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Dynamic Complex-to-Complex Transformations of Heterobimetallic Systems Influence the Cage Structure or Spin State of Iron(II) Ions

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Abstract: Two new heterobimetallic cages, a trigonal bipyramidal and a cubic one, were assembled from the same mononuclear metalloligand adopting the molecular library approach, using iron(II) and palladium(II) building blocks. The ligand system was designed to readily assemble through subcomponent self-assembly. It allowed the introduction of steric strain at the iron(II) centres, which stabilizes its paramagnetic high-spin state. This steric strain was utilized to perform dynamic complex-to-complex transformations with both, the metalloligand and heterobimetallic cages. Addition of sterically less crowded subcomponents as a chemical stimulus transformed all complexes to their previously reported low-spin analogues. The metalloligand and bipyramid incorporated the new building block more readily than the cubic cage, probably because the geometric structure of the sterically crowded metalloligand favours the cube formation. Furthermore it was possible to provoke structural transformations upon addition of more favourable chelating ligands, converting the cubic structures into bipyramidal ones.

Metallosupramolecular chemistry[1] has produced many beautiful structures with defined shapes[2] and fascinating functionality.[3] Within metallosupramolecular chemistry, a powerful tool is the subcomponent self-assembly approach, in which aggregates emerge from assembling two ligand subunits that form feasible ligands and their complexes *in situ*. These are formed via the reversible formation of covalent bonds.[4] This approach was used to prepare numerous structures adopting various properties and features,[5] e.g. host-guest chemistry[6] and switchable systems.[6c,7] The tuning of complex properties is often facilitated by varying one distinct ligand subunit and exchanging one building block.[6b,8] In combination with the reversible character of the covalent bonds, these properties can also allow for building block exchanges *in situ*, resulting in complex-to-complex transformations.[7a,9] Besides subcomponent exchanges, also ligand exchanges[10], solvent dependencies[11], or light irradiation[12] were successfully used to perform complex-to-complex transformations.

Aside from indisputably beautiful homometallic structures, the subcomponent self-assembly approach also proved useful for the formation of heterobimetallic cages within the meaning of the complex-as-a-ligand strategy.[13] Thus, it is possible to transfer all advantages of the subcomponent self-assembly approach to systems consisting of more than one type of metal cation. However, to date only a few examples for heterobimetallic complexes were reported that built up from subcomponents.[5c,13e,14]

Previously, Drago *et al.* introduced a ligand system that can be prepared from commercially available building blocks *tris*(2-aminoethyl)amine (TREN), 2-formylpyridine, 2-formyl-6-methylpyridine and iron(II) salts.[15] 2-Formyl-6-methylpyridine containing complexes show a stabilization of the high-spin state of iron(II) cations at room temperature, due to steric strain between the methyl groups and nearby pyridine rings, as well as spin-crossover behaviour in solid state.[15,16] These aldehydes were also used to develop 3D architectures with different shapes and sizes that show complex-to-complex transformations by replacing 2-formyl-6-methylpyridine with less bulky 2-formylpyridine. These transformations resulted in a change of the spin state of iron(II) cations from high-spin to low-spin, due to shortening of the Fe-N bond lengths.[9b,17] The decrease of steric strain might be responsible for the preferential incorporation of 2-formylpyridine over 2-formyl-6-methylpyridine.[9b,17]

In this work we investigated the dynamic behaviour of heterobimetallic structures that assemble through subcomponent self-assembly. These complexes contain sterically strained iron(II) centres in the paramagnetic high-spin state. We adopted previously reported subcomponent exchanges and expanded these principles to heterometallic systems. Chemical stimuli transferred the heterobimetallic paramagnetic complexes to their diamagnetic analogues upon reduction of steric strain. In addition, we could perform ligand exchange reactions, resulting in structural transformations from cubic to bipyramidal cages.

Ditopic building block **1** was selected to achieve the formation of C_3 symmetric iron(II)-*tris*(pyridylimine) moieties[18] as well as C_2 and C_4 symmetric palladium(II)-pyridine moieties. Reaction of 3 equivalents of aldehyde **1** with 1 equivalent of TREN **2** and 1 equivalent of iron(II) tetrafluoroborate hexahydrate in acetonitrile yielded the mononuclear complex **ML-1**$(BF_4)_2$ as a bright red solid (Scheme 1). This mononuclear complex was characterised by ^{1}H-NMR- and UV-Vis spectroscopy, ESI-MS spectrometry, vibrating sample magnetometry and single crystal X-ray diffraction (see SI). Mixing 1 equivalent of **ML-1**$(BF_4)_2$ with 1.5 equivalents of

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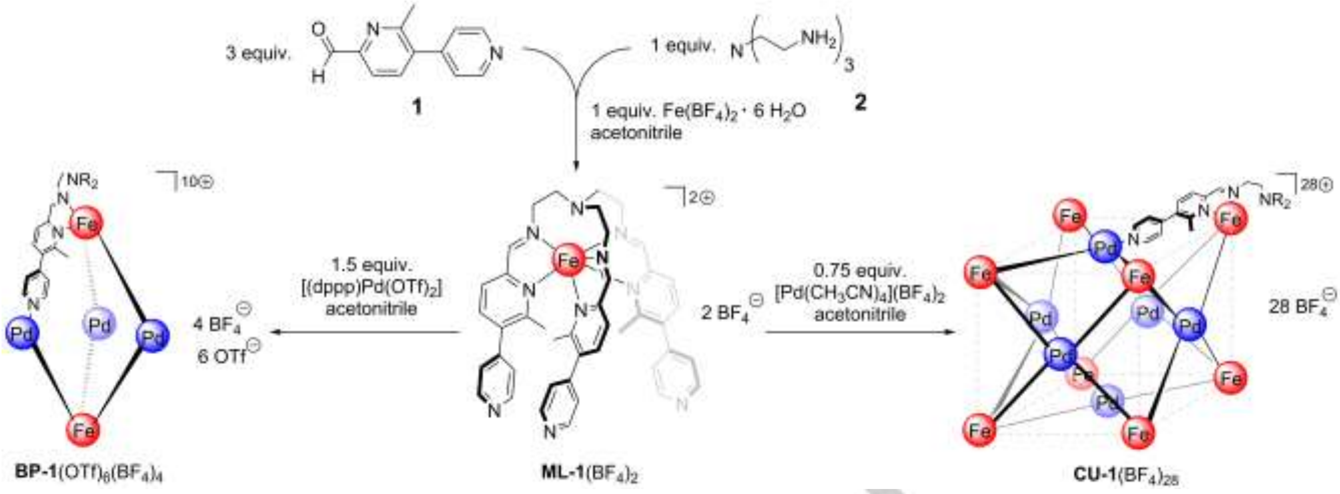


Scheme 1. Stepwise self-assembly of **BP-1**$(OTf)_6(BF_4)_4$ and **CU-1**$(BF_4)_{28}$ via formation of **ML-1**$(BF_4)_2$ from **1** and **2**.

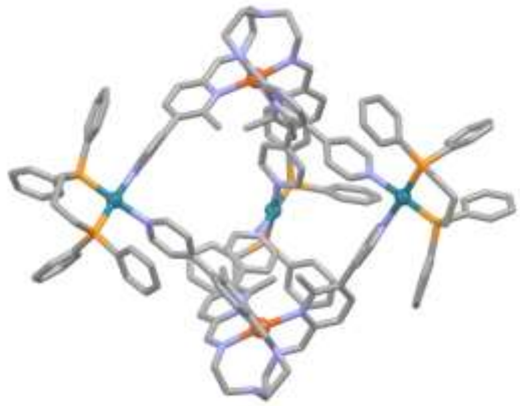


Figure 1. Structure of bipyramidal complex **BP-1**$(OTf)_6(BF_4)_4$ as determined by single crystal X-ray diffraction (hydrogen atoms, counter ions and solvent molecules are omitted for clarity; colour code: grey – carbon, blue – nitrogen, yellow-orange – phosphorus, dark orange – iron, petrol – palladium).

1,3-bis(diphenylphosphino)propane palladium(II) triflate ($[(dppp)Pd(OTf)_2]$) or 0.75 equivalents of *tetrakis*(acetonitrile) palladium(II) tetrafluoroborate ($[Pd(CH_3CN)_4](BF_4)_2$) in acetonitrile resulted in the formation of heterometallic pentanuclear bipyramidal assembly **BP-1**$(OTf)_6(BF_4)_4$ or the tetradecanuclear cubic assembly **CU-1**$(BF_4)_{28}$, respectively, each as a bright red microcrystalline solid in high yields (Scheme 1).

The identity and purity of bipyramid **BP-1**$(OTf)_6(BF_4)_4$ were proven by ^{1}H-NMR and UV-Vis spectroscopy and ESI-MS (see SI). Vibrating sample magnetometry and employing the Evans' method[19] revealed a magnetic susceptibility of $X_mT = 6.0\ cm^3\ K\ mol^{-1}$, which is in very good agreement with the expected value for two uncoupled iron(II) cations in the high-spin state ($6.001\ cm^3\ K\ mol^{-1}$).[20] Slow diffusion of diethyl ether into a concentrated solution of **BP-1**$(OTf)_6(BF_4)_4$ in acetonitrile gave X-ray diffraction quality single crystals that could be used to determine its crystal structure (Figure 1). The mixed anionic cage **BP-1**$(OTf)_6(BF_4)_4$ crystallises in the monoclinic space group C2/c, with both homochiral enantiomers [(Δ,Δ) and (Λ,Λ)] present in the unit cell as racemic mixture and is best described as a trigonal bipyramid or helicate[21] (for more details, see SI).

The iron cations are coordinated in an octahedral ligand sphere with an average Fe-N bond length of 2.179 Å, consistent with a paramagnetic high-spin iron(II) complex.[22] The palladium centres form the equatorial plane of the complex and are settled in a square-planar ligand sphere, each coordinated by a bidentate dppp ligand and two 4-pyridyl moieties.

The identity of the heterobimetallic cube **CU-1**$(BF_4)_{28}$ could also be proven by ^{1}H-NMR and UV-Vis spectroscopy and ESI-MS (see SI). An Evans' experiment revealed a magnetic susceptibility of $X_mT = 24.1\ cm^3\ K\ mol^{-1}$, proving its fully paramagnetic character.[20] Interestingly, the self-assembly of **CU-1**$(BF_4)_{28}$ was completed after only 16 hours at 50 °C whereas

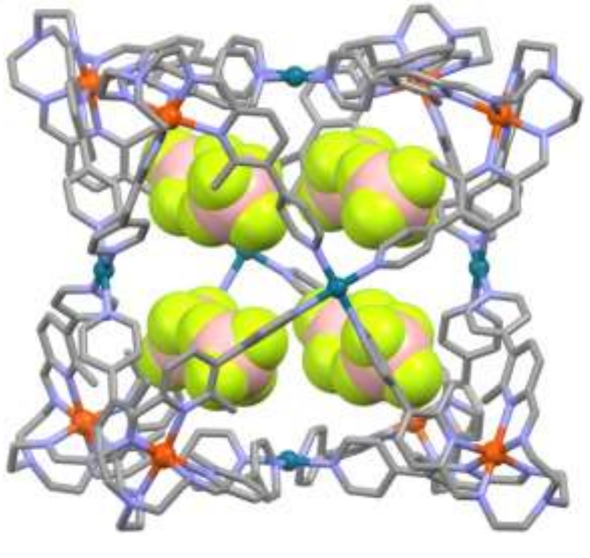


Figure 2. Structure of cube **CU-1** as determined by single crystal X-ray diffraction using synchrotron radiation. Eight tetrafluoroborate anions occupy the inner void. (hydrogen atoms, solvent molecules and counter ions outside the cavity are omitted for clarity; colour code: grey – carbon, blue – nitrogen, light green – fluorine, brown-beige – boron, dark orange – iron, petrol – palladium).

the self-assembly process of a previously reported diamagnetic analogue[13e] of this heterobimetallic cube took 120 hours under the same conditions. We attribute this tremendously shorter reaction time of **CU-1**$(BF_4)_{28}$ to the larger opening angle of **ML-1**$(BF_4)_2$, compared to the metalloligand without the additional methyl groups on the pyridine binding to the iron(II) ion. Due to the steric strain around the iron centre the opening angle becomes larger, and therefore, should be better preorganized to form the heterobimetallic cube.

Very slow evaporation of solvent from an acetonitrile solution of **CU-1**$(BF_4)_{28}$ over 3 months yielded single crystals, which diffracted up to 1.2 Å using synchrotron radiation[23] and allowed for unambiguous structure determination (Figure 2).

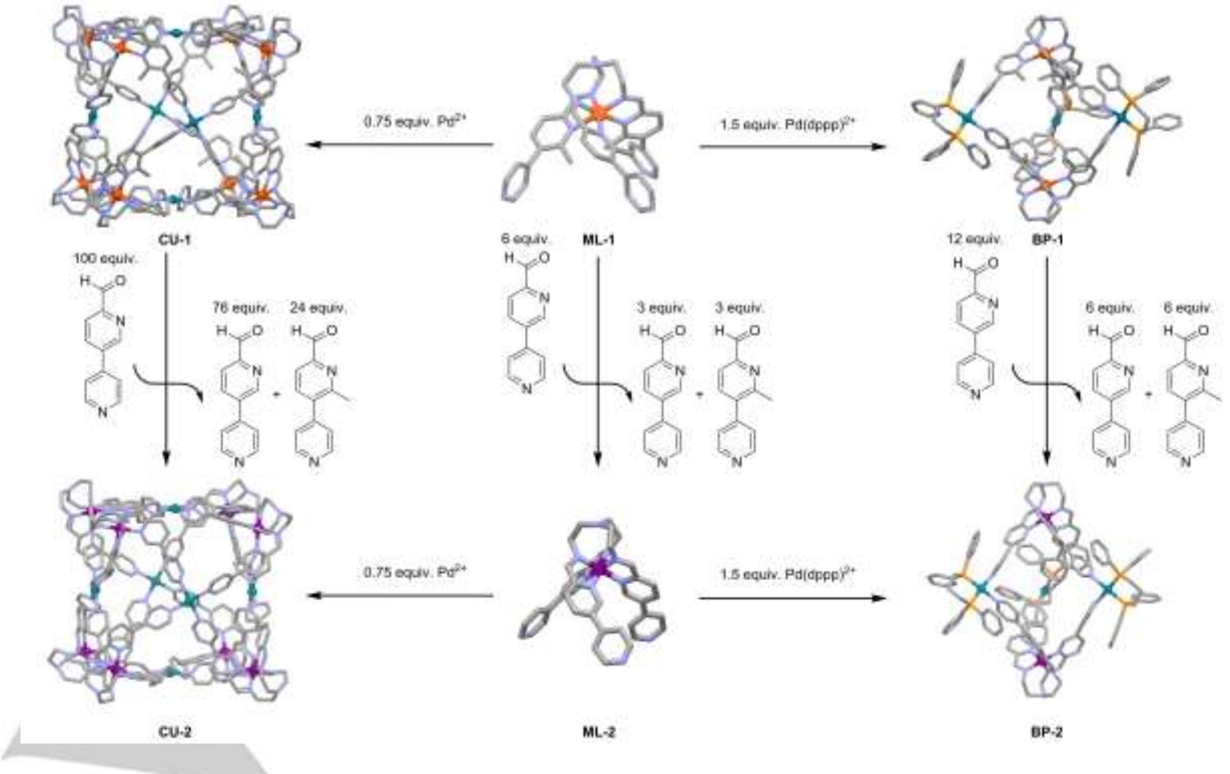
CU-1$(BF_4)_{28}$ crystallises in the cubic space group Fm-$\bar{3}$c with both homochiral enantiomers [all (Δ) and all (Λ)] present in the unit cell as racemic mixture. Only one third of one ligand and one iron ion is found in the asymmetric unit due to the 3-fold symmetry axis. All three Fe-N bonds are crystallographically equivalent and show a bond length of 2.105(11) Å, which is consistent with a high-spin iron(II) complex. The tetravalent palladium ions with their four coordinated pyridine moieties are located on the 4-fold symmetry axes of the cubic cage. Eight tetrafluoroborate anions occupy the void of the cage, adapting the cubic arrangement themselves.

The steric strain in **ML-1**, **BP-1** and **CU-1** results in an elongation of the Fe-N bond lengths and the stabilization of the paramagnetic high-spin state.[9b,15,17] Still the situation is energetically unfavourable, and hence, can be used to perform thermodynamically-driven complex-to-complex transformations during which the steric strain is reduced. The transformation reactions were performed by the addition of a twofold access of sterically less crowded 2-formyl-5-(4’-pyridyl)pyridine **3** (per exchangeable methyl substituted aldehyde component) to the complex solutions and were tracked by ^{1}H-NMR spectroscopy. In such a scenario a quantitative incorporation of **3** would lead to a 50:50 or 1:1 ratio of both free aldehydes **1** and **3**. Please note that we had to analyse the signals of the individual aldehyde subcomponents as probes here as integration of ^{1}H-NMR signals of paramagnetic species is generally not possible, if mixed species with different magnetic properties are present.

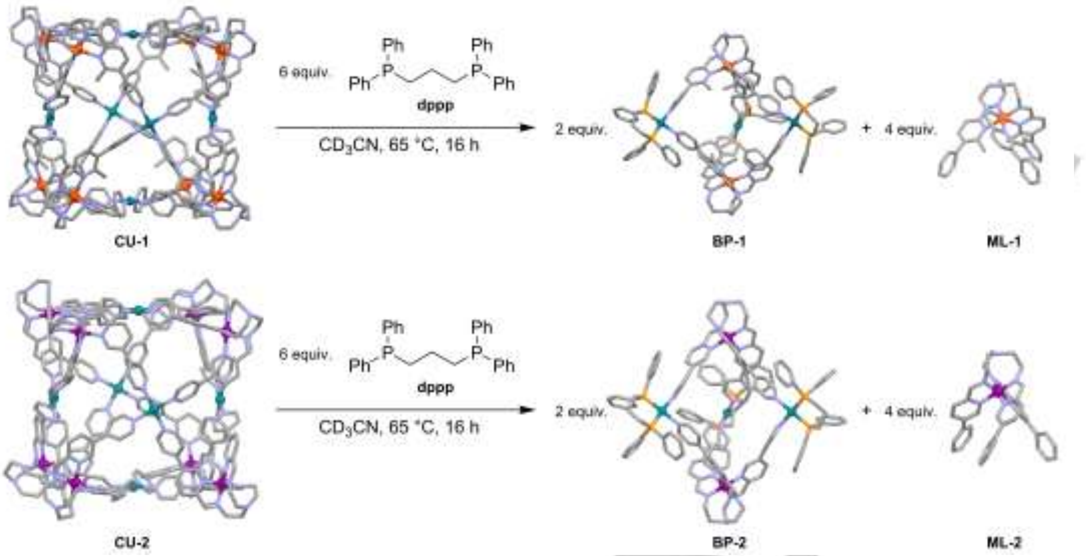
Following this approach, addition of 6 equivalents of **3** to a solution of **ML-1**$(BF_4)_2$ released free 3 equivalents of subcomponent **1** when **3** was incorporated almost quantitatively into the complex, resulting in the formation of previously reported diamagnetic metalloligand **ML-2**$(BF_4)_2$ in a high yield (Scheme 2).

Progress of this reaction was indicated by a colour change of the solution from bright red to dark purple. After 16 hours at 40 °C the mixture reached equilibrium with free subcomponents **3** and **1** in a 56:44 ratio and a new set of signals in the ^{1}H-NMR spectrum referring to **ML-2**$(BF_4)_2$ (see SI).

The same chemical stimulus can be used to transfer paramagnetic **BP-1**$(OTf)_6(BF_4)_4$ quantitatively into the corresponding diamagnetic cage **BP-2**$(OTf)_6(BF_4)_4$. After 16 hours at 40 °C the equilibrium ratio of **3** and **1** was determined to be 1:1 and ^{1}H-NMR signals arised that can be assigned to **BP-2**$(OTf)_6(BF_4)_4$ (see SI). Also the formation of **BP-2**$(OTf)_6(BF_4)_4$ could be shown by UV-Vis spectroscopy (see SI). This transformation impressively demonstrates the strong driving force of this subcomponent exchange and the highly dynamic behaviour of this heterobimetallic system. To conduct this exchange reaction one covalent imine bond, two coordinative



Scheme 2. Sterically driven complex-to-complex transformations. Red atoms mark iron(II) in the high-spin state, purple atoms mark iron(II) in the low-spin state.



Scheme 3. Structural transformations of cubic cages into bipyramidal ones, producing the metalloligands as side products.

Fe-N bonds and one coordinative Pd-N bond have to be broken, the new building block has to align and to reform all formerly cleaved bonds again for each exchanged subcomponent.

Similar treatment of cubic cage **CU-1**(BF$_4$)$_{28}$ with a higher excess of 100 equivalents of **3** resulted in the transformation to the analogues diamagnetic cube **CU-2**(BF4)$_{28}$. Unlike with **ML-1**(BF$_4$)$_2$ and **BP-1**(OTf)$_6$(BF$_4$)$_4$, however, the subcomponent exchange took noticeable more time. After three days at 65 °C an equilibrium ratio between **1** and **3** of 30:70 was determined, which is close to the expected 24:76 ratio. However, using only 48 equivalents of **3** did not lead to a complete transformation (see SI). Therefore, these experiments show that incorporation of **3** into the cubic assembly is slightly more favoured than incorporation of **1**, but less pronounced than in the case of the bipyramidal assemblies.

Hence, in case of the cubic cage the sterically stressed complex probably is not as disfavoured as for **ML-1**(BF$_4$)$_2$ and **BP-1**(OTf)$_6$(BF$_4$)$_4$. The larger opening angle of **ML-1**(BF$_4$)$_2$ caused by the additional methyl groups seems to be a better preorganization to assemble cubic structures than the smaller opening angle in **ML-2**(BF$_4$)$_2$. This assumption is corroborated by the much faster formation of **CU-1**(BF$_4$)$_{28}$ compared to that of **CU-2**(BF$_4$)$_2$ although it is difficult to dissect whether this is due to the kinetics or the thermodynamics of the assembly process.

Besides sterically driven subcomponent exchange reactions that influence the spin state of iron(II) cations, the system also allows for structural conversions upon a chemical stimulus, maintaining the initial spin state of the complexes (see SI). The addition of dppp as a chelating ligand to cubic cages **CU-1** and **CU-2** leads to complex-to-complex transformations, yielding the bipyramidal complexes **BP-1** and **BP-2** and excess metalloligands **ML-1** and **ML-2**, respectively (Scheme 3, SI). In these reactions two 4-pyridyl donors at palladium(II) cations are replaced by one bidentate dppp ligand, leading to major structural changes. Since the contingent of iron(II) cations in the cubic assemblies is higher than in the bipyramidal cages, excess metalloligand is produced as a side product in these transformations. Addition of 6 equivalents of dppp transforms one cubic cage into two bipyramidal assemblies and four free metalloligands, increasing the overall entropy of the system, which might be an additional driving force for this reaction besides the enthalpically strongly preferred coordination of the dppp ligand to palladium(II) cations to facilitate these conversions.[24]

In conclusion, we presented the stepwise assembly of two heterobimetallic cages **BP-1** and **CU-1** from the same C_3-symmetric metalloligand **ML-1** adopting the well implemented molecular library approach. Compared to previously reported diamagnetic complexes **ML-2**, **BP-2** and **CU-2**[13e] the simple addition of a methyl group in 6-position of the pyridyl ring leads to a substantial amount of steric strain and changed the spin state of the iron(II) cations from diamagnetic low to paramagnetic high-spin. This impressively shows how rather small changes of the ligand system can cause tremendous changes of the complex properties.

Paramagnetic complexes **ML-1** and **BP-1** showed a very high tendency to undergo subcomponent exchange reactions, resulting in the first reported complex-to-complex transformations of heterobimetallic complexes to heterobimetallic complexes in which metal-bridging components are exchanged. In this case, 2-formyl-6-methyl-5-(4'-pyridyl)-pyridine **1** could be replaced by sterically less crowded 2-formyl-5-(4'-pyrdiyl)pyridine **3**, transforming the high-spin complexes into their low-spin analogues.[13e] The cubic cage **CU-1**, however, was found to exchange **1** much less readily, probably because the opening angle of the sterically crowded metalloligand is kinetically and thermodynamically favourable to assemble the cubic structure.

Addition of bidentate dppp to cubic assemblies **CU-1** and **CU-2** led to a ligand exchange reaction, in which two 4-pyridyl donors around palladium(II) cations were replaced by the chelating ligand. These exchanges resulted in complex-to-complex transformations to the bipyramidal cages **BP-1** and **BP-2**, respectively, maintaining the spin state of iron(II). Since the iron(II) to palladium(II) ratio decreases from the cubic to the bipyramidal cages, the corresponding free metalloligands **ML-1** and **ML-2** are formed as side products in these transformations. The presented complex-to-complex transformations beautifully show the highly dynamic behaviour of the shown heterobimetallic systems, allowing the change of magnetic or structural properties upon certain chemical stimuli.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: supramolecular Chemistry • self-assembly • subcomponent self-assembly • iron complexes • palladium complexes

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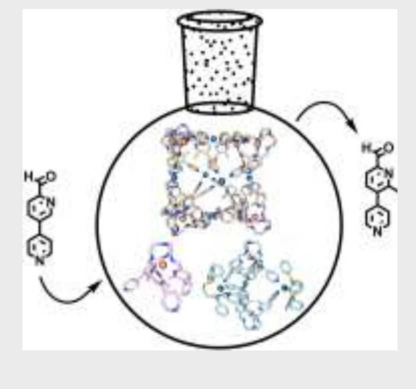
COMMUNICATION

Lively Exchanges: Two new heterobimetallic cages with incorporated iron(II) cations in a sterically strained coordination sphere undergo complex-to-complex transformation upon addition of chemical stimuli. Subcomponent exchanges by sterically less crowded building blocks changed the spin state of iron(II) from high to low-spin, whereas ligand exchanges with chelating ligands provoked major structural transformations, transforming cubic to bipyramidal cages.



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Dynamic Complex-to-Complex Transformations of Heterobimetallic Systems Influence the Cage Structure or Spin State of Iron(II) Ions