

## Self-Assembly of {2}-Metallacryptands and {2}-Metallacryptates

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Reaction of H<sub>2</sub>L (**1**) with potassium or strontium hydride, or lanthanum(III) chloride, followed by iron(III) chloride, yielded the {2}-ironcryptates **2a–c**. The mono-, di-, and trivalent guest cations are endohedrally encapsulated. In contrast, the dinuclear trispyridinium ironcryptand **2d** was

generated from the reaction of H<sub>2</sub>L (**1**) with only iron(III) chloride. The potassium metallacryptate **2a'** was formed from the triple-helicate **2d** by addition of potassium carbonate. The new compounds **2b**, **2c**, and **2d** were unequivocally characterised by X-ray diffraction analyses.

## Introduction

The selective complexation of guest molecules and metal cations is an essential prerequisite for the proper functioning of enzymes and biological receptors. In order to mimic the geometric and electronic requirements necessary for selective complexation as observed in nature, many different model compounds with cavities of variable size and electronic structure have been constructed<sup>[1]</sup>. Examples are the well-known crown ethers, cryptands, spherands and their inclusion complexes<sup>[1][2]</sup>, along with the corresponding metallatopomers, which are easily accessible by self-organisation<sup>[3][4][5]</sup>. Recently, the bicyclic metallacryptate [K<sub>2</sub>Fe<sub>2</sub>L<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub> (**2a**) was synthesised and characterised by X-ray crystallographic analysis<sup>[6][7][8]</sup> (Scheme 1).

## Results and Discussion

Herein we describe the formation of the bicyclic ironcryptates **2b** and **2c**, with endohedrally encapsulated divalent alkaline earth or trivalent rare earth metal ions, and the cation-free trispyridinium {2}-ironcryptand **2d** (Scheme 1). Upon reaction of H<sub>2</sub>L (**1**)<sup>[9]</sup> in THF with strontium hydride or lanthanum(III) chloride, followed by iron(III) chloride, and subsequent workup with dichloromethane, a dark-red solid was isolated. The FAB-MS spectra (FAB-MS = Fast Atom Bombardment) of the solid materials showed

peaks at *m/z* 1187 and 985, corresponding to the dication [Sr<sub>2</sub>Fe<sub>2</sub>L<sub>3</sub>]<sup>2+</sup> of **2b**, and the trication [La<sub>3</sub>Fe<sub>2</sub>L<sub>3</sub>]<sup>3+</sup> of **2c**, indicating the formation of strontium- and lanthanum-containing bicyclic metallacryptates, respectively. Ruby-red crystals of the strontium complex, suitable for X-ray analysis, were prepared by a slightly modified procedure. Strontium chloride was added to a solution of H<sub>2</sub>L (**1**; R = *t*Bu) and iron(III) chloride in THF, and the crude material was crystallised from dichloromethane by diffusion of a mixture of diethyl ether and hexanes (1:5). The X-ray diffraction analysis of these crystals proved the formation of a strontium-containing bicyclic ironcryptate [(Sr·H<sub>2</sub>O)CFe<sub>2</sub>L<sub>3</sub>][FeCl<sub>4</sub>]<sub>2</sub> (**2b**) with two ferric tetrachloride counterions (Figure 1).

The encapsulated strontium dication does not lie perfectly on the iron–iron axis (Fe–Sr–Fe 174.39°). Strontium is deca-coordinated by six oxygen and three nitrogen atoms of the three ligands, and one molecule of water. In addition, water forms a hydrogen bond to a molecule of diethyl ether solvent. The ligands are approximately octahedrally coordinated to the iron center in a helical fashion. In the chiral complex of racemic **2b**, both iron centers are identically coordinated. Therefore, **2b** is either a (Δ,Δ)-*fac*- or (Λ,Λ)-*fac*-{2}-metallacryptate. The crystals obtained were composed of the homochiral {2}-metallacryptate **2b**. The iron–iron distance in **2b** (715 pm) is identical to the Fe–Fe distance observed in the potassium-containing ironcryptate **2a**.

[◇] Part 12: Ref.<sup>[5]</sup>

Scheme 1. Reaction scheme for the formation of  $[M\subset Fe_2L_3]Y_n$  [**2a**: R = *t*Bu, M = K<sup>+</sup>, Y<sub>n</sub> = PF<sub>6</sub><sup>−</sup>; **2a'**: R = *t*Bu, M = K<sup>+</sup>, Y<sub>n</sub> = FeCl<sub>4</sub><sup>−</sup>; **2b**: R = *t*Bu, M = (Sr<sup>2+</sup>·H<sub>2</sub>O), Y<sub>n</sub> = (FeCl<sub>4</sub><sup>−</sup>)<sub>2</sub>; **2c**: R = Me, M = (La<sup>3+</sup>·H<sub>2</sub>O·THF), Y<sub>n</sub> = (FeCl<sub>4</sub><sup>−</sup>)<sub>3</sub>] and  $[Fe_2(LH^N)_3]Y_n$  [**2d**: Y<sub>n</sub> = (FeCl<sub>4</sub><sup>−</sup>)<sub>3</sub>]

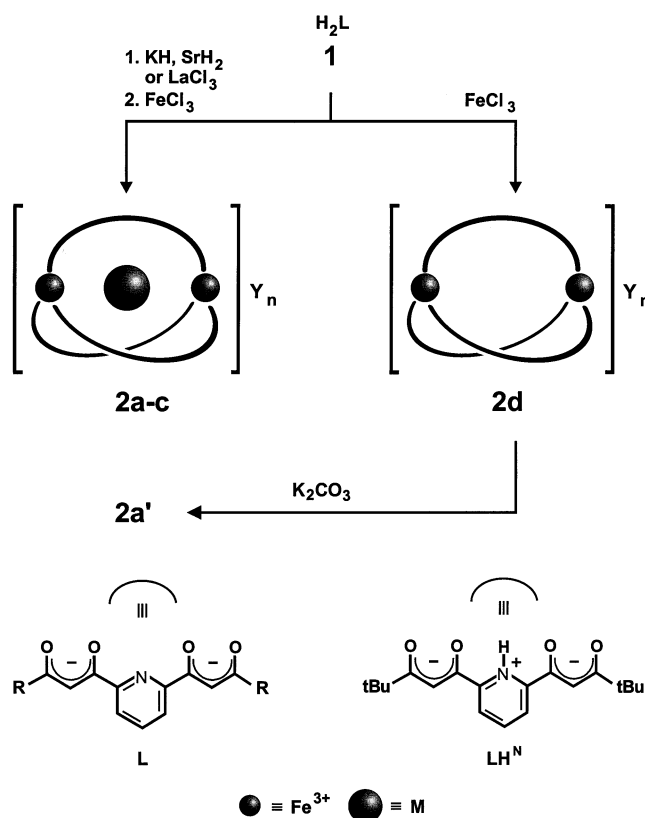
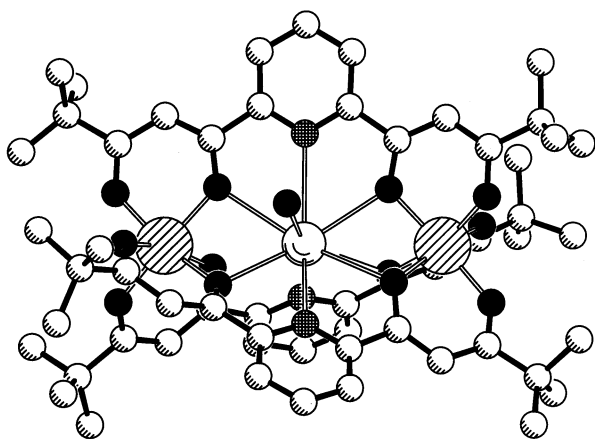


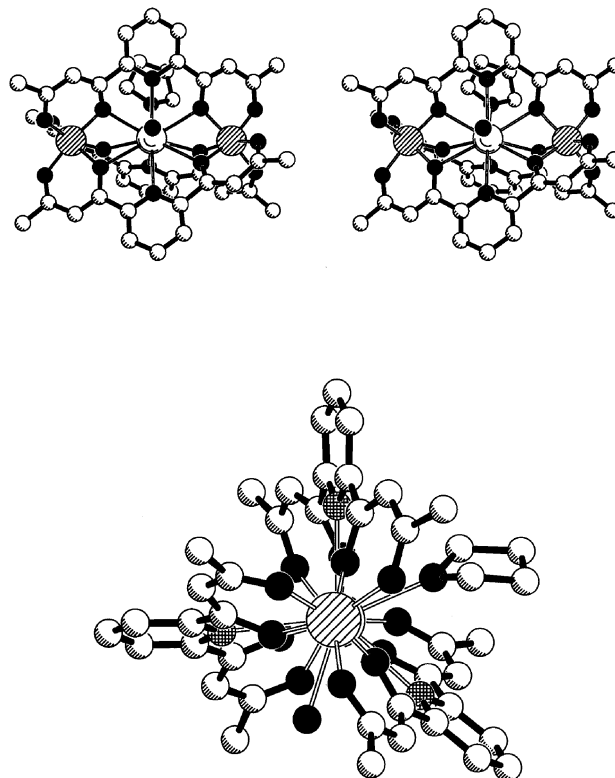
Figure 1. Molecular structure of the dication  $[(Sr\cdot H_2O)\subset Fe_2L_3]^{2+}$  of {2}-ironcryptate **2b** (hydrogen atoms, counterions and solvent molecules omitted for clarity; O atoms black, C atoms shaded, N atoms net, Sr atoms segment, Fe atoms diagonal)



Single crystals suitable for an X-ray diffraction analysis of the chiral racemic lanthanum-containing compound were obtained by diffusion of diethyl ether into a dichloromethane solution of **2c**. There are two slightly different, independent, homochiral ironcryptates ( $\Delta,\Delta$ - or ( $\Lambda,\Lambda$ -

$[(La\cdot THF\cdot H_2O)\subset Fe_2L_3][FeCl_4]_3$  (**2c**) of the same chirality present in the asymmetric unit (Figure 2).

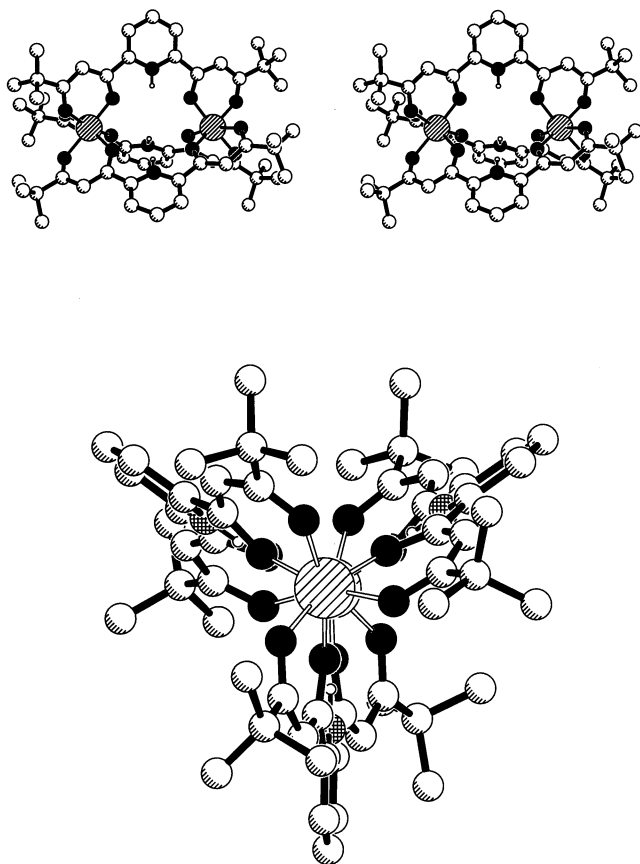
Figure 2. Molecular structure of the trication  $[(La\cdot H_2O\cdot THF)\subset Fe_2L_3]^{3+}$  of {2}-ironcryptate **2c**; top: stereo view; bottom: view along the Fe–Fe axis (hydrogen atoms, counterions and solvent molecules omitted for clarity; O atoms black, C atoms shaded, N atoms net, La atoms segment, Fe atoms diagonal)



The two iron(III) cations ( $d_{Fe-Fe} = 719$  pm) in the molecule are each approximately octahedrally coordinated by six oxygen atoms of three ligands. They are located on the idealised  $C_3$  axis of the  $D_{3h}$ -symmetric molecule. The incorporated lanthanum(III) cation is eleven-coordinate. The six internal oxygen atoms of the ligands form a trigonal prismatic coordination sphere around the lanthanum center. The three nitrogen atoms of the ligands, a THF molecule, and a water molecule coordinate the lanthanum center equatorially in a near perfect plane. The lanthanum–iron distances are similar within each molecule ( $\bar{d}_{Fe-La} = 360$  pm). The encapsulated lanthanum trication lies almost on the Fe–Fe axis (Fe–La–Fe  $176.93^\circ$ ). In contrast to the aforementioned potassium-containing ( $\Delta,\Lambda$ )-*fac* (*meso*) ironcryptate **2a**, the lanthanum-containing analogue **2c** forms a racemic mixture of the homochiral ( $\Delta,\Delta$ )-*fac* and ( $\Lambda,\Lambda$ )-*fac* stereoisomers.

Upon addition of iron(III) chloride to a solution of H<sub>2</sub>L (**1**; R = *t*Bu) in dry THF, followed by workup with dichloromethane, and crystallisation by diffusion of diethyl ether into a dichloromethane solution of the crude solid material, ruby crystals were obtained. The crystal structure determination revealed the formation of bicyclic metallacryptand  $[Fe_2(LH^N)_3][FeCl_4]_3$  (**2d**). In **2d** the pyridine nitrogen atoms of the three ligands are protonated, and the re-

Figure 3. Molecular structure of the trication  $[\text{Fe}_2(\text{LH}^{\text{N}})_3]^{3+}$  of {2}-ironcryptand **2d**; top: stereo view; bottom: view along the Fe–Fe axis (pyridinium hydrogen atoms shown; counterions and solvent molecules omitted for clarity; H atoms void, O atoms black, C atoms shaded, N atoms net, Fe atoms diagonal)



sulting charge of the complex is compensated by three  $\text{FeCl}_4^-$  counterions. In addition to the two molecules of **2d** in the asymmetric unit, there are four dichloromethane molecules (Figure 3).

The mean Fe–Fe distance of **2d** (642 pm) is much smaller than those in the metallacryptates **2a**, **b**, and **c** (715 and 719 pm). Inclusion of a cation in **2a**, **b**, and **c** causes an expansion of the ligands of the metallacryptates, and an elongation of the iron–iron distances. The average N–N distance for **2d** (539 pm) is considerably larger than that of the ironcryptate **2c** (481 pm). In the chiral, racemic complex **2d**, both iron centers are identically coordinated to six oxygen atoms. Therefore, the {2}-metallacryptand **2d** is either a  $(\Delta, \Delta)$ -*fac* or  $(\Lambda, \Lambda)$ -*fac* dinuclear triple helicate. A racemic mixture of complex **2d** self-selectively sorts by chirality to generate an enantiomerically pure crystal. As only one crystal was analysed by X-ray, there possibly exists crystals of opposite chirality, forming a conglomerate.

The {2}-ironcryptand **2d** can be converted into the potassium {2}-ironcryptate  $[\text{K}(\text{Fe}_2\text{L}_3)][\text{FeCl}_4]$  (**2a'**) on addition of an excess of potassium carbonate to a solution of complex  $[\text{Fe}_2(\text{LH}^{\text{N}})_3][\text{FeCl}_4]_3$  (**2d**) in THF. After stirring of the reaction mixture for one day at room temperature and workup with dichloromethane, a red solid was obtained,

which was characterised by FAB-MS, microanalysis, and IR to be **2a'**.

## Conclusion

In summary, a series of bicyclic ironcryptates with encapsulated alkaline, alkaline earth, and rare earth metal cations was synthesised, as was a bicyclic metallacryptand with pyridinium units in the ligands. According to X-ray analyses, the strontium- and lanthanum-containing ironcryptates and the bicyclic pyridinium ironcryptand form helical structures, in contrast to the known *meso*-potassium ironcryptate. Future work will concentrate on possible interesting physical and chemical properties of rare earth metallacryptates and the potential use of the ironcryptates as selective complexation agents for certain cations.

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## Experimental Section

**General:** The compounds  $\text{H}_2\text{L}$  (**1**) [1,1'-(2,6-pyridyl)bis-1,3-butanedione and 1,1'-(2,6-pyridyl)bis-4,4'-dimethyl-1,3-pentanedione] were prepared according to a literature procedure<sup>[9]</sup>. – IR: Bruker IFS 25. – FAB-MS: Micromass ZabSpec. – Microanalysis: Heraeus CHN-Mikroautomat; **2a–d** lose crystal solvent during drying.

**General Procedure for the Synthesis of the Dinuclear Iron(III) Complexes 2b and 2c:** To a solution of  $\text{H}_2\text{L}$  (**1**) (2 mmol) in 75 ml of dry THF, 359 mg (4 mmol) of strontium hydride, or 491 mg (4 mmol) of lanthanum(III) chloride was added. The mixture was stirred for 15 min at 20°C. Iron(III) chloride (216 mg, 1.33 mmol) was then added, and the dark red solution was stirred for 16 h at 20°C. The solvent was removed in vacuo, and the residue was suspended in 50 ml of dichloromethane. After standing for 16 h at 20°C, the red solution was filtered, the solvent removed, and the remaining crude product dried under vacuum (oil pump).

$[(\text{Sr} \cdot \text{H}_2\text{O})\text{C}(\text{Fe}_2\text{L}_3)][\text{FeCl}_4]_2 \cdot \text{CH}_2\text{Cl}_2 \cdot \text{Et}_2\text{O}$  (**2b**): Ruby-coloured crystals were obtained according to the general procedure using 634 mg (4 mmol) of strontium chloride instead of strontium hydride and diffusion of a mixture of diethyl ether and hexanes into a dichloromethane solution. Yield 676 mg (76%), m. p. > 250°C (decomp.). – IR ( $\text{CHBr}_3$ ):  $\tilde{\nu} = 1721 \text{ cm}^{-1}$  (C=O), 1553, 1515 (C=C). – FAB MS (3-nitrobenzyl alcohol matrix);  $m/z$ : 1222 ( $\text{SrC}(\text{Fe}_2\text{L}_3) \cdot 2\text{H}_2\text{O}$ ), 1187 ( $\text{SrC}(\text{Fe}_2\text{L}_3)$ ). –  $\text{C}_{63}\text{H}_{85}\text{Cl}_{12}\text{Fe}_4\text{N}_3\text{O}_{14}\text{Sr}$  (1844,77): calcd. C 41.02, H 4.64, N 2.28; found C 40.81, H 4.71, N 2.02.

$[(\text{La} \cdot \text{THF} \cdot \text{H}_2\text{O})\text{C}(\text{Fe}_2\text{L}_3)][\text{FeCl}_4]_3 \cdot 2\text{CH}_2\text{Cl}_2$  (**2c**): Ruby-coloured tablets were obtained by diffusion of diethyl ether into a dichloromethane solution. Yield 898 mg (80%), m. p. > 250°C (decomp.). – IR ( $\text{CHBr}_3$ ):  $\tilde{\nu} = 1736 \text{ cm}^{-1}$  (C=O), 1603, 1586 (C=C). – FAB MS (3-nitrobenzyl alcohol matrix);  $m/z$ : 1020 ( $\text{LaC}(\text{Fe}_2\text{L}_3) \cdot 2\text{H}_2\text{O}$ ), 985 ( $\text{LaC}(\text{Fe}_2\text{L}_3)$ ), 757 ( $\text{LaC}(\text{Fe}_2\text{L}_2 \cdot \text{H}_2\text{O})$ ). –  $\text{C}_{43}\text{H}_{45}\text{Cl}_{12}\text{Fe}_5\text{LaN}_3\text{O}_{14}$  (1687.41): calcd. C 30.61, H 2.69, N 2.49; found C 30.71, H 3.12, N 2.31.

$[\text{Fe}_2(\text{LH}^{\text{N}})_3][\text{FeCl}_4]_3 \cdot 2\text{CH}_2\text{Cl}_2$  (**2d**): To a solution of 662 mg (2 mmol) of  $\text{H}_2\text{L}$  (**1**) in 75 ml of dry THF, 216 mg (1.33 mmol) of iron(III) chloride was added and the dark red solution was stirred

for 16 h at 20°C. The solvent was removed in vacuo and the residue was suspended in 50 ml of dichloromethane. After standing for 16 h at 20°C, the red solution was filtered, the solvent removed and the remaining crude product dried under vacuum (oil pump). Ruby-coloured crystals were obtained by diffusion of diethyl ether into a dichloromethane solution. Yield 1094 mg (97%), m. p. > 250°C (decomp.). – IR (CHBr<sub>3</sub>):  $\tilde{\nu}$  = 3217 cm<sup>-1</sup> (N=H), 1587 (C=O), 1494 (C=C). – FAB MS (3-nitrobenzyl alcohol matrix); *m/z*: 1155 [Fe<sub>2</sub>(LH<sup>N</sup>)<sub>3</sub>Fe], 1099 (Fe<sub>2</sub>L<sub>3</sub>), 771 (Fe<sub>2</sub>L<sub>2</sub>). – C<sub>57</sub>H<sub>72</sub>Cl<sub>12</sub>Fe<sub>5</sub>N<sub>3</sub>O<sub>12</sub> (1695.88): calcd. C 40.37, H 4.28, N 2.48; found C 39.93, H 4.52, N 2.70.

[KCF<sub>2</sub>L<sub>3</sub>][FeCl<sub>4</sub>] (**2a'**): To a solution of 102 mg (0.06 mmol) of [Fe<sub>2</sub>(LH<sup>N</sup>)<sub>3</sub>][FeCl<sub>4</sub>] (**2d**) in 50 ml of dry THF, 24 mg (0.18 mmol) of potassium carbonate was added and the dark-red solution was stirred for 16 h at 20°C. The solvent was removed in vacuo, and the residue was suspended in 25 ml of dichloromethane. After standing for 16 h at 20°C, the red solution was filtered, the solvent removed, and the remaining crude product dried under vacuum (oil pump). Ruby-coloured microcrystals of **2a'** were obtained by diffusion of diisopropyl ether into a dichloromethane solution. Yield 67 mg (72%), m. p. > 250°C (decomp.). – IR (CHBr<sub>3</sub>):  $\tilde{\nu}$  = 1723 cm<sup>-1</sup> (C=O), 1573, 1514 (C=C). – FAB MS (3-nitrobenzyl alcohol matrix); *m/z*: 1138 ([KCF<sub>2</sub>L<sub>3</sub>]), 809 ([KCF<sub>2</sub>L<sub>2</sub>]). – C<sub>69</sub>H<sub>93</sub>Cl<sub>5</sub>Fe<sub>3</sub>KN<sub>3</sub>O<sub>15</sub> ([KCF<sub>2</sub>L<sub>3</sub>][FeCl<sub>4</sub>]·3THF; 1552.96): calcd. C 53.37, H 6.04, N 2.71; found C 53.44, H 5.99, N 2.62.

**Crystal Structure Determination of Compound 2b:** C<sub>61</sub>H<sub>81</sub>Cl<sub>8</sub>Fe<sub>4</sub>N<sub>3</sub>O<sub>14</sub>Sr, *M* = 1674.91, monoclinic, space group *P*<sub>2</sub><sub>1</sub>/*c*, *a* = 1735.6(4), *b* = 1925.7(4), *c* = 2299.6(5) pm, β = 98.35(3)°, *V* = 7.60(1) nm<sup>3</sup>, *Z* = 4, ρ<sub>calcd.</sub> = 1.463 Mg/m<sup>3</sup>, *F*(000) = 3432, λ = 71.073 pm, *T* = 133 K, μ(Mo-Kα) = 1.781 mm<sup>-1</sup>, min/max transmission: 0.470/0.776, crystal dimensions 0.50 × 0.28 × 0.15 mm; 3.48° ≤ 2θ ≤ 50.00°; 110590 measured reflections of which 13252 were independent (*R*<sub>int</sub> = 0.0672) and employed in the structure refinement (884 parameters, 492 restraints). The *R* values are *R*<sub>1</sub> = Σ|*F*<sub>o</sub> – *F*<sub>c</sub>|/Σ*F*<sub>o</sub> = 0.0465 [*I* > 2σ(*I*)] and *wR*<sub>2</sub> = [Σ(*w*(*F*<sub>o</sub><sup>2</sup> – *F*<sub>c</sub><sup>2</sup>)/Σ*wF*<sub>o</sub><sup>4</sup>)<sup>1/2</sup>] = 0.0831 (all data); min/max residual electron density: –599 e nm<sup>-3</sup>/602 e nm<sup>-3</sup>. Two *tert*-butyl groups show two different rotameric conformations. One tetrachloroferrate anion is disordered over two sites<sup>[18]</sup>.

**Crystal Structure Determination of Compound 2c:** C<sub>45</sub>H<sub>47</sub>Cl<sub>16</sub>Fe<sub>5</sub>LaN<sub>3</sub>O<sub>14</sub>, *M* = 1839.27, triclinic, space group *P* $\bar{1}$ , *a* = 1535.04(7), *b* = 2131.21(9), *c* = 2175.03(9) pm, α = 102.948(1), β = 91.732(1), γ = 97.320(1)°, *V* = 6.8654(5) nm<sup>3</sup>, *Z* = 2, ρ<sub>calcd.</sub> = 1.78 g/cm<sup>3</sup>, *F*(000) = 3636.00, λ = 71.069 pm, *T* = 182 K, μ(Mo-Kα) = 0.2312 mm<sup>-1</sup>, min/max transmission: 0.899/0.670, crystal dimensions 0.35 × 0.18 × 0.08 mm, 3.00° ≤ 2θ ≤ 46.5°; 29795 collected reflections of which 19097 were independent (*R*<sub>int</sub> = 0.046) and employed in the structure refinement (11762 parameters, 0 restraints). The *R* values are: *R*<sub>1</sub> = *R* = Σ *F*<sub>o</sub> – *F*<sub>c</sub> / Σ *F*<sub>o</sub> = 0.057 [*I* > 3σ(*I*)] and *wR*<sub>2</sub> = *R*<sub>w</sub> = [Σ(*w*(*F*<sub>o</sub><sup>2</sup> – *F*<sub>c</sub><sup>2</sup>) / Σ*wF*<sub>o</sub><sup>2</sup>)<sup>1/2</sup>] = 0.065 (all data), where

$$w = \frac{1}{\sigma^2(F_o^2)} = \frac{4F_o^2}{\sigma^2(F_o^2)};$$

max/min residual electron density: 0.76 e<sup>-</sup>/Å<sup>3</sup> / –0.86 e<sup>-</sup>/Å<sup>3</sup>.

Crystal data were collected using a Siemens SMART diffractometer equipped with a CCD area detector. Data were integrated using SAINT and were corrected for Lorentz- and polarization effects. An empirical absorption correction was applied using XPREP (ellipsoidal model); equivalent reflections were

merged. The structure was solved by direct methods and was refined on *F* using the teXsan crystallographic software package. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined.

**Crystal Structure Determination of Compound 2d:** C<sub>59</sub>H<sub>76</sub>Cl<sub>16</sub>Fe<sub>5</sub>N<sub>3</sub>O<sub>12</sub>, *M* = 1875.68, monoclinic, space group *P*<sub>2</sub><sub>1</sub>, *a* = 1467.8(3), *b* = 4000.1(8), *c* = 1511.4(3) pm, β = 111.20(3)°, *V* = 8.27(1) nm<sup>3</sup>, *Z* = 4, ρ<sub>calcd.</sub> = 1.498 Mg/m<sup>3</sup>, *F*(000) = 3796, λ = 71.073 pm, *T* = 133 K, μ(Mo-Kα) = 1.4251 mm<sup>-1</sup>, min/max transmission: 0.467/0.675, crystal dimensions 0.63 × 0.40 × 0.30 mm, 3.54° ≤ 2θ ≤ 50.34°; 93692 measured reflections of which 23822 were independent (*R*<sub>int</sub> = 0.0381) and employed in the structure refinement (1878 parameters, 1027 restraints). The *R* values are *R*<sub>1</sub> = 0.0518 [*I* > 2σ(*I*)] and *wR*<sub>2</sub> = 0.1136 (all data); min/max residual electron density: –752 e nm<sup>-3</sup>/727 e nm<sup>-3</sup>. Three *tert*-butyl groups and one tetrachloroferrate anion are disordered over two sites. Crystallographic data for **2b** and **2d** were collected with a Stoe-Siemens-Huber four-circle diffractometer with Siemens CCD area detector by using φ and ω scans on a shock-cooled crystal in an oil drop<sup>[15]</sup>. Data integration was performed with the program SAINT. A semi-empirical absorption correction was applied. The structures were solved by direct methods (SHELXS-97)<sup>[16]</sup>. Refinement of *F*<sup>2</sup> was accomplished by the least-squares method<sup>[17]</sup>. All non-hydrogen atoms were refined anisotropically. For the hydrogen atoms, the riding model was used. The hydrogen atoms attached to the nitrogen atoms in **2d** could be located in the difference Fourier synthesis. NH distances were restrained to a target value of 95 pm. All disordered components were refined anisotropically with the assistance of distance and ADP restraints<sup>[18]</sup>.

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