# Assembly of High-Spin [$Fe_3$] Clusters by Ligand-Based Multielectron Reduction

Davide Toniolo[a], Rosario Scopelliti[a] Ivica Zivkovic[b] and Marinella Mazzanti[a]*

[a] Insititut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland

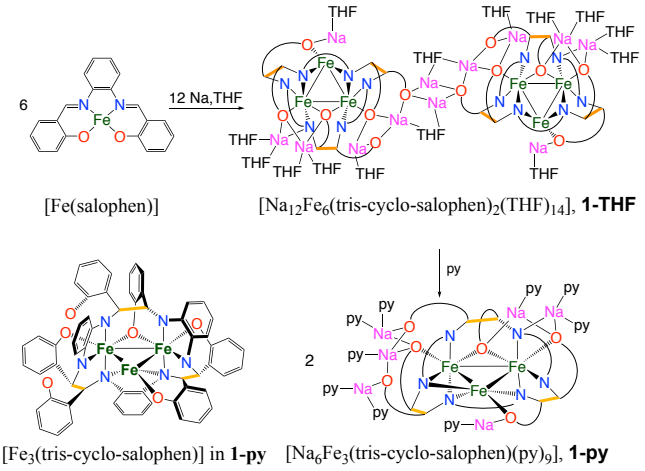
[b] Laboratory for Quantum Magnetism, Institute of Physics, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland.

*Supporting Information Placeholder*

**ABSTRACT:** The hexanuclear [$Na_{12}Fe_6$(tris-cyclo-salophen)$_2$(THF)$_{14}$], **1-THF,** and the trinuclear [$Na_6Fe_3$(tris-cyclo-salophen)(py)$_9$], **1-py,** Fe(II) clusters can be easily assembled in one-step from the ligand-based reduction of the [$Fe^{II}$(salophen)(THF)] complex. These complexes consist of triangular cores where three Fe(II) ions are held together, within range of bonding interaction, by the hexa-amide, hexa-phenolate macrocyclic ligand *tris-cyclo-salophen*$^{12-}$. The *tris-cyclo-salophen*$^{12-}$ ligand is perfectly suited for binding three Fe(II) centers at short distances allowing for strong magnetic coupling between the Fe(II) centers. The macrocyclic ligand is generated by the reductive coupling of the imino groups of three salophen ligands resulting in three new C–C bonds. The six electrons stored in the ligand become available for the reduction of carbon dioxide with selective formation of carbonate.

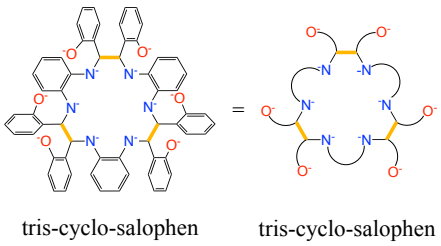
Polynuclear metal complexes have attracted intense interest because they can mediate multielectron transfer and facilitate the binding and activation of small molecules via multi-metallic cooperativity.[1] Moreover, polynuclear clusters can be used to promote strong magnetic coupling between metal ions resulting in fascinating magnetic properties.[2] However, the synthesis of well-defined polynuclear complexes remains a challenge and usually relies on the random self-assembly of mononuclear units. Alternatively, synthetically demanding pre-designed ligands which are capable of bringing several metal centers in close proximity can be used.[1e, 2a, 3] Redox-active ligands are increasingly used in combination with d- and f-block metal ions to promote multielectron transfer.[4] Interestingly, the use of tetradentate Schiff bases as redox-active ligands in d-[5] and f-block[6] chemistry was shown to promote the formation of intermolecular C-C bonds resulting in the assembly of dinuclear complexes with short metal-metal interactions. However, the possibility of accessing complexes of higher nuclearity using this route has been hardly explored.[7]

Here we show that the reduction of an easily prepared mononuclear Fe(II) Schiff base complex[8] provides a facile route to the synthesis of trinuclear Fe(II) complexes featuring short Fe-Fe separations. The reported complexes provide a rare example[2a, 9] of trinuclear clusters featuring close Fe-Fe interactions that produce a high spin state persistent at room temperature. Moreover, they can store, in three C-C bonds, six electrons that become available to mediate the reductive disproportionation of $CO_2$ to $CO_3^{2-}$ and CO.




**Scheme 1. Reduction of [Fe(salophen)] to yield 1-THF and 1-py.**

The reduction of [Fe(salophen)(THF)] with two equivalents of sodium metal in THF at room temperature (Scheme 1) affords an orange solid that could be recrystallized both from THF and pyridine, upon slow dissolution, to yield crystals of the hexanuclear heterometallic compound [$Na_{12}Fe_6$(tris-cyclo-salophen)$_2$(THF)$_{14}$], **1-THF** (Figure S6), in 84 % yield and the trinuclear complex [$Na_6Fe_3$(tris-cyclo-salophen)(py)$_9$], **1-py** in 72 % yield.




**Scheme 2. Structure of the tris-cyclo-salophen**

After slow dissolution of the orange powder formed in the reduction of [Fe(salophen)(THF)], the isolated **1-THF** and **1-py** turned out to be highly soluble in pyridine or THF. However, no signal could be detected in the $^1$H NMR spectrum in THF-d8 or in py-d5, from -40 °C to room temperature, probably as a result of the high magnetic moment of the complex, ($\chi_M T$ = 14.6 emu K/mol, $\mu_{eff}$ = 10.80 $\mu_B$ for **1-py** and $\chi_M T$ = 15.7 emu K/mol, $\mu_{eff}$ = 11.20 $\mu_B$ for **1-THF** as measured by Evan's method[10] at 298 K).

Complex **1-THF** crystallizes in the *P2$_1$/c* space group with half a molecule per asymmetric unit while **1-py** crystallizes in the *P1* space group with one molecule per asymmetric unit. The overall structure of **1-THF** (see Supporting information, Figure S6) is comprised of two identical trinuclear [$Na_6Fe_3$(tris-cyclo-salophen)(THF)$_7$] moieties which are held together by two sodium–aryloxide bonds. The structure of each trinuclear moiety is very similar to the structure of the trinuclear complex **1-py.** (Figure 1 and 2) The trinuclear moiety in **1-THF** and **1-py** consists of a triangular core of Fe(II) ions held together by the hexa-amide, hexa-phenolate macrocyclic ligand *tris-cyclo-salophen$^{12-}$* (Scheme 2). The macrocyclic ligand *tris-cyclo-salophen$^{12-}$* is generated by the reductive coupling of the imino groups of three distinct salophen ligands resulting in three new C–C bonds (average C-C distance: 1.564(6) Å for **1-THF** and 1.567(5) Å for **1-py**). Six inner sphere sodium counterions bind each trimeric unit in both structures.

In the trinuclear complex **1-py** (Figure 1) each Fe(II) ion presents a unique coordination environment (two iron ions present a distorted square pyramidal geometry and one iron ion present a distorted square planar geometry). The values of the Fe-N bond distances range from 2.289(3) Å to 1.961(3) Å and the values of the Fe-O distance range from 1.944(3) to 2.131(3) Å (2.05(6) Å average) with the longer distances found for an aryloxide binding two sodium cations. These values are in the range of those reported for Fe(II) amido[9] and phenolate[11] complexes. The C-N bond distances in **1-py** (1.450(5)-1.474(5) Å) are significantly longer compared to those reported for the [Fe(salophen)(EtOH)] complex (1.299(4) Å) which clearly indicates imine reduction.[12] The values of the Fe-Fe distances range from 2.4405(7) Å, 2.5054(9) Å and 2.7942(7) Å) with a longer Fe(3)-Fe(1) distance, indicative of a weaker bonding interaction. These values remain within range of bonding interactions[1h, 9, 13] and are similar to the Fe(II)-Fe(II) distances found in trinuclear complexes showing magnetic coupling arising from direct orbital overlap.[9, 14, 15]

Two distinct coordination environments are found in the trinuclear moiety of **1-THF** (Figure 2) for the Fe(II) ions with Fe-N and Fe-O bond distances comparable to those found in **1-py** (see Supporting information). The values of the Fe-Fe bond distances in **1-THF** (2.403(1) Å, 2.438(1) Å, and 2.703(1) Å) are shorter than those found in **1-py** and are within range of bonding interactions.[9, 13]

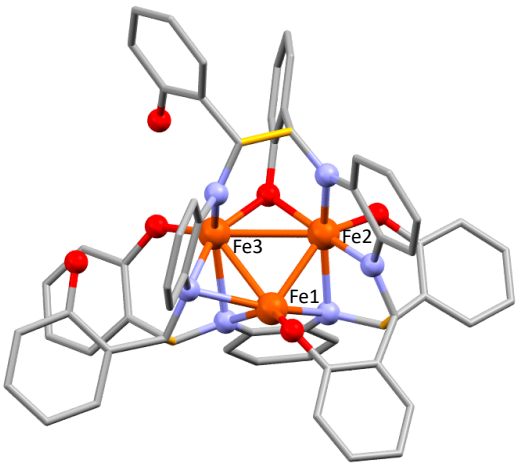



Figure 1. Molecular crystal structure of **1-py**. The three C-C bonds formed by reduction of salophen$^{2-}$ are shown in yellow. Hydrogen atoms, sodium cations and Na-bound pyridine molecules have been omitted for clarity.

The structures of **1-THF** and **1-py** show that the reduction of the [Fe(salophen)(THF)] complex does not lead to the reduction of the metal center, but affords in one simple step a sophisticated macrocyclic ligand that holds together within bonding distance three Fe(II) centers.

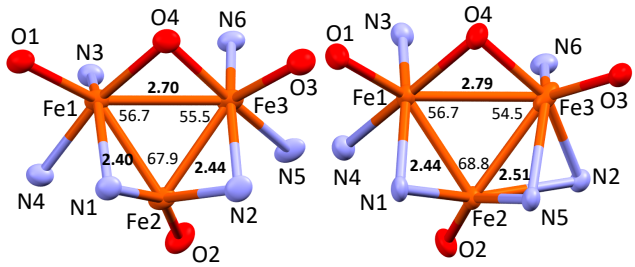



Figure 2. View of the trinuclear core in the molecular crystal structures of **1-THF** (left) and **1-py** (right) with Fe-Fe distances in Å (bold), Fe-Fe-Fe angles in degrees (normal) (50% probability ellipsoids).

The presence of potential magnetic Fe-Fe interactions was investigated by measuring variable temperature (5-300 K) magnetic susceptibility data for **1-THF** and **1-py** under an applied magnetic field of 1 T. The values of $\chi_M T$ remain relatively constant in the temperature range 60-300 K (Figure 3) while they drop rapidly for both complexes below 60 K to reach a value of about 10 emu K/mol at 5 K probably due to Zeeman effect and zero field splitting.

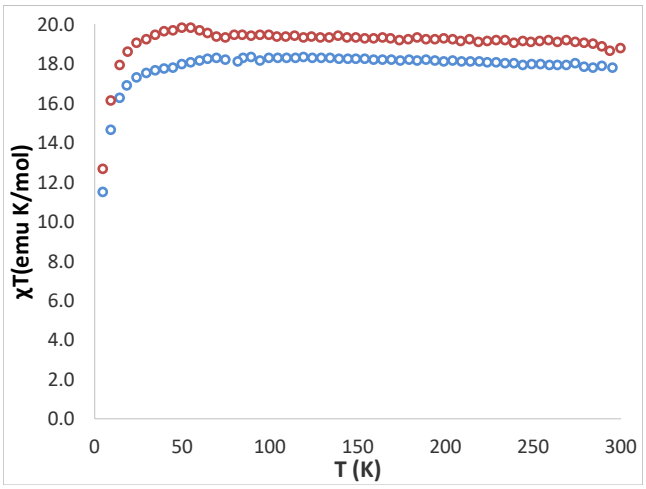


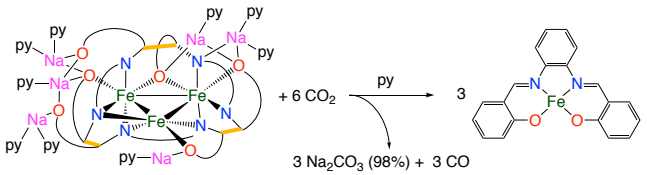

Figure 3. $\chi_M T$ *vs.* T graphic for **1-THF** (blue) and **1-py** (red) ($10^3$ Oe, 300-5 K)

The values of $\chi_M T$ and $\mu_{eff}$ found for **1-THF** ($\chi_M T$ = 19.4 emuK/mol and $\mu_{eff}$ = 12.45 $\mu_B$ at 300 K) and **1-py** ($\chi_M T$ = 17.7 emuK/mol and $\mu_{eff}$ = 11.90 $\mu_B$ at 300 K) are much higher than the expected value for three non-interacting Fe (II) ($\chi_M T$ = 9 emuK/mol and $\mu_{eff}$ = 8.50 $\mu_B$) with g = 2. This suggests the presence of a strong ferromagnetic interaction between the Fe centers in the core which is maintained at room temperature. These values are only slightly lower than the 21 emuK/mol expected for a system with S = 6 ground state (g = 2). Only one example of a trinuclear Fe(II) cluster with a stable high spin state (S = 6) at room temperature was previously reported.[9] The previously reported triangular system supported by an hexamido ligand showed Fe(II)-Fe(II) distances comparable to complexes **1-THF** and **1-py** and a similar weak-field environment. A high-spin state was previously reported for weak-field tri- and hexa-nuclear iron clusters. This was interpreted in terms of weak Fe-Fe interactions that result in three or six atom clusters behaving as a large single spin [2a, 16 9, 17] approximating that of a single metal ion.[18] A similar type of direct magnetic exchange is likely to be at the origin of the high-spin state in **1-THF** and **1-py.**

One of the most attractive properties of metal complexes supported by non-innocent ligands is their ability to store electrons. However, the storage of a large number of electrons remains a key challenge in the field.[4c, 4d] Notably, we recently demonstrated that the electrons stored in C-C bonds, which are formed from the reduction of Schiff base complexes of cobalt, can become available for reduction of $CO_2$. However, the reaction proceeds with the addition of $CO_2$ to the ligand framework.[7]

In contrast, **1-py** can transfer six electrons stored in three C-C bonds of the *tris-cyclo-salophen*$^{12-}$ ligand to

carbon dioxide to yield carbonate whilst restoring the original [Fe(salophen)(THF)] complex.




[$Na_6Fe_3$(tris-cyclo-salophen)$py_9$], **1-py** [Fe(salophen)]

**Scheme 3. Reaction of 1-py with $CO_2$.**

The trimer **1-py** reacts at room temperature with 6 equiv. of $^{13}CO_2$ to yield the [Fe(salophen)] complex, as identified by $^1$H NMR spectroscopy (see supporting information) and the concomitant formation of an insoluble product (Scheme 3). The quantitative $^{13}$C NMR spectrum of the residue dissolved in $D_2O$ (pD = 13.4) showed a signal at 168 ppm assigned[19] to $CO_3^{2-}$ formed in 100 % conversion (see SI). The quantitative formation of carbonate indicates that the complex **1-py** promotes the reductive disproportionation of $CO_2$ to carbonate and CO. The signal of $^{13}$CO could not be detected in the used reaction conditions.

The reduction of the [Fe(salophen)(THF)] to yield the trimer **1-py** can also be effected electrochemically rendering this system well poised for the development of electrocatalysts.

In conclusion, we have presented a novel and convenient one step route for the assembly of three Fe(II) centers in a trinuclear cluster. In this approach the reduction of a mononuclear Fe(II) complex of a tetradentate Schiff base leads to the formation of a macrocyclic dodecadentate ligand perfectly suited for binding three Fe(II) centers at short distances allowing for strong magnetic coupling. Moreover, six electrons are stored in the ligand and these electrons become available for the reduction of carbon dioxide with selective formation of carbonate. The facile synthetic route presented, together with the vast library of Schiff base ligands available in the literature, will provide easy access to trinuclear iron complexes with different magnetic properties and high reactivity towards small molecules.

## ASSOCIATED CONTENT

**Supporting Information**.

X-ray data for **1-THF** and **1-py**, (CIF) and additional crystallographic details, Experimental procedures, NMR spectra, magnetic data (PDF).

"This material is available free of charge via the Internet at http://pubs.acs.org.".

## AUTHOR INFORMATION

### Corresponding Author

* marinella.mazzanti@epfl.ch.

### Author Contributions

The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript.

## ACKNOWLEDGMENT

We acknowledge support from the Swiss National Science Foundation grant number 200021_178793 and the Ecole Polytechnique Fédérale de Lausanne (EPFL). We thank Dr. Euro Solari for carrying out the elemental analyses, Farzaneh Fadaei-Tirani for important contributions to the X-ray single crystal structure analyses.

## REFERENCES

1. (a) Lee, Y.; Sloane, F. T.; Blondin, G.; Abboud, K. A.; Garcia-Serres, R.; Murray, L. J., Dinitrogen Activation Upon Reduction of a Triiron(II) Complex. *Angew. Chem. Int. Ed. Engl.* **2015,** *54*, 1499-1503; (b) Anderton, K. J.; Knight, B. J.; Rheingold, A. L.; Abboud, K. A.; Garcia-Serres, R.; Murray, L. J., Reactivity of hydride bridges in a high-spin $Fe_3(\mu\text{-}H)_3^{3+}$ cluster: reversible $H_2$/CO exchange and Fe-H/B-F bond metathesis. *Chem. Sci.* **2017,** *8*, 4123-4129; (c) Chiang, K. P.; Bellows, S. M.; Brennessel, W. W.; Holland, P. L., Multimetallic cooperativity in activation of dinitrogen at iron-potassium sites. *Chem. Sci.* **2014,** *5*, 267-274; (d) Powers, T. M.; Betley, T. A., Testing the Polynuclear Hypothesis: Multielectron Reduction of Small Molecules by Triiron Reaction Sites. *J. Am. Chem. Soc.* **2013,** *135*, 12289-12296; (e) Ferreira, R. B.; Murray, L. J., Cyclophanes as Platforms for Reactive Multimetallic Complexes. *Acc. Chem. Res.* **2019,** *52*, 447-455; (f) Speelman, A. L.; Coric, I.; Van Stappen, C.; DeBeer, S.; Mercado, B. Q.; Holland, P. L., Nitrogenase-Relevant Reactivity of a Synthetic Iron-Sulfur-Carbon Site. *J. Am. Chem. Soc.* **2019,** *141*, 13148-13157; (g) McWilliams, S. F.; Bill, E.; Lukat-Rodgers, G.; Rodgers, K. R.; Mercado, B. Q.; Holland, P. L., Effects of $N_2$ Binding Mode on Iron-Based Functionalization of Dinitrogen to Form an Iron(III) Hydrazido Complex. *J. Am. Chem. Soc.* **2018,** *140*, 8586-8598; (h) Tereniak, S. J.; Carlson, R. K.; Clouston, L. J.; Young, V. G.; Bill, E.; Maurice, R.; Chen, Y. S.; Kim, H. J.; Gagliardi, L.; Lu, C. C., Role of the Metal in the Bonding and Properties of Bimetallic Complexes Involving Manganese, Iron, and Cobalt. *J. Am. Chem. Soc.* **2014,** *136*, 1842-1855; (i) Falcone, M.; Chatelain, L.; Scopelliti, R.; Zivkovic, I.; Mazzanti, M., Nitrogen reduction and functionalization by a multimetallic uranium nitride complex. *Nature* **2017,** *547*, 332-335; (j) Zhang, H. T.; Hatzis, G. P.; Moore, C. E.; Dickie, D. A.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M., $O_2$ Activation by a Heterobimetallic Zr/Co Complex. *J. Am. Chem. Soc.* **2019,** *141*, 9516-9520; (k) Falcone, M.; Barluzzi, L.; Andrez, J.; Tirani, F. F.; Zivkovic, I.; Fabrizio, A.; Corminboeuf, C.; Severin, K.; Mazzanti, M., The role of bridging ligands in dinitrogen reduction and functionalization by uranium multimetallic complexes. *Nat. Chem.* **2019,** *11*, 154–160; (l) Cammarota, R. C.; Vollmer, M. V.; Xie, J.; Ye, J. Y.; Linehan, J. C.; Burgess, S. K.; Appel, A. M.; Gagliardi, L.; Lu, C. C., A Bimetallic Nickel-Gallium Complex Catalyzes $CO_2$ Hydrogenation via the Intermediacy of an Anionic $d^{10}$ Nickel Hydride. *J. Am. Chem. Soc.* **2017,** *139*, 14244-14250; (m) Krogman, J. P.; Foxman, B. M.; Thomas, C. M., Activation of $CO_2$ by a Heterobimetallic Zr/Co Complex. *J. Am. Chem. Soc.* **2011,** *133*, 14582-14585; (n) Cooper, O.; Camp, C.; Pécaut, J.; Kefalidis, C. E.; Maron, L.; Gambarelli, S.; Mazzanti, M., Multimetallic Cooperativity in Uranium-Mediated $CO_2$ Activation. *J. Am. Chem. Soc.* **2014,** *136*, 6716-6723.

2. (a) Sanchez, R. H.; Bartholomew, A. K.; Powers, T. M.; Menard, G.; Betley, T. A., Maximizing Electron Exchange in a [$Fe_3$] Cluster. *J. Am. Chem. Soc.* **2016,** *138*, 2235-2243; (b) Zhao, Q. L.;

Betley, T. A., Synthesis and Redox Properties of Triiron Complexes Featuring Strong Fe-Fe Interactions. *Angew. Chem. Int. Ed. Engl.* **2011,** *50*, 709-712; (c) Hogue, R. W.; Singh, S.; Brooker, S., Spin crossover in discrete polynuclear iron(ii) complexes. *Chem. Soc. Rev.* **2018,** *47*, 7303-7338; (d) Powell, A. K.; Heath, S. L.; Gatteschi, D.; Pardi, L.; Sessoli, R.; Spina, G.; Delgiallo, F.; Pieralli, F., Synthesis, Structures, and Magnetic Properties of Fe2, Fe17, and Fe19 Oxo-Bridged Iron Clusters - the Stabilization of High Ground State Spins by Cluster Aggregates. *J. Am. Chem. Soc.* **1995,** *117*, 2491-2502; (e) Sanchez, R. H.; Betley, T. A., Thermally Persistent High-Spin Ground States in Octahedral Iron Clusters. *J. Am. Chem. Soc.* **2018,** *140*, 16792-16806.

3. (a) Arnold, P. L.; Stevens, C. J.; Bell, N. L.; Lord, R. M.; Goldberg, J. M.; Nichol, G. S.; Love, J. B., Multi-electron reduction of sulfur and carbon disulfide using binuclear uranium(III) borohydride complexes. *Chem. Sci.* **2017,** *8*, 3609-3617; (b) Arnold, P. L.; Patel, D.; Blake, A. J.; Wilson, C.; Love, J. B., Selective Oxo Functionalization of the Uranyl Ion with 3d Metal Cations. *J. Am. Chem. Soc.* **2006,** *128*, 9610-9611; (c) Rao, P. V.; Holm, R. H., Synthetic Analogues of the Active Sites of Iron-Sulfur Proteins. *Chem. Rev.* **2004,** *104*, 527-559.

4. (a) Coughlin, E. J.; Zeller, M.; Bart, S. C., Neodymium(III) Complexes Capable of Multi-Electron Redox Chemistry. *Angew. Chem. Int. Ed. Engl.* **2017,** *56*, 12142-12145; (b) Anderson, N. H.; Odoh, S. O.; Yao, Y. Y.; Williams, U. J.; Schaefer, B. A.; Kiernicki, J. J.; Lewis, A. J.; Goshert, M. D.; Fanwick, P. E.; Schelter, E. J.; Walensky, J. R.; Gagliardi, L.; Bart, S. C., Harnessing redox activity for the formation of uranium tris(imido) compounds. *Nat. Chem.* **2014,** *6*, 919-926; (c) Chirik, P. J.; Wieghardt, K., Radical Ligands Confer Nobility on Base-Metal Catalysts. *Science* **2010,** *327*, 794-795; (d) Broere, D. L. J.; Plessius, R.; van der Vlugt, J. I., New avenues for ligand-mediated processes - expanding metal reactivity by the use of redox-active catechol, o-aminophenol and o-phenylenediamine ligands. *Chem. Soc. Rev.* **2015,** *44*, 6886-6915; (e) Kiernicki, J. J.; Ferrier, M. G.; Pacheco, J. S. L.; La Pierre, H. S.; Stein, B. W.; Zeller, M.; Kozimor, S. A.; Bart, S. C., Examining the Effects of Ligand Variation on the Electronic Structure of Uranium Bis(imido) Species. *J. Am. Chem. Soc.* **2016,** *138*, 13941-13951.

5. (a) DeAngelis, S.; Solari, E.; Gallo, E.; Floriani, C.; ChiesiVilla, A.; Rizzoli, C., Formation of carbon-carbon-bonded dimers in the reduction of [Co(II)salophen] [salophen equals N,N'-o-phenylenebis(salicylideneaminato)]: Their reactivity with electrophiles to form Co-C bonds. *Inorg. Chem.* **1996,** *35*, 5995-6003; (b) Franceschi, F.; Solari, E.; Scopelliti, R.; Floriani, C., Metal-Mediated Transfer of Electrons between Two Different C-C Single Bonds That Function as Electron-Donor and Electron-Acceptor Units. *Angew. Chem. Int. Ed. Engl.* **2000,** *39*, 1685-1686; (c) Floriani, C.; Solari, E.; Franceschi, F.; Scopelliti, R.; Belanzoni, P.; Rosi, M., Metal-metal and carbon-carbon bonds as potential components of molecular batteries. *Chem. Eur. J.* **2001,** *7*, 3052-3061; (d) Gambarotta, S.; Mazzanti, M.; Floriani, C.; Zehnder, M., A Tetranuclear Polyfunctional Sodium-Vanadium(III) Complex Containing a Vanadium(III)-Vanadium(III) Double-Bond. *J. Chem. Soc., Chem. Commun.* **1984**, 1116-1118.

6. (a) Camp, C.; Mougel, V.; Horeglad, P.; Pecaut, J.; Mazzanti, M., Multielectron Redox Reactions Involving C-C Coupling and Cleavage in Uranium Schiff Base Complexes. *J. Am. Chem. Soc.* **2010,** *132*, 17374-17377; (b) Camp, C.; Andrez, J.; Pecaut, J.; Mazzanti, M., Synthesis of Electron-Rich Uranium(IV) Complexes Supported by Tridentate Schiff Base Ligands and Their Multi-Electron Redox Chemistry. *Inorg. Chem.* **2013,** *52*, 7078-7086; (c) Camp, C.; Guidal, V.; Biswas, B.; Pecaut, J.; Dubois, L.; Mazzanti, M., Multielectron redox chemistry of lanthanide Schiff-base complexes. *Chem. Sci.* **2012,** *3*, 2433-2448.

7. Andrez, J.; Guidal, V.; Scopelliti, R.; Pecaut, J.; Gambarelli, S.; Mazzanti, M., Ligand and Metal Based Multielectron Redox Chemistry of Cobalt Supported by Tetradentate Schiff Bases. *J. Am. Chem. Soc.* **2017,** *139*, 8628-8638.

8. Niswander, R. H.; Martell, A. E., Pyridine Adducts of Iron(II)-Schiff Base Complexes. *Inorg. Chem.* **1978,** *17*, 2341-2344.

9. Eames, E. V.; Harris, T. D.; Betley, T. A., Modulation of magnetic behavior *via* ligand-field effects in the trigonal clusters ($^{Ph}$L)$Fe_3L_3^*$ ($L^*$ = thf, py, $PMe_2Ph$). *Chem. Sci.* **2012,** *3*, 407-415.

10. Evans, D. F., The Determination of the Paramagnetic Susceptibility of Substances in Solution by Nuclear Magnetic Resonance. *J. Chem. Soc.* **1959**, 2003-2005.

11. Adelhardt, M.; Chalkley, M. J.; Heinemann, F. W.; Sutter, J.; Scheurer, A.; Meyer, K., Synthesis and Characterization of Iron Trisphenolate Complexes with Hydrogen-Bonding Cavities. *Inorg. Chem.* **2014,** *53*, 2763-2765.

12. Nabei, A.; Kuroda-Sowa, T.; Shimizu, T.; Okubo, T.; Maekawa, M.; Munakata, M., Ferromagnetic interaction in iron(II)-bis-Schiff base complexes. *Polyhedron* **2009,** *28*, 1734-1739.

13. (a) Murillo, C. A., *Multiple Bonds Between Metal Atoms*. 3rd ed. ed.; Springer: New York, 2005; (b) Hess, C. R.; Weyhermuller, T.; Bill, E.; Wieghardt, K., [{Fe(tim)}$_2$] : An Fe-Fe Dimer Containing an Unsupported Metal-Metal Bond and Redox-Active $N_4$ Macrocyclic Ligands. *Angew. Chem. Int. Ed. Engl.* **2009,** *48*, 3703-3706; (c) Zall, C. M.; Zherebetskyy, D.; Dzubak, A. L.; Bill, E.; Gagliardi, L.; Lu, C. C., A Combined Spectroscopic and Computational Study of a High-Spin S=7/2 Diiron Complex with a Short Iron-Iron Bond. *Inorg. Chem.* **2012,** *51*, 728-736; (d) Cotton, F. A.; Daniels, L. M.; Matonic, J. H.; Murillo, C. A., Highly distorted diiron(II,II) complexes containing four amidinate ligands. A long and a short metal-metal distance. *Inorg. Chim. Acta* **1997,** *256*, 277-282; (e) Fohlmeister, L.; Liu, S. S.; Schulten, C.; Moubaraki, B.; Stasch, A.; Cashion, J. D.; Murray, K. S.; Gagliardi, L.; Jones, C., Low-Coordinate Iron(I) and Manganese(I) Dimers: Kinetic Stabilization of an Exceptionally Short Fe-Fe Multiple Bond. *Angew. Chem. Int. Ed. Engl.* **2012,** *51*, 8294-8298; (f) Pick, F. S.; Leznoff, D. B.; Fryzuk, M. D., Redox behaviour of ([fc( $NP^iPr_2$)$_2$] Fe)$_2$, formation of an iron- iron bond and cleavage of azobenzene. *J. Chem. Soc.-Dalton Trans.* **2018,** *47*, 10925-10931.

14. Powers, T. M.; Fout, A. R.; Zheng, S.-L.; Betley, T. A., Oxidative Group Transfer to a Triiron Complex to Form a Nucleophilic $\mu^3$-Nitride, [$Fe_3(\mu^3\text{-N})]^-$. *J. Am. Chem. Soc.* **2011,** *133*, 3336-3338.

15. Bartholomew, A. K.; Teesdale, J. J.; Sanchez, R. H.; Malbrecht, B. J.; Juda, C. E.; Menard, G.; Bu, W.; Iovan, D. A.; Mikhailine, A. A.; Zheng, S. L.; Sarangi, R.; Wang, S. G.; Chen, Y. S.; Betley, T. A., Exposing the inadequacy of redox formalisms by resolving redox inequivalence within isovalent clusters. *Proc Natl Acad Sci USA* **2019,** *116*, 15836-15841.

16. Sanchez, R. H.; Betley, T. A., Meta-Atom Behavior in Clusters Revealing Large Spin Ground States. *J. Am. Chem. Soc.* **2015,** *137*, 13949-13956.

17. Zhao, Q. L.; Harris, T. D.; Betley, T. A., [($^H$L)$_2Fe_6$(NCMe)$_m$]$^{n+}$ (m = 0, 2, 4, 6; n = -1, 0, 1, 2, 3, 4, 6): An Electron-Transfer Series Featuring Octahedral $Fe_6$ Clusters Supported by a Hexaamide Ligand Platform. *J. Am. Chem. Soc.* **2011,** *133*, 8293-8306.

18. Rau, I. G.; Baumann, S.; Rusponi, S.; Donati, F.; Stepanow, S.; Gragnaniello, L.; Dreiser, J.; Piamonteze, C.; Nolting, F.; Gangopadhyay, S.; Albertini, O. R.; Macfarlane, R. M.; Lutz, C. P.; Jones,

B. A.; Gambardella, P.; Heinrich, A. J.; Brune, H., Reaching the magnetic anisotropy limit of a 3d metal atom. *Science* **2014,** *344*, 988-992.

19. Clouston, L. J.; Siedschlag, R. B.; Rudd, P. A.; Planas, N.; Hu, S. X.; Miller, A. D.; Gagliardi, L.; Lu, C. C., Systematic Variation of Metal-Metal Bond Order in Metal-Chromium Complexes. *J. Am. Chem. Soc.* **2013,** *135*, 13142-13148.