High-Fidelity, Narcissistic Self-Sorting in the Synthesis of Organometallic Assemblies from Poly-NHC Ligands

Narayan Sinha, Tristan T. Y. Tan, Eduardo Peris, and F. Ekkehardt Hahn*

Abstract: *Highly selective, narcissistic self-sorting has been observed in the one-pot synthesis of three organometallic molecular cylinders of type* $[M_3\{L\text{-}(NHC)_3\}_2](PF_6)_3$ *(M = Ag^+, Au^+; L = 1,3,5-benzene, triphenylamine, or 1,3,5-triphenylbenzene) from* $L\text{-}(NHC)_3$ *and silver(I) or gold(I) ions. The molecular cylinders contain only one type of tris-NHC ligand with no crossover products detectable. Transmetalation of the tris-NHC ligands from* Ag^+ *to* Au^+ *in a one-pot reaction with retention of the supramolecular structures is also demonstrated. High-fidelity self-sorting was also observed in the one-pot reaction of benzene-bridged tris-NHC and tetrakis-NHC ligands with* Ag_2O. *This study for the first time extends narcissistic self-sorting in metal–ligand interactions from Werner-type complexes to organometallic derivatives.*

Self-sorting, described as the high-fidelity recognition of self from non-self, is often observed in biological systems where specific functions are performed by selected compounds in spite of the presence of various chemical entities simultaneously competing for the same interaction sites. This selectivity arises from specific features encoded in the chemical structure of the interacting species.[1] The formation of the DNA double-helix, for example, requires the base-pairing and thus recognition and sorting of complementary nucleobases[2] thereby allowing the storage of genetic information. Even more complex sorting is observed in a cell where numerous small and large molecules self-sort to generate different types of compartmentalization which in turn allow the different functional architectures to act independently.

Compared to the elaborate self-sorting phenomena found in biological architectures, artificial self-assembled systems are normally less complex and comprise fewer components.[3] The relationship between the chemical structure of the components (or building blocks) and the resulting self-sorted architectures, however, is often not well established

and even the simplest systems have outcomes that are often guided more by serendipity than by design. High-fidelity self-sorting processes have been described based on reversible covalent bonds,[4] solvophobic effects,[5] hydrogen bonding,[6] and metal–ligand interactions,[7] to name a few. The steric and electronic information encoded in each of the molecular components often forces the mixture to arrange into only one defined metallosupramolecular assembly. Self-sorting systems can be classified in two categories. Self-recognition or "narcissistic" self-sorting is observed for molecules with an affinity towards like species[7e] while self-discrimination, also named "social" self-sorting, is found for species favoring the formation of self-discrimination products (mixed assemblies or heterocomplexes).[6c] Both types of self-sorting can be achieved by using metal ions and polydentate ligands featuring differences in size, topology, or coordination angles under kinetic or thermodynamic control.

Obviously, metal–ligand self-sorting becomes more challenging when the ligands used are very similar or even feature identical coordination motifs. Social self-sorting in metal–ligand coordination assemblies is not uncommon and various complex structures such as polyhedra, polygons, catenanes, and knots have emerged from social self-sorting procedures.[1, 7e,g,j,l,m] Narcissistic self-sorting in metal–ligand coordination assemblies, on the other hand, is still less common and less developed. A first impressive example of narcissistic self-sorting was described by Lehn and co-workers who reacted a mixture of oligobipyridine ligand strands containing two to five 2,2′-bipyridine donor groups with Cu^I ions to obtain a self-sorted mixture of double-stranded helicates, each containing two ligand strands with an identical number of 2,2′-bipyridine groups.[7a] Later, Raymond and co-workers[7b] and others[7c,d] showed that differently linked bis(catecholamide) ligands form M₂L₃-type triple helicates in a one-pot reaction, each containing only one type of ligand. Another impressive example for narcissistic self-sorting was reported by Fujita and co-workers in 2010, who synthesized M₂₄L₄₈ or M₁₂L′₂₄ cages from a mixture of two ligands L and L′ and Pd^II by a simple variation of the ratio of ligands having different bite angles.[7h]

Up to now, all of the known metal–ligand self-sorting systems are based on Werner-type interactions featuring coordinative bonds between the metal atoms and oxygen, nitrogen, sulfur, or phosphorus donor atoms of the polydentate ligands. Ligands composed of carbon donors have not been studied in self-sorting reactions until recently, since the metal–carbon bonds are normally obtained in a nonreversible manner preventing dynamic self-correction in the case that the thermodynamically preferred product is not formed initially. The situation is different for complexes of N-

[*] Dr. N. Sinha, T. T. Y. Tan, Prof. Dr. F. E. Hahn
Institut für Anorganische und Analytische Chemie and
NRW Graduate School of Chemistry
Westfälische Wilhelms-Universität Münster
Corrensstrasse 30, 48149 Münster (Germany)
E-mail: fehahn@uni-muenster.de
Homepage: http://www.uni-muenster.de/Chemie.ac/hahn/
index.html
Prof. Dr. E. Peris
Institute of Advanced Materials (INAM), Universitat Jaume I
Avenida Vicente Sos Baynat, 12071 Castellon (Spain)

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heterocyclic carbenes (NHCs)[8] where particularly C_{NHC}–Ag^+ interactions have been found to be rather labile and upon cleavage generate a stable metal ion and a stable free NHC ready to form again a C_{NHC}–M bond.[9] Consequently, poly-NHC ligands are promising candidates for self-sorting studies. They have already been utilized for the preparation of different metallosupramolecular architectures such as molecular cylinders[10] and molecular squares and rectangles.[11] While the lability of the C_{NHC}—Ag^+ bond would encourage the use of poly-NHC ligands in self-sorting reactions, such self-sorting phenomena in metallosupramolecular architectures featuring poly-NHC ligands are currently unknown. Herein we describe narcissistic and consecutive self-sorting phenomena observed during the formation of organometallic molecular cylinders from a mixture of poly-NHC ligands and silver(I) or gold(I) ions.

For the first part of the self-sorting study, we selected three tris-NHC precursors ([1-Et](PF$_6$)$_3$, [2-Et](PF$_6$)$_3$, and [3-Et](PF$_6$)$_3$, Scheme 1) featuring different spacers but a similar ligand topology and an identical number of donor groups. Upon triple deprotonation of these salts, the resulting tris-NHC ligands feature identical coordination motifs but differ in the size of the spacer between the donor groups. The one-pot reaction of 2 equiv each of [1-Et](PF$_6$)$_3$, [2-Et](PF$_6$)$_3$, and [3-Et](PF$_6$)$_3$ with 9 equiv of Ag$_2$O in acetonitrile at 60°C for 2 d under exclusion of light gave the three trinuclear Ag^I hexacarbene molecular cylinders [4-Et](PF$_6$)$_3$, [5-Et](PF$_6$)$_3$,

and [6-Et](PF$_6$)$_3$, each containing only one type of tris-NHC ligand (for structural and spectroscopic details of the individual complexes see Refs. [10d,e] for [4-Et](PF$_6$)$_3$, Ref. [10b] for [6-Et](PF$_6$)$_3$, and the Supporting Information for [5-Et]-(PF$_6$)$_3$). Since the three tris-NHC ligands feature identical donor groups and a very similar topology, a distinct probability for the formation of mixed-ligand or oligomeric reaction products does exist. However, no such crossover products were observed. The Ag···Ag separation in complexes [4-Et](PF$_6$)$_3$, [5-Et](PF$_6$)$_3$, and [6-Et](PF$_6$)$_3$ increases steadily and therefore narcissistic self-sorting was achieved by the controlling size of the ligand backbone. This finding contrasts recent results regarding the reorganization of [6-Et](PF$_6$)$_3$ when mixed together with a similar-shaped cyclinder-like complex built from two tris-MIC ligands (MIC = mesoionic carbene), where a random distribution of both tris-NHC and tris-MIC ligands about the metals and thus no self-sorting was observed.[10a]

The exclusive formation of the three homoligand Ag^I hexacarbene cylinders in the one-pot reaction was confirmed by ^{1}H NMR spectroscopy and high-resolution electrospray ionization (HR-ESI) mass spectrometry. The ^{1}H NMR spectrum obtained from the one-pot reaction mixture features only resonances previously obtained for the individual complexes (Figure 1). HR-ESI mass spectrometry also confirmed the exclusive formation of only three Ag^I hexacarbene complexes with no trace of mixed-ligand species detectable.
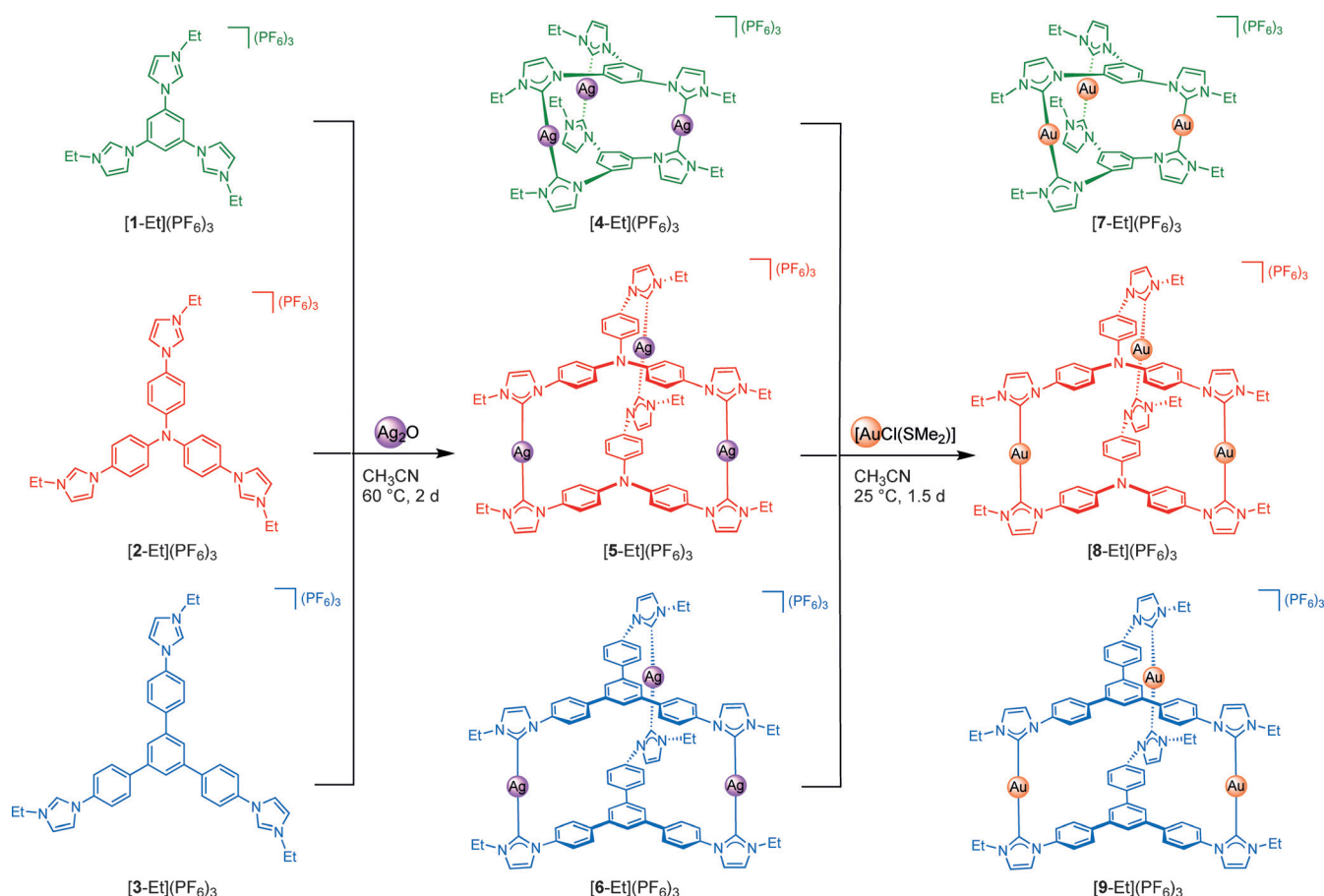
Scheme 1. Consecutive narcissistic self-sorting of organometallic cylinders featuring tris-NHC ligands with different backbones.
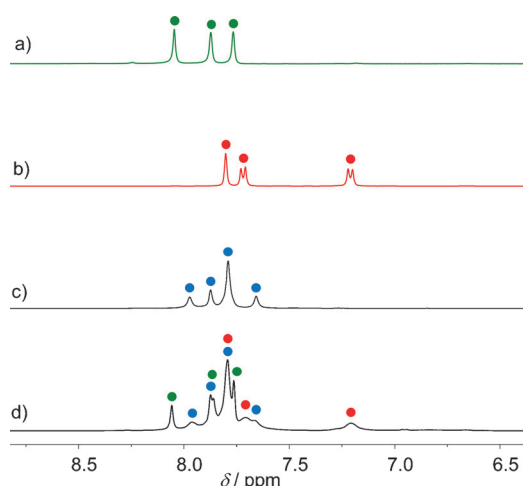
Figure 1. Section of the ¹H NMR spectra (400 MHz, 300 K, [D₆]DMSO) of a) complex [**4**-Et](PF₆)₃, b) complex [**5**-Et](PF₆)₃, c) complex [**6**-Et]-(PF₆)₃, and d) the mixture of reaction products of the one-pot reaction.

Figure 2. ESI mass spectrum (positive ions) of the complex mixture [**7**-Et](PF₆)₃, [**8**-Et](PF₆)₃, and [**9**-Et](PF₆)₃ obtained after transmetalation of [**4**-Et](PF₆)₃, [**5**-Et](PF₆)₃, and [**6**-Et](PF₆)₃ with [AuCl(SMe₂)].

In the HR-ESI mass spectrum of the complex mixture (Figure S2 in the Supporting Information) the most intense peaks were detected for the cations [**4**-Et]³⁺, [**5**-Et]³⁺, [**6**-Et]³⁺, [[**4**-Et](PF₆)]²⁺, [[**5**-Et](PF₆)]²⁺, and [[**6**-Et](PF₆)]²⁺ with the experimentally observed isotope patterns perfectly matching the calculated ones.

Transmetalation is a common procedure for the transfer of NHC ligands form silver(I) to other transition metals.[9,10b–e] However, transmetalation for a mixture of different NHC complexes has not been observed yet. Reaction of the complex mixture [**4**-Et](PF₆)₃, [**5**-Et](PF₆)₃, and [**6**-Et](PF₆)₃ with 9.0 equiv of [AuCl(SMe₂)] in acetonitrile gave a mixture of the trinuclear gold(I) hexacarbene complexes [**7**-Et](PF₆)₃, [**8**-Et](PF₆)₃, and [**9**-Et](PF₆)₃ (Scheme 1). Again, no crossover products were observed. The exclusive formation of the three Auᴵ–NHC complexes was also confirmed by ¹H NMR spectroscopy and HR-ESI mass spectrometry. The ¹H NMR spectrum of the complex mixture features only the resonances for the individual trinuclear Auᴵ hexacarbene complexes (Figure S3 in the Supporting Information). The HR-ESI mass spectrum of the complex mixture shows only peaks attributed to the molecular cylinders [**7**-Et](PF₆)₃, [**8**-Et](PF₆)₃, and [**9**-Et](PF₆)₃, respectively (Figure 2). Not only do the three NHC ligands undergo narcissistic self-sorting during the formation of the trinuclear silver(I) complexes but the self-recognition is maintained during the successive transmetalation reaction. Such unique behavior has not yet been described for any metallosupramolecular compound.

In order to gain more insight into this unprecedented narcissistic self-sorting phenomenon, we have studied a second set of poly-NHC ligands. Benzene-bridged NHC ligand precursors [**1**-Et](PF₆)₃ and [**10**-Et](PF₆)₄ were used for this study. Both poly-NHC ligand precursors feature a benzene backbone, that is, they are similar in size, but after deprotonation they will generate different coordination motifs due to the difference in the number and orientation of donor sites (Scheme 2).

Reaction of [**1**-Et](PF₆)₃ (1 equiv) and [**10**-Et](PF₆)₄ (1 equiv) with 3.5 equiv of Ag₂O in CH₃CN at 60°C for 2 d
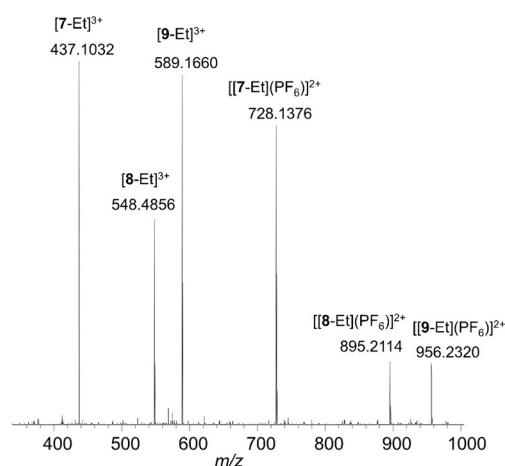
under exclusion of light gave exclusively the two organometallic molecular cylinders [**4**-Et](PF₆)₃ and [**11**-Et](PF₆)₄. Again, no crossover products were observed. Here, the inherently different coordination motifs of the ligands acted as molecular code to control the narcissistic self-sorting. The high-fidelity self-recognition was confirmed by comparison of
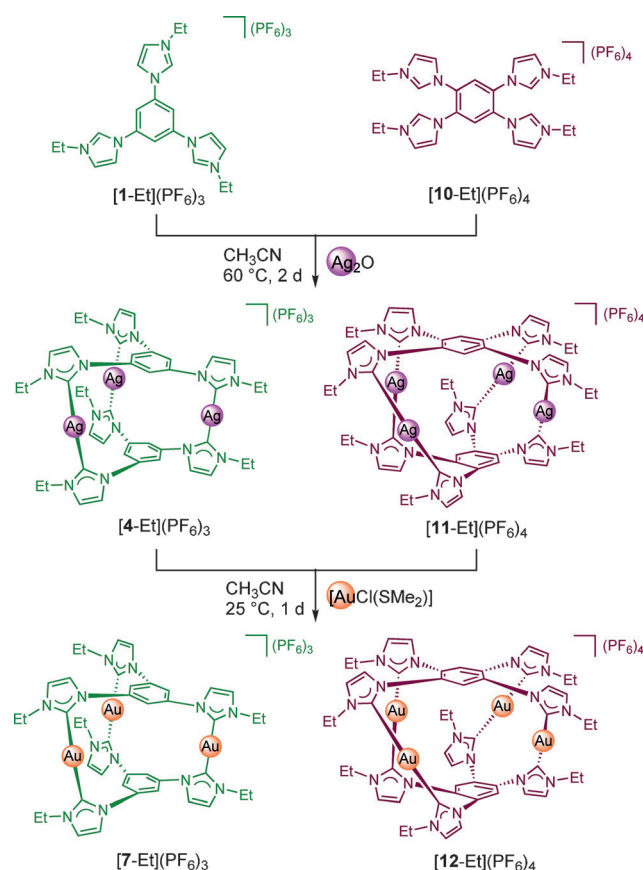
Scheme 2. Narcissistic self-sorting in the formation of organometallic molecular cylinders from poly-NHC ligands with a different number of donor groups.

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the ^{1}H NMR spectra of the individual complexes[10d,e] with the spectrum of the complex mixture (Figure S5 in the Supporting Information). The HR-ESI mass spectrum of reaction products of the one-pot reaction showed only peaks for the hexacarbene cylinder [**4**-Et](PF$_6$)$_3$ and the octacarbene cylinder [**11**-Et](PF$_6$)$_4$ (Figure 3).
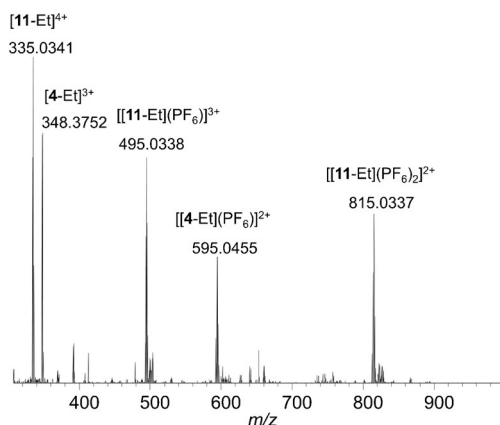
Figure 3. ESI mass spectrum (positive ions) of the complex mixture [**4**-Et](PF$_6$)$_3$ and [**11**-Et](PF$_6$)$_4$.

The transmetalation of the of the poly-NHC ligands from [**4**-Et](PF$_6$)$_3$ and [**11**-Et](PF$_6$)$_4$ with gold(I) using [AuCl(SMe$_2$)] to give the Au^I–NHC complexes [**7**-Et](PF$_6$)$_3$ and [**12**-Et](PF$_6$)$_4$ was also performed (Scheme 2). As expected, the ^{1}H NMR spectrum of the reaction products of the one-pot transmetalation reaction (Figure 4) features only the resonances previously recorded for the individual complexes [**7**-Et](PF$_6$)$_3$ and [**12**-Et](PF$_6$)$_4$.[10d,e] The HR-ESI mass spectrum of the mixture of complexes (Figure S8 in the Supporting Information) provided additional evidence for perfect self-sorting and no indications for crossover reaction products during the transmetalation were detected.

We have demonstrated for the first time that poly-NHC ligands, similar to polydentate Werner-type ligands, form metallosupramolecular assemblies controlled by narcissistic
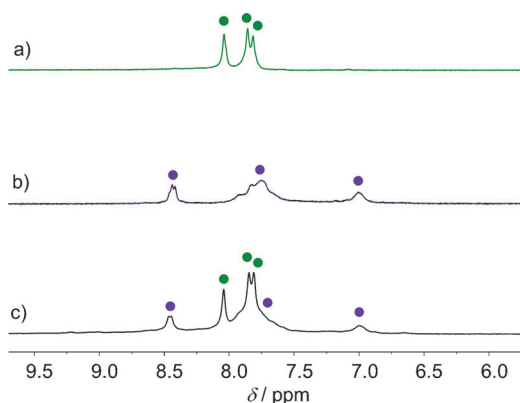
and consecutive self-sorting. Three tris-NHC ligands with different backbones react in a one-pot reaction with Ag^I to give by narcissistic self-sorting exclusively the three homoligand molecular cylinders [**4**-Et](PF$_6$)$_3$, [**5**-Et](PF$_6$)$_3$, and [**6**-Et](PF$_6$)$_3$. Consecutive self-sorting was observed in the transmetalation of the tris-NHC ligands from silver(I) to gold(I) in a one-pot procedure. Such transmetalation behavior starting from a mixture of silver–NHC complexes with retention of the individual metallosupramolecular structures has not been observed previously. Finally, high-fidelity self-sorting has also been demonstrated with two poly-NHC ligands featuring a central phenyl group and three or four NHC donors. Based on the different coordination motifs these two ligands reacted in a one-pot procedure with silver(I) ions to give by high-fidelity self-sorting the trinuclear molecular cylinder [**4**-Et](PF$_6$)$_3$ and the tetranuclear molecular cylinder [**11**-Et]-(PF$_6$)$_4$. We have shown that narcissistic self-sorting is not limited to the formation of Werner-type complexes but that proper ligand design and selection of metal ions allows the transfer of this methodology to organometallic compounds.

Conflict of interest

The authors declare no conflict of interest.

Figure 4. Section of the ^{1}H NMR spectra (400 MHz, 300 K, [D$_6$]DMSO) of a) complex [**7**-Et](PF$_6$)$_3$, b) complex [**12**-Et](PF$_6$)$_4$, and c) complex mixture [**7**-Et](PF$_6$)$_3$ and [**12**-Et](PF$_6$)$_4$ obtained by transmetalation of [**4**-Et](PF$_6$)$_3$ and [**11**-Et](PF$_6$)$_4$ with [AuCl(SMe$_2$)].

[1] M. M. Safont-Sempere, G. Fernández, F. Würthner, *Chem. Rev.* **2011**, *111*, 5784–5814.

[2] J. D. Watson, F. H. C. Crick, *Nature* **1953**, *171*, 737–738.

[3] a) A. Wu, L. Isaacs, *J. Am. Chem. Soc.* **2003**, *125*, 4831–4835; b) P. Mukhopadhyay, A. Wu, L. Isaacs, *J. Org. Chem.* **2004**, *69*, 6157–6164; c) Z. He, W. Jiang, C. A. Schalley, *Chem. Soc. Rev.* **2015**, *44*, 779–789.

[4] a) S. Klotzbach, F. Beuerle, *Angew. Chem. Int. Ed.* **2015**, *54*, 10356–10360; *Angew. Chem.* **2015**, *127*, 10497–10502; b) K. Acharyya, S. Mukherjee, P. S. Mukherjee, *J. Am. Chem. Soc.* **2013**, *135*, 554–557.

[5] N. A. Schnarr, A. J. Kennan, *J. Am. Chem. Soc.* **2003**, *125*, 667–671.

[6] a) A. Wu, A. Chakraborty, J. C. Fettinger, R. A. Flowers II, L. Isaacs, *Angew. Chem. Int. Ed.* **2002**, *41*, 4028–4031; *Angew. Chem.* **2002**, *114*, 4200–4203; b) Y. Ma, S. V. Kolotuchin, S. C. Zimmerman, *J. Am. Chem. Soc.* **2002**, *124*, 13757–13769; c) D. Ajami, J.-L. Hou, T. J. Dale, E. Barrett, J. Rebek, Jr., *Proc. Natl. Acad. Sci. USA* **2009**, *106*, 10430–10434.

[7] a) R. Krämer, J.-M. Lehn, A. Marquis-Rigault, *Proc. Natl. Acad. Sci. USA* **1993**, *90*, 5394–5398; b) D. L. Caulder, K. N. Raymond, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1440–1442; *Angew. Chem.* **1997**, *109*, 1508–1510; c) E. J. Enemark, T. D. P. Stack, *Angew. Chem. Int. Ed.* **1998**, *37*, 932–935; *Angew. Chem.* **1998**, *110*, 977–981; d) M. Albrecht, M. Schneider, H. Röttele, *Angew. Chem. Int. Ed.* **1999**, *38*, 557–559; *Angew. Chem.* **1999**, *111*, 512–515; e) P. N. Taylor, H. L. Anderson, *J. Am. Chem. Soc.* **1999**, *121*, 11538–11545; f) N. K. Al-Rasbi, I. S. Tidmarsh, S. P. Argent, H. Adams, L. P. Harding, M. D. Ward, *J. Am. Chem. Soc.* **2008**, *130*, 11641–11649; g) Y.-R. Zheng, H.-B. Yang, K. Ghosh, L. Zhao, P. J. Stang, *Chem. Eur. J.* **2009**, *15*, 7203–7214; h) Q.-F. Sun, J. Iwasa, D. Ogawa, Y. Ishido, S. Sato, T. Ozeki, Y. Sei, K. Yamaguchi, M. Fujita, *Science* **2010**, *328*, 1144–1147; i) V. E. Campbell, X. de Hatten, N. Delsuc, B. Kauffmann, I. Huc, J. R. Nitschke, *Nat. Chem.* **2010**, *2*, 684–687; j) B. Brusilowskij, E. V. Dzyuba, R. W. Troff, C. A. Schalley, *Chem. Commun.* **2011**, *47*, 1830–1832; k) M. D. Ward, P. R. Raithby, *Chem. Soc. Rev.* **2013**, *42*, 1619–1636; l) M. L. Saha, S. De, S. Pramanik, M. Schmittel, *Chem. Soc. Rev.* **2013**, *42*, 6860–6909; m) Q.-F. Sun, S. Sato, M. Fujita, *Angew. Chem. Int. Ed.* **2014**, *53*, 13510–13513; *Angew. Chem.* **2014**, *126*, 13728–13731; n) M. Frank, L. Krause, R. Herbst-Irmer, D. Stalke, G. H. Clever, *Dalton Trans.* **2014**, *43*, 4587–4592; o) T. K. Ronson, D. A. Roberts, S. P. Black, J. R. Nitschke, *J. Am. Chem. Soc.* **2015**, *137*, 14502–14512.

[8] a) M. Melaimi, M. Soleilhavoup, G. Bertrand, *Angew. Chem. Int. Ed.* **2010**, *49*, 8810–8849; *Angew. Chem.* **2010**, *122*, 8992–9032; b) L. Mercs, M. Albrecht, *Chem. Soc. Rev.* **2010**, *39*, 1903–1912; c) F. E. Hahn, M. C. Jahnke, *Angew. Chem. Int. Ed.* **2008**, *47*, 3122–3172; *Angew. Chem.* **2008**, *120*, 3166–3216.

[9] J. C. Y. Lin, R. T. W. Huang, C. S. Lee, A. Bhattacharyya, W. S. Hwang, I. J. B. Lin, *Chem. Rev.* **2009**, *109*, 3561–3598.

[10] a) C. Mejuto, G. Guisado-Barrios, D. Gusev, E. Peris, *Chem. Commun.* **2015**, *51*, 13914–13917; b) N. Sinha, F. Roelfes, A. Hepp, C. Mejuto, E. Peris, F. E. Hahn, *Organometallics* **2014**, *33*, 6898–6904; c) C. Segarra, G. Guisado-Barrios, F. E. Hahn, E. Peris, *Organometallics* **2014**, *33*, 5077–5080; d) A. Rit, T. Pape, A. Hepp, F. E. Hahn, *Organometallics* **2011**, *30*, 334–347; e) A. Rit, T. Pape, F. E. Hahn, *J. Am. Chem. Soc.* **2010**, *132*, 4572–4573.

[11] a) Y.-F. Han, G.-X. Jin, F. E. Hahn, *J. Am. Chem. Soc.* **2013**, *135*, 9263–9266; b) M. Schmidtendorf, T. Pape, F. E. Hahn, *Angew. Chem. Int. Ed.* **2012**, *51*, 2195–2198; *Angew. Chem.* **2012**, *124*, 2238–2241.

[12] CCDC 1533675 for [**8**-Bu](PF$_6$)$_3$·9Et$_2$O contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.