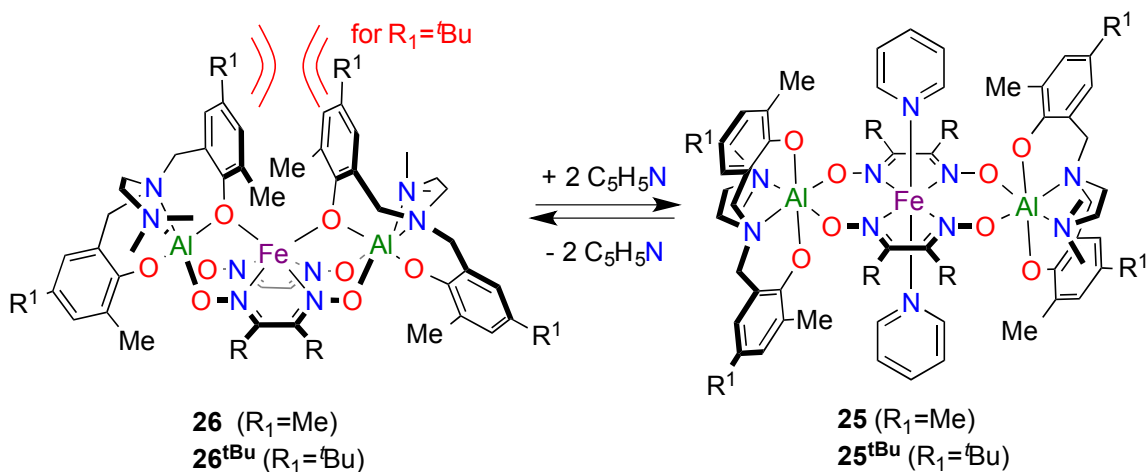


Figure 5.1. Solid-state structure of **26**. Hydrogen atoms and solvent molecules have been omitted for clarity; thermal ellipsoids are displayed at the 50% probability.

Scheme 5.2: Ancillary and Axial Ligand effects on Fe Coordination



Compound **25** was dissolved in benzene and analyzed by UV-Vis spectroscopy (Figure 5.2). Two absorptions, at 461 and 548 nm were observed. Addition of pyridine led to an increase in the intensity of the band at 548 nm and decrease of the band at 461 nm. The 548 nm band is in the range previously reported for iron bisglyoximate complexes, with coplanar oximes.^{26,54,55} The observed spectral shift in the presence of pyridine is consistent with an equilibrium between **25** and **26** plus free pyridine.

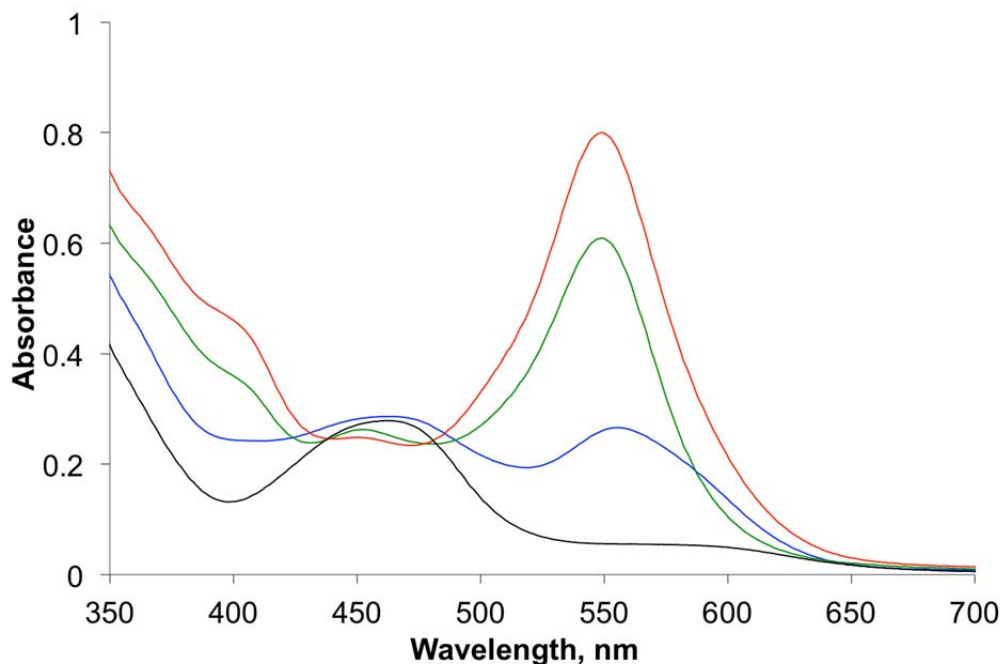


Figure 5.2. UV-Vis spectra at 70 μM of complexes **26** (black), **25** (blue), **25^{tbu}** (green) and **25** plus excess pyridine (2 mM, red).

The structural change from **25** and **26** is accompanied by a spin change from diamagnetic to paramagnetic and a change in the electronic absorption spectrum (Figure 5.2). The change in the iron coordination geometry from square bipyramid to trigonal prism is expected to lead to a smaller d-d splitting because none of the d orbitals have all lobes pointing to ligands.^{56,57} Consequently a high-spin species was generated. The band at 548 nm (**25**) is consistent with a d- π^* charge transfer, as previously assigned.^{54,55,58} The observed shift to higher energy is likely due to an increase in the energy of the glyoxime π^* orbital due to more direct interactions with d orbitals.

Analysis of the solid-state structure of **26** shows that the two bridging phenoxides are spatially close to each other. In order to disfavour phenoxide bridges and facilitate intermolecular binding of ligands, a bulkier phenoxide was utilized. A

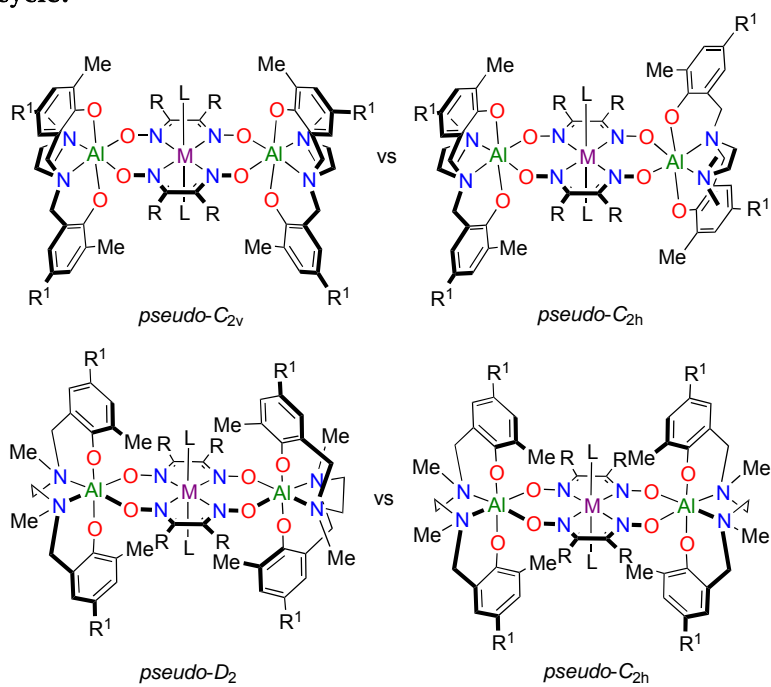
variant with tert-butyl instead of methyl groups in the para position vs. the phenoxide oxygens was employed. Species **25^{tbu}** was prepared analogously to **25** and investigated by UV-Vis spectroscopy (Figure 5.2). Without added pyridine the peak at 548 nm, corresponding to the d- π^* transition in **25^{tbu}**, is almost as intense as the 548 nm peak of **25** upon addition of excess pyridine. This indicates that the increased steric bulk on the ligand periphery affects the coordination environment at the iron center, disfavoring the formation of phenoxide bridges (Scheme 5.2).

The geometry of the ancillary ligand bound to the aluminum center affects the overall symmetry of the metallomacrocycle. A tripodal N(O₂N) ligand generates an aluminium precursor of *pseudo-C₃* symmetry (**21**, Scheme 5.1). Since two aluminium centres are part of the metallomacrocycle, the symmetry can be *pseudo-C_{2v}* or *pseudo-C_{2h}* (approximating the macrocycle as planar) dependent on the relative orientation of the Al[N(O₂N)] moiety (Scheme 5.3). If the four donors of the diphenoxide diamines ligands are linked in a linear fashion (NO)₂, the resulting aluminium complexes display *pseudo-C₂*-symmetry rendering the metal centres chiral. Again, depending on the stereochemistry at aluminium, two types of macrocycles are possible, with *pseudo-D₂* or *pseudo-C_{2h}* symmetry. It was envisioned that the stereochemistry at aluminium could be set by a chiral centre in the ligand backbone, such as defined by a *trans*-1,2-diaminocyclohexane moiety. Control of the stereochemistry by the ancillary ligand was expected to favour the chiral, *pseudo-D₂* structure.

To examine the stereochemistry of complexes with *C₂* symmetric ancillary ligands on aluminium, precursors^{7,10} supported by linear diphenoxide diamine ligands were prepared using 1,2-ethylenediamine or (*R,R*)-*trans*-1,2-diaminocyclohexane backbones (Scheme 5.3). Attempts to prepare iron complexes ligated by

aluminiummacrocycles with ethylenediamine backbones resulted in a mixture of diamagnetic products likely due to the formation of both *pseudo-D₂* and *pseudo-C_{2h}* structures. Nevertheless, one isomer can be enriched by precipitation. Since NMR spectroscopy does not allow for determination of the symmetry of the isolated product, an XRD study was performed and showed a *pseudo-D₂* structure in the solid-state (**29^{bu}**). The iron coordination environment is *pseudo*-octahedral, with the phenoxide oxygens coordinated only to aluminium. This geometry at iron is consistent with the sharp, diamagnetic NMR spectra, and the vibrant purple colour. Since a variant with methyl groups in the position para to the phenoxide oxygen was not prepared, it is not clear if the macrocycle binding mode is a consequence of the bulky substituent or the steric demands of the linear ligand set bound to aluminium. The metallomacrocycle appears to be larger than boron or hydrogen linked versions.^{59,60} The O1-O3 and O2-O4 distances in **29^{bu}** are ca. 0.4 Å larger than the corresponding ones in difluoroborate and proton linked iron diglyoximato species (average 2.90 vs. 2.57 and 2.52 Å respectively).^{59,60} This ring expansion is due to the larger aluminium centre. Ruffling of the metalocycle is observed and contrasts with the flat geometry observed for bisglyoximato complexes bridged by protons or boron moieties. This distortion could be due to *C₂*-twists caused by the aluminium centres or the larger size of the macrocycle.

Scheme 5.3. Effect of the ancillary ligand of aluminum on the symmetry of the metallomacrocyclic.



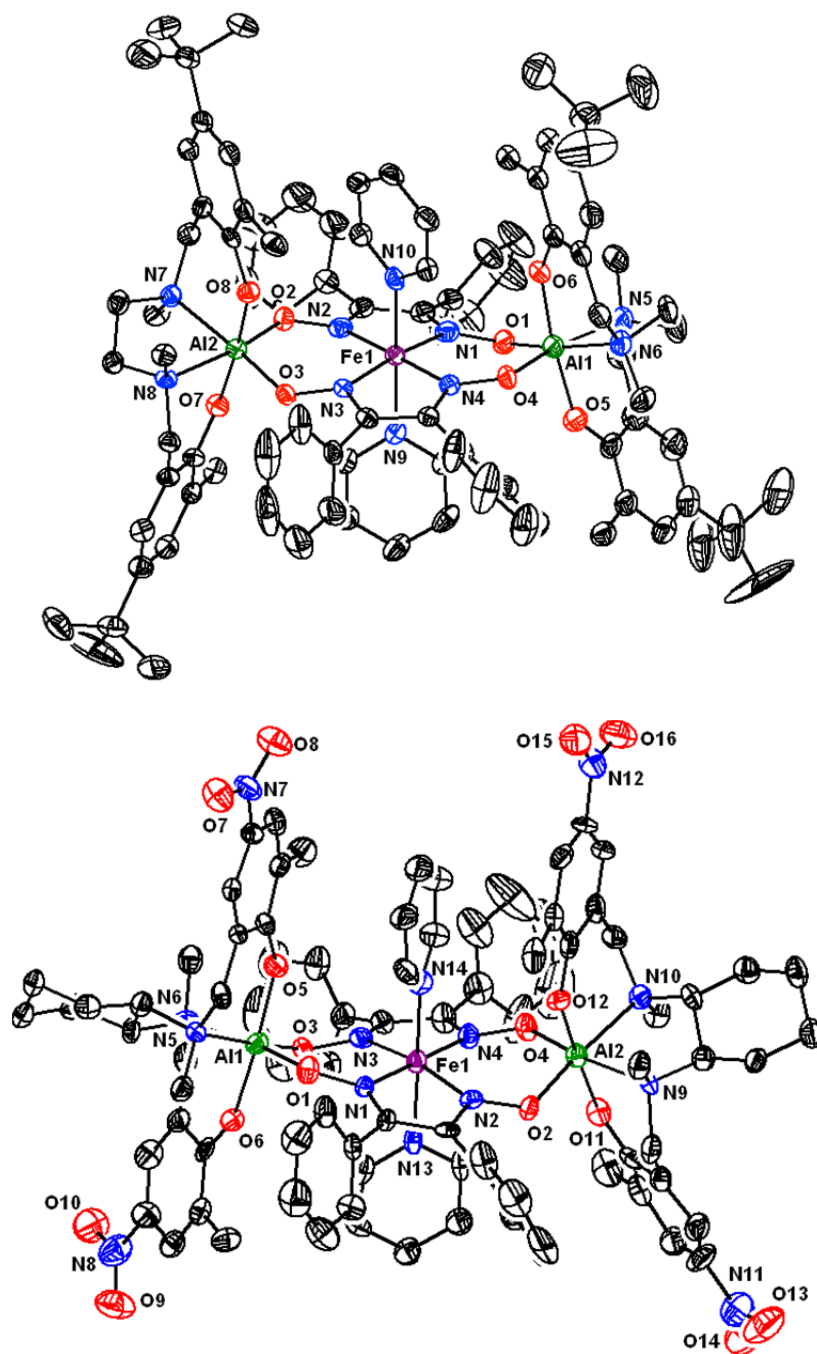


Figure 5.3. Solid state structures of 29^{tBu} and 32^{NO_2} . Hydrogen atoms and solvent molecules have been omitted for clarity; thermal ellipsoids are displayed at the 50% probability.

Utilization of enantiopure (*R,R*)-*trans*-1,2-diaminocyclohexane backbones results in significantly cleaner reactions for the synthesis of iron complexes ligated by aluminiummacrocycles, **32^{tBu}** and **32^{NO₂}** (1H NMR spectroscopy). Analysis of **31^{tBu}** by ²⁷Al NMR gives a broad peak ca. 74 ppm consistent with a five coordinate aluminium center as described in literature.^{52,61-63} Mixing **31^{tBu}** with diphenyl glyoxime forms the **31^{tBu}** macrocycle, which gives a broad ²⁷Al NMR peak ca. 14 ppm consistent with aluminium coordination to the glyoxime oxygens. Subsequent metallation and carbonyl coordination to form **32^{tBu}** and **33^{tBu}** does not substantially change the shift in the ²⁷Al NMR (14 and 12 ppm respectively).⁶¹⁻⁶³ Ligand variants with *para*-NO₂ and *para*-*tert*-butyl substitution were employed for the phenoxides. An XRD study of complex **32^{NO₂}** revealed a *pseudo-D₂* structure. Similar to complex **29^{tBu}** supported by the ethylenediamine backbone, **32^{NO₂}** shows ruffling of the macrocycle departing from an idealized *D₂* structure. The control of the overall symmetry of the metallomacrocycle by the ancillary ligand on aluminium is notable as it affords enantiopure macrocycles.^{18,64}

Remote substituents on the phenoxide rings were found to affect the coordination environment around the central iron, likely due to steric interactions (vide supra). To complement those findings, complexes **32^{tBu}** and **32^{NO₂}** allow for studies of the electronic effect of remote groups on aluminium-bound phenoxide on chemistry at the iron centre. Cyclic voltammetry of **32^{tBu}** shows waves between 0.5 and 1 V vs. [FeCp₂]⁺ / FeCp₂, which are assigned to phenoxide based redox events (Figure 5.4). Metal-bound trialkyl phenoxides were reported previously to have reduction potentials in the above range.^{65,66} Complex **32^{NO₂}** displays a positive shift of these potentials consistent with the presence of electron withdrawing nitro groups that

disfavouring ligand oxidation. A large peak is seen close to 1 V in **32**^{NO₂}, which is assigned to the oxidation of the nitro substituted phenoxides on the ancillary aluminium centers as the **31**^{NO₂} diphenylglyoxime macrocycle also contains a large oxidation wave in that region (Figure 5.5). The redox event at -0.34 V for **32**^{Bu} was assigned to the Fe^{III}/Fe^{II} couple. This is 0.32 V more negative compared to proton-bridged iron diglyoximato species (-0.02 V vs. [FeCp²]⁺ / FeCp²). It is not clear if this a consequence of increasing electron density at iron when six-coordinate aluminium bridges are present or of the larger macrocycle size with aluminium.⁶⁷ The presence of four *para*-NO₂ groups in **32**^{NO₂} led to a Fe^{III}/Fe^{II} couple at -0.07 V. The significant 0.27 V shift of the Fe^{III}/Fe^{II} reduction potential compared to **32**^{Bu} supports the notion that the redox properties of the central atom can be affected by remote substituents at the periphery of the macrocycle.

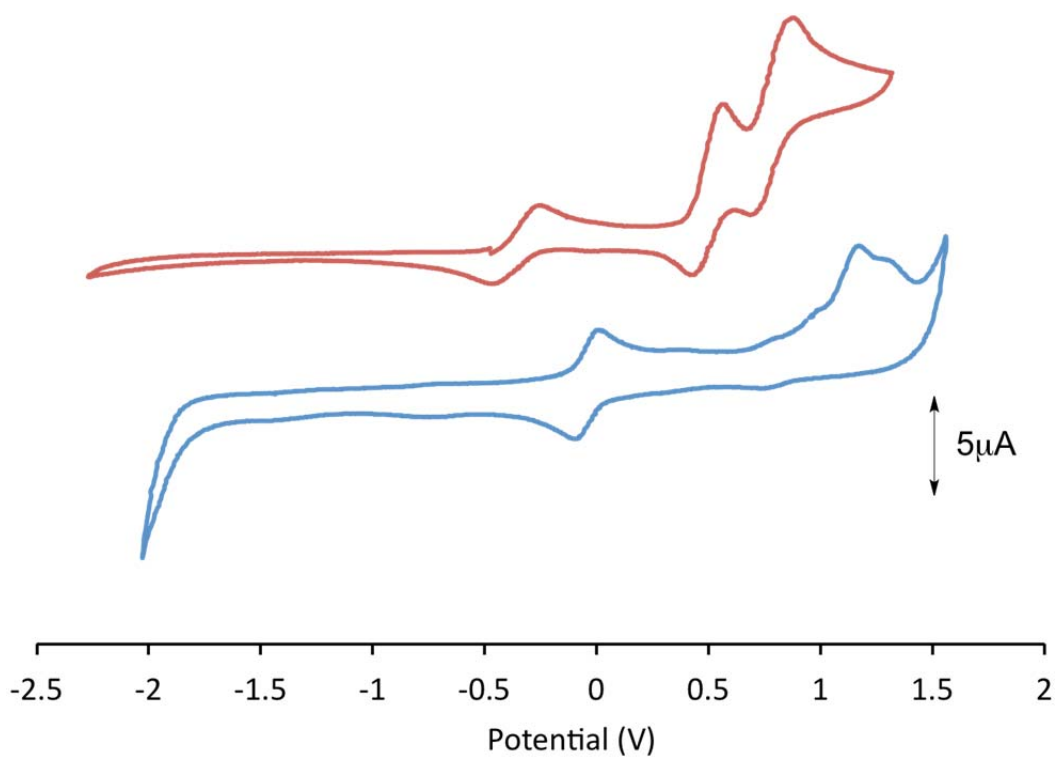


Figure 5.4. Cyclic voltammograms of complexes 32^{tbu} (red) and 32^{no_2} (blue) (1 mM in 1:1 DCM:MeCN solution, 0.1 M $n\text{Bu}_4\text{ClO}_4$, 0.01 M AgNO_3 reference electrode, platinum working electrode, Pt wire counter electrode, referenced to $\text{FcCp}^2/[\text{FcCp}^2]^+$).

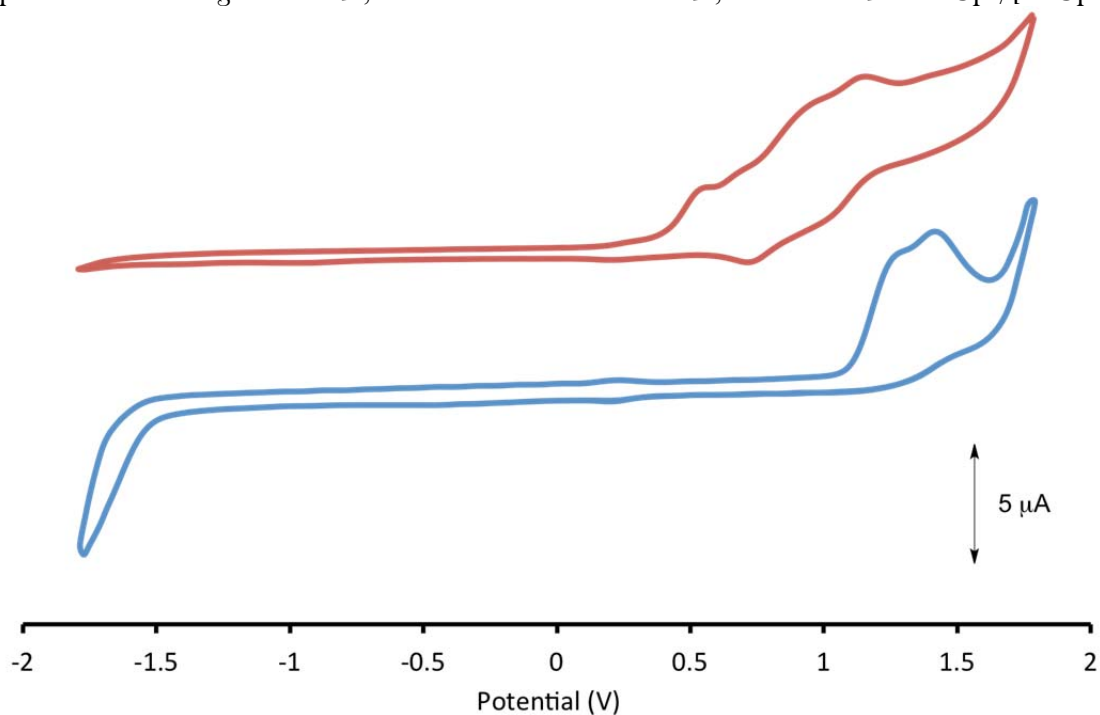
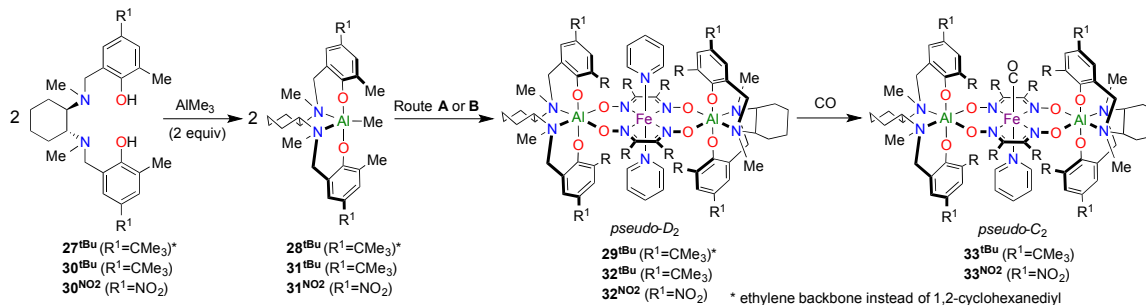


Figure 5.5. Cyclic voltammograms of complexes 31^{no_2} (blue) and 31^{tbu} (red), 1 mM solutions of each using a 100 mV/s scan rate, both referenced to Fc/Fc^+ .



Scheme 5.4. Synthesis of iron complexes supported by aluminium macrocycles with C_2 -symmetric ancillary ligands.

Treatment of complexes 32^{tBu} and 32^{NO_2} with CO generated new species cleanly by 1H NMR spectroscopy (Scheme 5.4). The number of peaks corresponding to the diphenoxide diamine ligands is doubled, consistent with a decrease in molecular symmetry. For example, the methyl groups ortho to the phenoxide oxygen display two singlets rather than one in 32^{tBu} or 32^{NO_2} . Displacement of one pyridine with CO leads to a *pseudo-C₂* structure. The two different ligands located on the C_2 axis, CO and pyridine, render chemically different the two halves of the molecule delimited by the Fe-diglyoximato moiety.²⁶ The carbonyl C-O stretch for complexes 33^{tBu} and 33^{NO_2} (Scheme 5.4) appears at 2019 and 2020 cm^{-1} , respectively. The carbon monoxide adduct of the proton-bridged iron diglyoximato species (**24**) shows a C-O stretch at 2004 cm^{-1} in THF.²⁶ The cyclic voltammograms of the CO adducts 33^{NO_2} and 33^{tBu} show a large shift in the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ couple in comparison with the dipyrindine complexes 32^{NO_2} and 32^{tBu} . The $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ couple in 33^{NO_2} shows up as an irreversible oxidation at 0.71 V, which is ca. 700 mV more positive than that observed in 32^{NO_2} . Similarly, the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ couple in the 33^{tBu} complex is shifted, albeit obscured by the phenoxide oxidation peaks. The shift in the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ couple is similar to what is seen in a boron-bridged

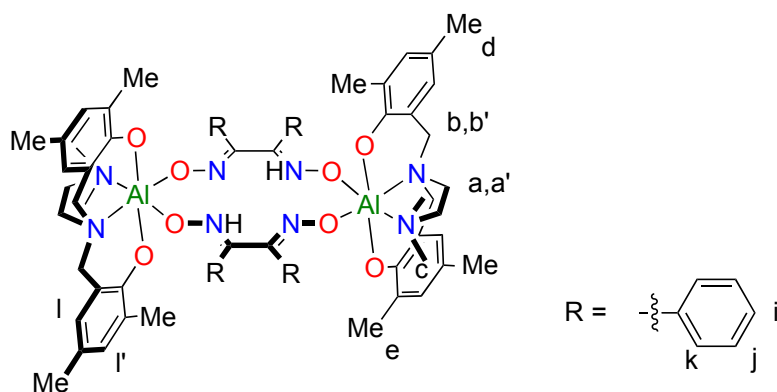
iron bisdimethylglyoxime system³⁸ and metal porphyrin systems upon the binding of carbon monoxide.^{68,69} The similar values for **33**^{tbu} and **33**^{NO₂} suggest that although the iron reduction potential is affected by the substituents, the electron density of the metal is affected to a greater extent by interactions with the carbonyl ligand. Compared to proton bridged system, **33**^{tbu} and **33**^{NO₂} both appear less electron rich on the central metal based on the C-O stretch.

CONCLUSIONS:

In summary, metallomacrocycles consisting of dialuminium diglyoximate frameworks were synthesized and utilized as ligands for iron. These iron complexes were also prepared independently by first binding two glyoximate units to a central metal followed by reaction with alkyl aluminium precursors. The overall symmetry of the products is affected by the ancillary ligands bound to aluminium. Utilization of enantiopure, C_2 -symmetric backbones facilitates the formation of a single, chiral isomer. The steric bulk of remote substituents was found to affect the conformation of the free metallomacrocycles as well as the coordination geometry around the central metal. For iron, complexes with trigonal prismatic and square bipyramidal coordination modes were characterized. Additionally, the electronic properties of the substituents on ligands bound to aluminium significantly influence the reduction potentials of the central metal. The present synthetic strategies and properties suggest that metallomacrocycles with a variety of ancillary ligands can be prepared and designed to affect chemistry at the central atom both sterically and electronically.

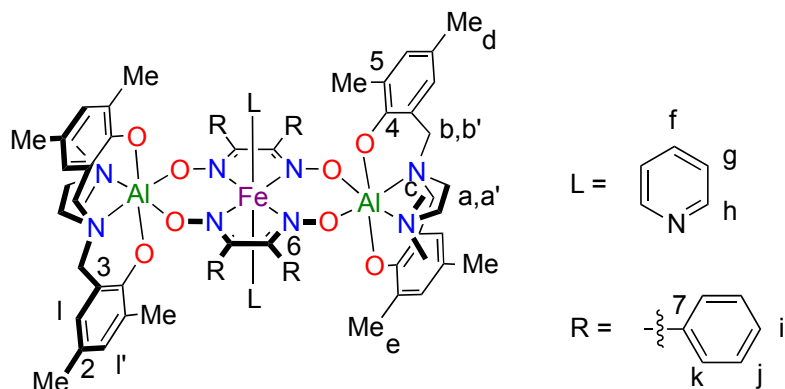
EXPERIMENTAL SECTION:

General Considerations. Unless otherwise specified, all compounds were manipulated using a glove box under a nitrogen atmosphere. Solvents for all reactions were dried by Grubbs' method. Benzene- d_6 was purchased from Cambridge Isotope Laboratories and vacuum distilled from sodium benzophenone ketyl. Chloroform- d and dichloromethane- d_2 were also purchased from Cambridge Isotope Laboratories and vacuum distilled from calcium hydride. Alumina and Celite were activated by heating under vacuum at 200 °C for 12 h. Tetradentate salan ligands (**21^{bu}**), methyl aluminum complexes (**22**, **22^{bu}**, and **27^{bu}**), and metal glyoxime precursors (**24**) were all synthesized according to literature procedures.²⁻⁴ All other materials were used as received. All ^1H , ^{13}C , and 2D NMR spectra were recorded on Varian Mercury 300 MHz, Varian 400 MHz, or Varian INOVA-500 or 600 MHz spectrometers at room temperature, unless denoted otherwise. Chemical shifts are reported with respect to internal solvent: 7.16 ppm and 128.06 (t) ppm (C_6D_6), 7.26 ppm and 77.16 ppm (CDCl_3), and 5.32 ppm and 53.84 ppm (CD_2Cl_2) for ^1H and ^{13}C NMR data, respectively. The chemical shifts in the ^{27}Al NMR data were referenced to a 1.1 M solution of $\text{Al}(\text{NO}_3)_3$ in D_2O . Electrochemical measurements were recorded in a glovebox under a N_2 atmosphere using a Pine Instrument Company Bipotentiostat, at 1mM of the complex of interest, in DCM containing 0.1 M $n\text{Bu}_4\text{N}(\text{ClO}_4)$ as the supporting electrolyte. For the electrochemistry a platinum working electrode, a platinum wire auxiliary electrode, and a 0.01M Ag/AgNO_3 nonaqueous reference electrode were used for all measurements. Elemental analysis was performed by Midwest Microlab, LLC (Indianapolis, IN).



Synthesis of **23**

A stirring solution of **2** (0.158 g, 0.387 mmol) in THF was treated with a slurry of diphenylglyoxime (0.096 g, 0.398 mmol) in THF. The solution was stirred for 3 hours over which the solution became yellow. The solvent was removed *in vacuo* to yield a pale yellow solid. The macrocycle **22** was used as isolated without any further purification. Yield 0.211 g, 88 %. $^1\text{H NMR}$ (300 MHz, C_6D_6) δ 14.41 (2H, s, *NH*), 7.86 (8H, m, k) 6.98 (4H, t, J = 7.6 Hz, i), 6.83 (8H, m, j), 6.76 (4H, s, l, l'), 6.69 (4H, s, l, l'), 4.89 (4H, d, J = 12.9 Hz, b, b'), 2.79 (4H, d, J = 13.1 Hz, b, b'), 2.38 (12H, s, e), 2.32 (4H, m, a, a'), 2.18 (12H, s, c), 2.15 (12H, s, d), 1.75 (4H, m, a, a') ppm. Anal. Calcd for $\text{C}_{72}\text{H}_{82}\text{Al}_2\text{N}_8\text{O}_8$: C, 69.66; H, 6.66; N, 9.03; Found: C, 69.07; H, 6.69; N, 8.69 %.

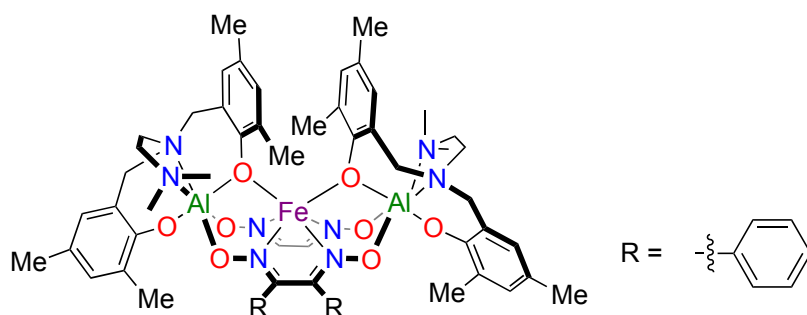


Synthesis of **25**

Route B: In a 20 ml vial (0.043 g, 0.062 mmol) of **24** was stirred in about 2 ml of THF. To this was added (0.050 g, 0.126 mmol) of **22** as a solution in a small amount of THF. The reaction was stirred at ambient temperature for 3 days. Over the reaction time the solid **24** became soluble. The volatiles were removed under vacuum and the resulting purple solid was washed with Et₂O and benzene. The benzene was removed from the benzene fraction via vacuum and the resulting solid was dissolved in minimal amounts of THF. Small amounts of hexanes were added to the saturated solution resulting in precipitation of a purple solid. The solid was collected via filtration over a fine frit. Yield 0.033 g, 36 %.

Route A: Sodium hexamethyldisilazide (0.030 g, 0.163 mmol) was added to a solution of **23** (0.100 g, 0.081 mmol) in THF. The solution was stirred for 2 hours and the solvent was removed via vacuum. The resulting white residue was washed with pentane to remove the bis(trimethylsilyl)amine. The bis(trimethylsilyl)amine free solid was taken up in THF and mixed with a solution of FeCl₂ (0.010 g, 0.079 mmol) in THF. The solution immediately turned a dark purple and was stirred for an hour. After an hour excess pyridine was added to the solution upon which the color changed from dark purple to a reddish purple. The solvent was removed *in vacuo* yielding the a

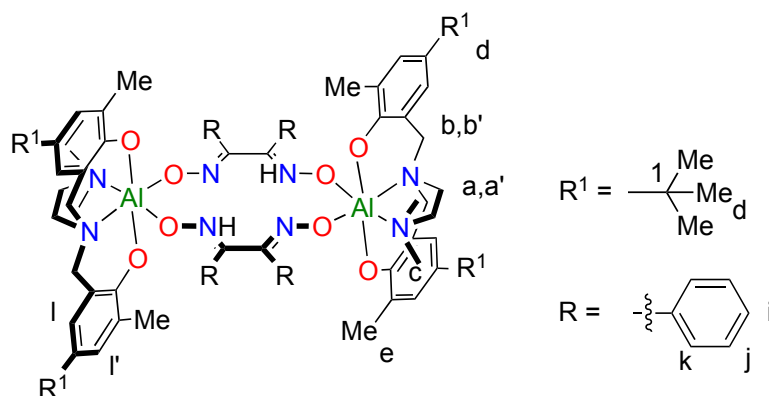
purple red solid which was washed with ether. Yield 0.060 g, 52 %, about 90 % pure. To date, an analytically pure sample has yet to be obtained due to contamination of what is believed to be another isomer of the desired complex. ^1H NMR (500 MHz, C_6D_6) δ 9.30 (4H, d, $J=5.6$ Hz, h), 7.33 (4H, m, $J=5.8$ Hz, i), 6.98 (16H, m, j,l), 6.95 (4H, s, l'), 6.79 (2H, t, $J=8.2$ Hz, f), 6.63 (4H, m, g), 6.61 (4H, s, l), 4.61 (4H, d, $J=13.0$ Hz, b'), 2.61 (4H, d, $J=12.9$ Hz, b), 2.36 (6H, s, d), 2.15 (4H, m, a'), 1.97 (6H, s, e), 1.80 (6H, s, c), 1.64 (4H, m, a) ppm. $^{13}\text{C}\{^1\text{H}\}$ (126 MHz, C_6D_6) δ 159.08 (4), 158.35 (6), 156.67 (h), 135.70 (7), 134.57 (f), 131.41 (l'), 130.49 (i), 130.43 (k), 127.63 (j), 127.25 (l), 126.01 (5), 122.59 (g), 122.15 (3), 121.80 (2), 64.97 (b,b'), 58.18 (a,a'), 50.11 (a,a'), 47.68 (c), 20.89 (d), 16.74 (e) ppm. MS ESI (m/z): calcd, 1453.46 (M^+); found 1452.7 (M^+) (dipyridine) and 1390.2 (M^+) (monopyridine with an oxygen)



Synthesis of 26

A solution of **23** (0.248 g, 0.200 mmol) in THF was treated with a solution of Sodium hexamethyldisilazide (0.073 g, 0.400 mmol) also in THF. The solution was stirred for 3 hours over which the solution lost some of its color. After 3 hours the solvent was removed *in vacuo* resulting in a pale yellow white solid. The solid was washed with pentane resulting in a white THF soluble solid (0.116 g, 0.090 mmol, **23-Na₂**). To a THF solution of this disodium salt was added a slurry of FeCl_2 in THF (0.0115 g,

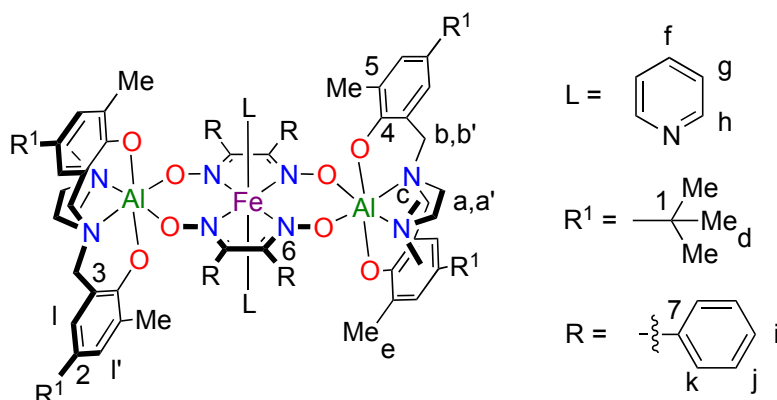
0.091 mmol). Upon addition the solution immediately became a dark black with an orange hue. The solution was stirred for 4 hours and the THF was removed *in vacuo*. The resulting dark brown solid was washed with diethyl ether resulting in an orange solid which was extracted using DCM. The DCM was removed *in vacuo* resulting in a dark orange solid paramagnetic material. Alternatively, **26** can be synthesized by removing the pyridines from **25**, by dissolving **25** in a high boiling solvent and removing the solvent *in vacuo*. Crystals were grown from a concentrated solution of **25** in THF layered with hexanes. Yield 0.066 g, 57 %. $^1\text{H NMR}$ (300 MHz, CD_2Cl_2) δ 18.46, 15.23, 12.84, 11.02, 10.67, 9.82, 8.97, 7.13, 6.68, 5.26, 4.96, 4.27 ppm.



Synthesis of **23**^{tbu}

The macrocycle was synthesized following the synthesis procedure for **23**. A stirring solution of **22**^{tbu} (0.100 g, 0.021 mmol) in THF was treated with a slurry of diphenylglyoxime (0.050 g, 0.021 mmol) in THF. The solution was stirred for 3 hours over which the solution became yellow. The solvent was removed *in vacuo* to yield a pale yellow solid. The $\text{Al}(\text{salan})_2(\text{diphenylglyoxime})_2$ macrocycle was used as isolated without any further purification. $^1\text{H NMR}$ (300 MHz, C_6D_6) δ 14.10 (2H, s, NH), 7.85 (4H, d, $J = 6.7$ Hz, l, l'), 7.61 (4H, t, $J = 7.6$ Hz, l, l'), 6.92 (8H, m, k), 6.82 (8H, m, j),

6.65 (4H, m, i), 4.82 (4H, d, $J = 12.7$ Hz, b,b'), 2.81 (4H, d, $J = 12.9$ Hz, b,b'), 2.32 (12H, s, e), 2.23 (4H, m, a,a'), 2.02 (12H, s, c), 1.78 (4H, m, a,a'), 1.48 (36H, s, d) ppm.



Synthesis of 25^{tBu}

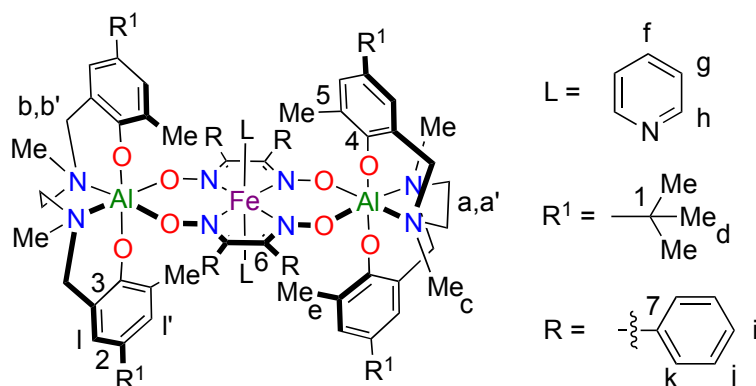
25^{tBu} was synthesized and purified according to the synthesis procedures of **25**.

Route A: In a 20 ml vial 0.072 g (0.010 mmol) of **24** was stirred in about 2 ml of THF. To this was added 0.110 g (0.023 mmol) of the 22^{tBu} complex as a solution in a small amount of THF. The reaction was stirred at ambient temperature for 16 days. Over the reaction time the solid **24** glyoxime became soluble. The volatiles were removed under vacuum and the resulting purple red solid was washed with hexanes, pentane, diethyl ether, and toluene. The toluene fraction was concentrated via vacuum and a small amount of hexanes was added to the saturated solution resulting in precipitation of a purple solid. The solid was collected via filtration over a fine frit. Yield 0.071 g, 44 %.

Route B: Sodium hexamethyldisilazide 0.036 g (0.200 mmol) was added to a solution of 23^{tBu} (0.141 g, 0.100 mmol) in THF. The solution was stirred for 2 hours and the solvent was removed via vacuum. The resulting white residue was washed with pentane

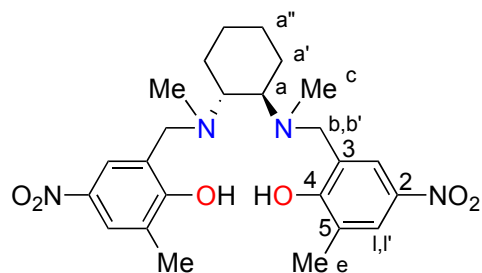
to remove the bis(trimethylsilyl)amine. The bis(trimethylsilyl)amine free solid (0.126 g, 0.090 mmol) was taken up in THF and mixed with a solution of Fe(II)Cl₂ (0.011 g, 0.090 mmol) in THF. The solution immediately turned a dark purple and was stirred for an hour. After an hour excess pyridine was added to the solution upon which the color changed from dark purple to a reddish purple. The solvent was removed in vacuo yielding a purple red solid, which was washed with pentane and hexanes and extracted with diethyl ether. Yield 0.098 g, 67 %

¹H NMR (300 MHz, C₆D₆): δ 9.26 (4H, d, *J*=5.5 Hz, h), 7.41 (4H, d, *J*=8.4 Hz, g), 7.21 (8H, s, k), 6.97 (8H, s, j), 6.89 (8H, s, l), 6.83 (4H, t, *J*=6.7 Hz, i), 6.58 (2H, t, *J*=6.7 Hz, f), 4.65 (4H, d, *J*=12.9 Hz, b,b'), 2.71 (4H, d, *J*=13.3 Hz, b,b'), 2.15 (4H, m, a,a'), 2.08 (6H, s, e), 1.81 (6H, s, c), 1.63 (4H, m, a,a'), 1.44 (36H, s, d) ppm. ¹³C{¹H} NMR (126 MHz, C₆D₆) δ 159.02 (4), 158.88 (6), 156.46 (h), 135.80 (7), 134.24 (2), 130.62 (f), 130.37 (k), 127.66 (j), 127.53 (i), 127.44 (l,l'), 125.67 (5), 123.18 (l,l'), 122.52 (g), 121.53 (3), 65.65 (b,b'), 58.10 (a,a'), 50.33 (a,a'), 47.64 (c), 33.90 (1), 32.33 (d), 17.12 (e) ppm. Anal. Calcd for C₉₄H₁₁₄Al₂FeN₁₀O₈: C, 69.62; H, 7.09; N, 8.64; Found C, 69.36; H, 7.33; N, 8.63



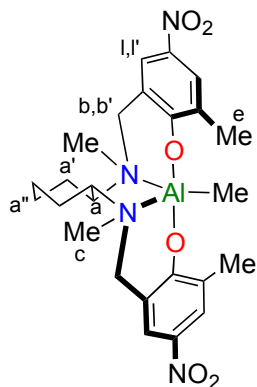
Synthesis of 29^{tBu}

In a round bottom flask **24** (0.692 g, 0.98 mmol) was stirred in 10 ml of toluene at ambient temperature. To this purple slurry was added a solution of the **28^{tBu}** (0.999 g, 2.08 mmol) in toluene. The solution was stirred for 14 hours. After 14 hours toluene was removed in vacuo yielding a purple solid. The solid was washed with hexanes, Et₂O, and toluene. The toluene washed was pumped down to a solid yielding clean **6**. Yield: 0.688 g, 43 % ¹H NMR (500 MHz, C₆D₆) δ 9.21 (4H, d, *J* = 4.9 Hz, h), 7.31 (8H, d, *J* = 7.3 Hz, k), 7.21 (4H, d, *J* = 2.4 Hz, l'), 7.01 (8H, t, *J* = 7.5 Hz, j), 6.94 (4H, m, i), 6.75 (2H, t, *J* = 7.6 Hz, f), 6.74 (4H, d, *J* = 2.5 Hz, l), 6.30 (4H, t, *J* = 7.0 Hz, g), 4.49 (4H, d, *J* = 12.8 Hz, b,b'), 2.69 (4H, d, *J* = 9.0 Hz, a,a'), 2.57 (4H, d, *J* = 13.1 Hz, b,b'), 2.14 (12H, s, e), 1.90 (12H, s, c), 1.38 (36H, s, d), 0.89 (4H, d, *J* = 9.1 Hz, a,a') ppm. ¹³C{¹H} NMR (126 MHz, C₆D₆) δ 158.90 (4), 157.44 (6), 156.83 (h), 135.99 (2), 135.87 (7), 134.16 (f), 130.58 (k), 127.75 (j), 127.43 (i), 126.90 (l'), 126.68 (5), 123.14 (l), 122.65 (g), 120.89 (3), 63.73 (b,b'), 49.97 (a,a'), 46.85 (c), 33.88 (1), 32.30 (d), 17.62 (e) ppm. Anal. Calcd for C₉₄H₁₁₄Al₂FeN₁₀O₈: C, 69.62; H, 7.09; N, 8.64; Found, C, 69.49; H, 6.96; N, 8.44;



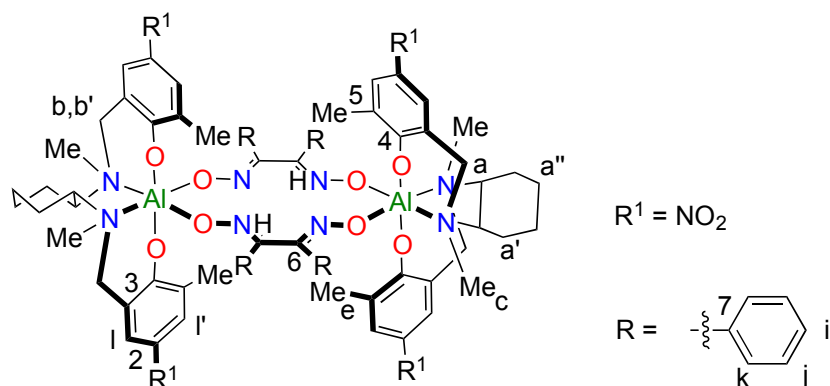
Synthesis of 30^{NO2}

This ligand variant was synthesized using a modified literature procedure.⁵ A solution of N,N'-dimethylcyclohexane-1,2-diamine (0.233 g, 1.63 mmol) and diisopropylethylamine (0.424 g, 3.28 mmol) in THF (7.5 ml) at 0°C (ice bath) was treated with a cold solution (ice bath) of 2-(chloromethyl)-6-methyl-4-nitrophenol (0.661 g, 3.28 mmol) in THF (5 ml). The solution was stirred for 16 hours during which a yellow precipitate formed. The resulting slurry was filtered using a medium glass frit and washed with 3x 20 ml of cold MeOH. The resulting off white solid was dried under vacuum. Yield 0.298 g, 38 % ¹H NMR (300 MHz, CDCl₃), δ 11.99 (2H, br s, OH) 8.01 (2H, d, J = 2.8 Hz, l,l'), 7.84 (2H, d, J = 2.4 Hz, l,l'), 3.91 (4H, d, J = 13.2 Hz, b,b'), 3.59 (2H, br s, b,b'), 2.83 (2H, m, a), 2.29 (6H, s, e), 2.14 (6H, s, c), 2.11 (2H, m, a''), 1.91 (2H, s, a'), 1.27 (4H, br m, a',a'') ppm. ¹³C{¹H} NMR (from 2D spectra, 126 MHz, (CD₃)₂SO) δ 166.98 (4), 135.74 (2), 126.12 (5), 125.81 (l'), 127.34 (l), 122.58 (3), 62.56 (b,b'), 25.54 (c), 22.78 (a), 16.68 (a), 16.53 (e) ppm from . ESI-MS Calc. (M) 472.2322 Found. 473.2 (MH⁺)



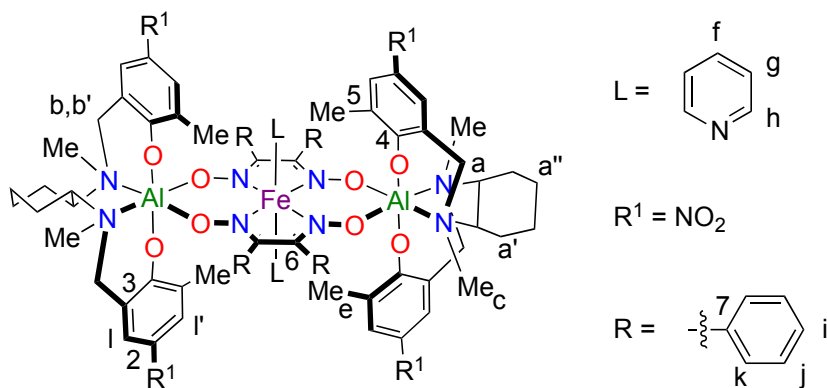
Synthesis of 31^{NO_2}

The synthesis of 31^{NO_2} was synthesized using trimethylaluminum following a published procedure for similar aluminium alkyl complexes.^{6,7} A freshly thawed slurry of 30^{NO_2} (0.024 g, 0.052 mmol) in toluene (5 ml) was treated with a thawed solution of trimethylaluminum (0.004g, 5.2 μl , 0.053 mmol). Upon mixing the solid particulates dissolved and the solution became a dark orange color which faded after a few minutes resulting in a light yellow solution. The solution was allowed to stir for 18 hours. During this time the solution became a slurry. The solvent was removed *in vacuo* resulting in a light yellow powder which was used without further purification. Yield 0.026 g, 99 % ^1H NMR (300 MHz, CD_2Cl_2), δ 8.04 (2H, m, l,l'), 7.85 (2H, m, l,l'), 4.00 (2H, $J = 13.4$ Hz, b,b'), 3.50 (2H, $J = 13.0$ Hz, b,b'), 2.95 (2H, m, a), 2.32 (3H, s, e), 2.28 (6H, m, e',c'), 2.18 (2H, m, a''), 2.10 (3H, s, c), 1.97 (2H, m, a'), 1.51(2H, m, a''), 1.25(2H, m, a'), -0.69 (3H, s, AlCH₃) ppm.



Synthesis of 31^{NO_2} Macrocycle

The macrocycle was synthesized following the synthesis procedure for **23**. A stirring solution of 31^{NO_2} (0.100 g, 0.019 mmol) in THF was treated with a slurry of diphenylglyoxime (0.046 g, 0.019 mmol) in THF. The solution was stirred for 3 hours over which the solution became yellow. The solvent was removed *in vacuo* to yield a pale yellow solid. 31^{NO_2} macrocycle was used as isolated without any further purification. Yield 0.139 g, 97 %. ^1H NMR (300 MHz, C_6D_6) δ 13.98 (2H, s, NH), 7.77 (4H, d, $J = 2.9$ Hz, l,l'), 7.59 (12H, m, i and j), 7.29 (12H, m, k and l,l'), 4.41 (4H, d, $J = 13.5$ Hz, b,b'), 3.25 (4H, d, $J = 13.6$ Hz, b,b'), 2.44 (4H, m, a), 2.06 (12H, s, e), 1.92 (12H, s, c), 1.72 (4H, m, a'), 1.59 (4H, m, a''), 1.03 (4H, m, a'), 0.80 (4H, m, a'') ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2) δ 165.86 (4), 149.36 (6), 136.44 (2), 130.11 (k), 128.28 (j), 127.97 (5), 127.40 (7), 126.39 (l'), 123.49 (l), 120.79 (3), 58.45 (b,b'), 56.39 (a), 39.97 (c), 24.01 (a''), 21.89 (a'), 16.18 (e) ppm. Anal. Calcd for $\text{C}_{76}\text{H}_{82}\text{Al}_2\text{FeN}_{12}\text{O}_{16}$: C, 61.95; H, 5.61; N, 11.41; Found: C, 61.91; H, 5.74; N, 11.29 %.

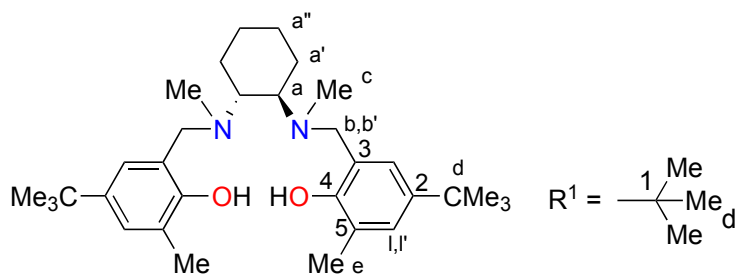


Synthesis of 32^{NO_2}

Route A: To a slurry of 31^{NO_2} (0.150 g, 0.302 mmol) in toluene (5 ml) was added **24** (0.101 g, 0.146 mmol) with THF (3 ml). The slurry was stirred for a total of 3 days, during which the solution took on a purple orange hue. From this colored solution a solid precipitated on the walls of the vial. After the allotted time the solvent was removed *in vacuo*. The solid was washed three times with hexanes to remove the excess toluene. The solid was washed with hexanes, diethylether, toluene, and THF. The desired product was found in the THF fraction. Yield 0.129 g, 52 %

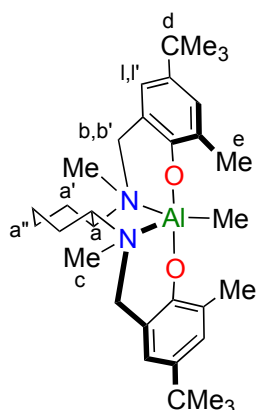
Route B: Sodium hexamethyldisilazide (0.030 g, 0.163 mmol) was added to a solution of 31^{NO_2} macrocycle (0.236 g, 0.160 mmol) in THF. The solution was stirred for 12 hours and the solvent was removed via vacuum. The resulting residue was washed with pentane to remove the bis(trimethylsilyl)amine. The bis(trimethylsilyl)amine free solid (0.217 g, 0.143 mmol) was taken up in THF and mixed with a solution of Fe(II)Cl_2 (0.019 g, 0.146 mmol) in THF. The solution immediately turned a dark purple. The dark purple solution was stirred for 3 hours after which excess pyridine was added. Upon addition of pyridine the solution color changed from dark purple to a reddish purple. The solvent was removed *in vacuo* yielding a purple solid which was washed with benzene and extracted with THF. Yield 0.174 g, 72 %

^1H NMR (500 MHz, CD_2Cl_2), δ 8.61 (4H, s, h), δ 7.83 (4H, l',), δ 7.63 (d, 4H), δ 7.28 (m, 20H), δ 7.02 (dd, 4H), δ 6.37 (m, 2H), δ 4.15 (d, 4H), δ 2.89 (d, 4H), δ 1.80 (s, 12H), δ 1.75 (s, 12H) $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2) δ 166.85 (4), 159.75 (6), 155.16 (h), 135.81 (2), 134.82 (k), 129.75 (j), 128.35 (5) 128.25 (7) 127.76 (f), 126.35 (l'), 123.88 (l), 123.05 (g), 121.54 (3), 58.48 (b,b') , 56.27 (a), 40.97 (c), 24.40 (a''), 22.06 (a'), 16.69 (e) ppm. Anal. Calcd for $\text{C}_{86}\text{H}_{90}\text{Al}_2\text{FeN}_{14}\text{O}_{16}$: C, 61.28; H, 5.38; N, 11.63; Found: C, 61.13; H, 5.46; N, 11.43 %



Synthesis of 30^{tBu}

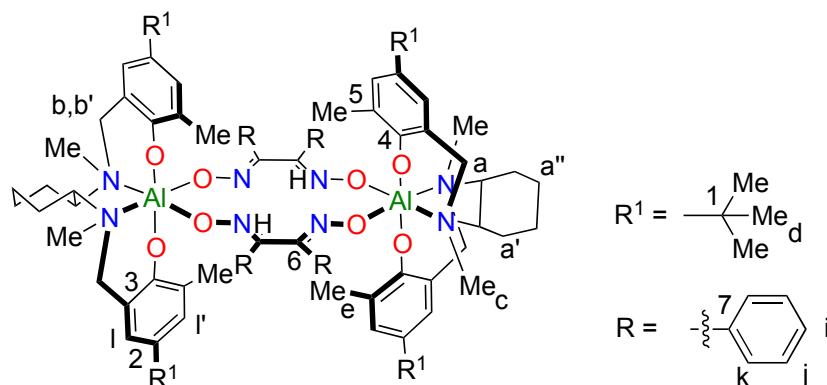
This compound was synthesized via a mannich condensation of the (*R,R*)-1,2-diammoniumcyclohexane mono-(+)-tartrate salt and 2-methyl-4-tert-butylphenol using a previously published procedure.^{7,8} The amines were methylated following the same procedure resulting in the compound 30^{tBu} . ^1H NMR (300 MHz, CDCl_3), δ 10.01 (2H, br s, *OH*), 7.05 (2H, d, $J = 2.1$ Hz, l,l'), 6.82 (2H, d, $J = 2.4$ Hz, l,l'), 3.77 (2H, d, $J = 13.2$ Hz, b,b'), 3.66 (2H, d, $J = 13.3$ Hz, b,b'), 2.70 (2H, m, a), 2.20 (6H, s, e), 2.17 (6H, s, c), 2.01 (2H, m, a''), 1.81 (2H, d, a'), 1.27 (18H, s, d), 1.17 (4H, m, a',a'') ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6) δ 154.06 (4), 140.74 (2), 127.17 (l'), 124.73 (5), 123.32 (l), 121.26 (3), 61.65 (b,b'), 33.66 (1), 31.60 (d), 25.05 (c), 21.99 (a,a',a''), 16.23 (e) ppm. ESI-MS Calc. (M) 494.3872 Found. 495.3 (MH⁺)



Synthesis of 31^{tBu}

Compound 31^{tBu} was synthesized using trimethylaluminum following a published procedure for similar aluminium alkyl complexes.^{6,7} A slurry of 30^{tBu} (0.956 g, 1.93 mmol) in toluene was frozen in a coldwell. Upon freezing the solution was allowed to thaw upon which a freshly thawed solution of trimethylaluminum (0.139 g, 1.93 mmol) in toluene (3 ml) was added slowly. This mixture was allowed to warm to room temperature and left stirring for 12 hours. After 12 hours the solvent was removed in vacuo, yielding an off white solid which was used without further purification. Yield: 0.900 g, 87 % 1H NMR (300 MHz, C_6D_6) δ 7.32, 7.29, 6.90, 6.82, and 6.78 (l,l'), 3.61, 3.54, 3.32, 3.27, 2.79, 2.75, and 2.70 (b,b'), 2.63 and 2.43 (e), 2.29 and 1.99 (a), 1.88, 1.68, and 1.66 (c), 1.41, 1.39, and 1.39 (d), 1.21, 0.60, and 0.48 (a',a''), -0.40 (AlCH₃) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2) δ 156.06 (4), 155.89 (4), 138.33 (2), 137.68 (2), 127.43 (l'), 127.29 (l'), 126.93 (l'), 126.68 (5), 126.55 (5), 126.01 (5), 123.04 (l), 122.84 (l), 120.03 (3), 118.54 (3), 63.81 (b,b'), 60.73 (b,b'), 60.26 (b,b'), 59.48 (b,b'), 42.67, 36.77, 33.57 (1), 31.51 (d), 24.79 (a''), 24.54 (a''), 23.13(a'), 22.89

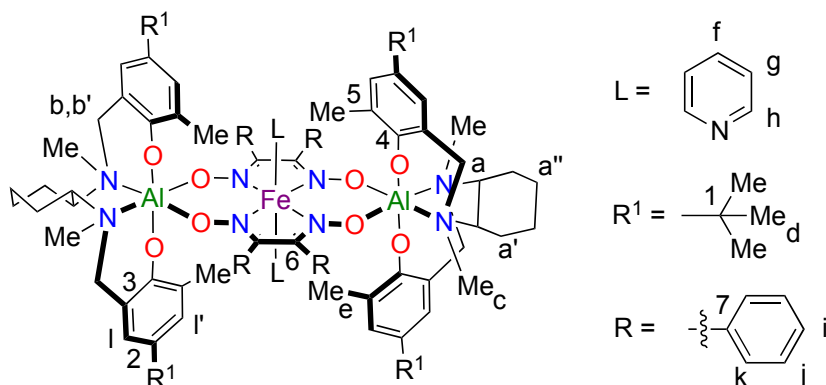
(a'), 22.72 (a'), 16.21 (e), 16.08 (e), 15.72 (AlCH₃) ppm multiple diastereomers in solution.²⁷Al NMR (104.7 MHz, 25 °C, CD₂Cl₂) δ 74.21 ppm, ω_{1/2} 6500 Hz.



Synthesis of **31^{tbu}** macrocycle

The macrocycle was synthesized following the synthesis procedure for **3a**. A stirring solution of **31^{tbu}** (0.105 g, 0.197 mmol) in THF was treated with a slurry of diphenylglyoxime (0.047 g, 0.196 mmol) in THF. The solution was stirred for 3 hours over which the solution became yellow. The solvent was removed in vacuo to yield a pale yellow solid. **31^{tbu}** macrocycle was used as isolated without any further purification. It can also be purified through precipitation from pentane. Yield 0.145 g, 98 %. ¹H NMR (300 MHz, C₆D₆) δ 14.20 (2H, s, NH), 7.67 (8H, d, J = 7.1 Hz, k), 7.29 (4H, s, l,l'), 6.91 (12H, m, j,i), 6.78 (4H, m, l,l'), 4.54 (4H, d, J = 13.0 Hz, b,b'), 2.88 (4H, d, J = 13.1 Hz, b,b'), 2.57 (4H, m, a), 2.34 (12H, s, e), 2.06 (12H, s, c), 1.45 (36H, s, d), 1.25 (8H, m, a', a''), 0.38 (8H, m, a',a'') ppm. ¹³C{¹H} NMR (126 MHz, CD₂Cl₂) δ 156.69 (4), 148.27 (6), 136.31 (7), 131.56 (2), 130.12 (k), 128.76 (j), 127.53 (i), 126.99 (l'), 125.54 (5), 123.17 (l), 120.29 (3), 59.40 (b,b'), 55.56 (a), 39.89 (c), 33.49 (1), 31.67 (d), 24.31 (a''), 21.83 (a'), 16.05 (e). ²⁷Al NMR (104.7 MHz, 25 °C, CD₂Cl₂) δ

14.40 ppm, $\omega_{1/2}$ 4150 Hz. Anal. Calcd for C₉₂H₁₁₈Al₂FeN₈O₈: C, 72.80; H, 7.84; N, 7.38; Found: C, 72.68; H, 7.60; N, 7.12 %



Synthesis of **32^{tbu}**

Route B: In a 100 mL round bottom, a solution of **30^{tbu}** (2.167 g, 4.05 mmol) was treated with a slurry of Fe(DPG)₂(Py)₂ (1.334 g, 1.93 mmol) in benzene at room temperature. The solution was stirred allowing for the produced methane to escape. After 24 hours the solvent was removed in vacuo. The crude solid was taken up in hexanes and filtered. The recovered solid was washed with diethyl ether and extracted with toluene. Purified **12^{tbu}** was precipitated from toluene by adding hexanes to the toluene mixture and cooling the mixture to -35 °C overnight. Another crop of purified solid can be obtained from the hexane fraction via cooling to -35 °C overnight. Yield 2.197 g, 66 %

Route A: Sodium hexamethyldisilazide (0.013 g, 0.069 mol) was added to a solution of **31^{tbu} macrocycle** (0.503 g, 0.033 mol) in THF. The solution was stirred for 2 hours and the solvent was removed via vacuum. The resulting residue was triterated with THF to remove the bis(trimethylsilyl)amine. The bis(trimethylsilyl)amine free solid was taken up in THF and mixed with a slurry of Fe(II)Cl₂ (0.005 g, 0.039 mmol) in THF. The

solution immediately turned a dark purple. The dark purple solution was stirred for one hour after which excess pyridine was added. Upon addition of pyridine the solution color changed from dark purple to a reddish purple. The solvent was removed in vacuo yielding a purple solid. The solid was washed with hexanes and a small amount of diethylether before it was extracted with toluene. The solvent was removed *in vacuo* yielding the same product as Route A. Yield 0.414 g, 72 %

^1H NMR (500 MHz, C_6D_6) δ 9.35 (4H, d, $J = 5.5$ Hz, h), 7.33 (8H, d, $J = 7.4$ Hz, k), 7.20 (4H, s, l'), 7.06 (8H, t, $J = 7.4$ Hz, j), 7.00 (4H, m, $J = 7.1$ Hz, i), 6.77 (2H, t, $J = 7.6$ Hz, f), 6.74 (4H, s, l), 6.34 (4H, t, $J = 6.7$ Hz, g), 4.54 (4H, d, $J = 13.2$ Hz, b'), 2.80 (4H, d, $J = 13.4$ Hz, b), 2.52 (4H, s, a), 2.17 (12H, s, e), 1.93 (12H, s, c), 1.35 (36H, s, d), 1.22 (4H, m, a'), 1.02 (4H, s, a''), 0.46 (4H, m, a'), 0.28 (4H, m, a'') ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (125.70 MHz, C_6D_6) δ 158.77 (6), 157.80 (4), 157.01 (h), 136.14 (7), 135.90 (2), 134.17 (f), 130.62 (k), 127.78 (j), 127.41 (i), 127.08 (l'), 126.17 (5), 122.82 (l), 122.56 (g), 121.27 (3), 59.90 (b,b'), 55.45 (a), 40.90 (c), 33.86 (1), 32.29 (d), 24.26 (a''), 21.78 (a'), 17.51 (e) ppm; ^{27}Al NMR (104.7 MHz, 25 °C, C_6D_6) δ 14.19 ppm, $\omega_{1/2}$ 9000 Hz. Anal. Calcd for $\text{C}_{102}\text{H}_{126}\text{Al}_2\text{FeN}_{10}\text{O}_8$: C, 70.82; H, 7.34; 8.10; Found C, 69.90; H, 7.24; N, 7.44 %

Table 4.1. Crystal and refinement data for complexes **26**, **29^{tbu}**, and **32^{NO2}**

	26	29^{tbu}	32^{NO2}
CCDC Number	861067		861069
Empirical formula	$C_{72}H_{80}N_8O_8Al_2Fe$	$C_{94}H_{114}Al_2FeN_{10}O_8$	$C_{86}H_{90}N_{14}O_{16}Al_2Fe \cdot C_4H_{10}O \cdot 3.5(C_6H_8O)$
Formula weight	1295.25	1621.76	2012.01
T (K)	100(2)	100(2)	100(2)
<i>a</i> , Å	22.511(4)	14.7358(11)	23.9420(6)
<i>b</i> , Å	10.8586(19)	20.2952(15)	27.0271(6)
<i>c</i> , Å	28.663(5)	33.354(3)	15.5154(3)
β, deg	90	77.202(2)	90
γ, deg	109.657(2)	88.031(2)	90
δ, deg	90	74.307(2)	90
Volume, Å ³	6598(2)	9361.2(12)	10039.7(4)
Z	4	4	4
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	C 2/c	P	P 2 ₁ 2 ₁ 2 (#18)
<i>d</i> _{calc} , g/cm ³	1.304 Mg/m ³	1.151 Mg/m ³	1.331 Mg/m ³
ρ range, deg	2.40 to 27.52	1.55 to 25.00	1.86 to 23.28
μ, mm ⁻¹	0.318	none	0.246
Abs. Correction	Semi-empirical from equivalents (TWINABS)	Semi-empirical from equivalents	None
GOF	1.423	1.009	1.681
<i>R</i> ₁ , ^a <i>wR</i> ₂ ^b [I>2σ(I)]	<i>R</i> ₁ = 0.0537 <i>wR</i> ₂ = 0.0804	<i>R</i> ₁ = 0.0650 <i>wR</i> ₂ = 0.1428	<i>R</i> ₁ = 0.0570 <i>wR</i> ₂ = 0.0558

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad ^b wR_2 = \frac{[\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)]}^{1/2}.$$

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