Supramolecular NHC Complexes

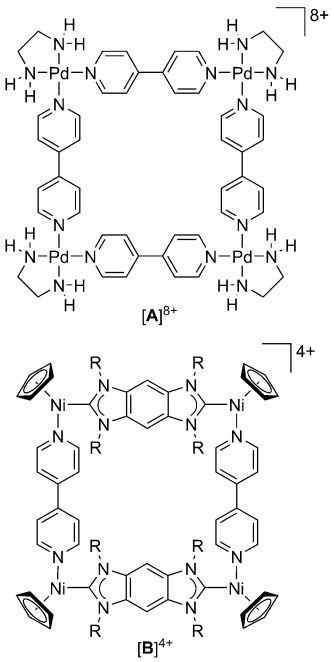
DOI: 10.1002/anie.201107227

Stepwise Preparation of a Molecular Square from NR,NR- and NH,O-Substituted Dicarbene Building Blocks**

*Markus Schmidtendorf, Tania Pape, and F. Ekkehardt Hahn**

Metallosupramolecular self-assembly has been a field of intensive research ever since Lehn et al. first demonstrated the spontaneous self-assembly of dinuclear helicates from bipyridine and copper(I).[1] Thereafter, different metallosupramolecular structures have been synthesized.[2] Some of these feature internal cavities suitable for the encapsulation of small molecules.[3] Reactive intermediates have been stabilized in such cavities[3b,f,k] and selected catalytic transformations have been carried out and accelerated inside metallosupramolecular assemblies.[3g–j]

The molecular square $[\mathbf{A}]^{8+}$ (Scheme 1) by Fujita et al. built up from end-capped Pd^{II} ions and 4,4′-bipyridine building blocks was among the first metallosupramolecular structures to be studied in detail.[4] Related molecular squares



Scheme 1. Molecular square $[\mathbf{A}]^{8+}$ and molecular rectangle $[\mathbf{B}]^{4+}$ (R=*n*-butyl).

were subsequently studied by Stang and Olenyuk[5] and other research groups.[6] Complex $[\mathbf{A}]^{8+}$ and most other metallosupramolecular assemblies described to date are derived from polydentate ligands featuring either nitrogen or oxygen donor atoms coordinating to the metal centers.[3] Supramolecular assemblies built from polydentate ligands with carbon donors are quite rare, although some examples with bridging diisocyanide,[7] acyclic diaminocarbene,[8] remote-NHC,[9] or α,ω-dicarbanion ligands[10] have been described.

The preparation of the molecular rectangle $[\mathbf{B}]^{4+}$,[11] which features rigid linear dicarbenes[12] and 4,4′-bipyridine linkers, as well as cylindrical structures synthesized from macrocyclic[13] and other poly-NHC ligands,[14] have only recently been reported, while N-heterocyclic carbenes have developed into an important class of ligands in organometallic chemistry over the last 30 years.[15] Herein we introduce a novel molecular square that is built up from four platinum(II) corners that are held together by bonds formed between platinum and the carbon atoms of two classical bis(diaminocarbene) and two di(NH,O-NHC) ligands. In contrast to the known metallosupramolecular structures featuring bridging ligands that form M–C bonds,[7–10] only $Pt–C_{carbene}$ bonds are employed for the formation of the molecular square.

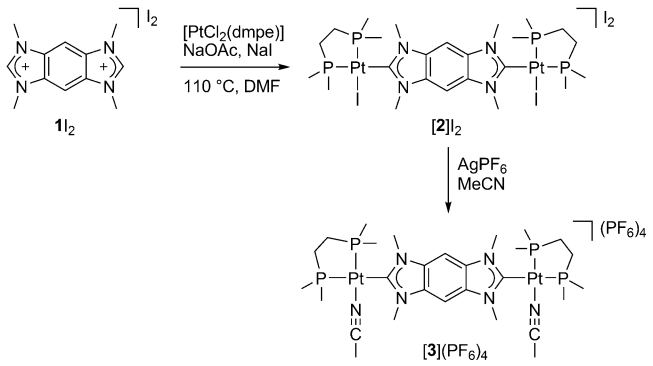
Previous studies have established that the reaction of square-planar platinum(II) with sterically demanding diphosphines and rigid linear dicarbenes, obtained by double deprotonation of benzobisimidazolium salts, yielded a mixture of dinuclear dicarbene-bridged *syn* (minor) and *anti* complexes (major).[16] Once formed, these isomers do not interconvert with the *anti* isomer being geometrically unfit for the construction of a molecular square. We have now found that a reduction of the steric demand of the ligands at platinum(II) leads to a lower barrier of rotation about the $Pt–C_{carbene}$ bond, thereby allowing the formation of the dinuclear complex with *syn* geometry by interconversion of the potential geometrical isomers.

The tetramethyl-substituted benzobisimidazolium salt $\mathbf{1}I_2$ was reacted with NaOAc[17] and $[PtCl_2(dmpe)]$ instead of the previously used $[PtCl_2(dppe)]$[16] to yield complex $[\mathbf{2}]I_2$ (Scheme 2; see Supporting Information; dmpe = bis(dimethylphosphino)ethane, dppe = bis(diphenylphosphino)-ethane). The complex was identified by the characteristic chemical shift for the carbene carbon atom at $\delta = 183.9$ ppm, which was recorded as a multiplet owing to coupling with the phosphorus atoms. The high-resolution mass spectrometry (ESI, positive ions) shows the mass of the cationic complex ion $[\mathbf{2}]^{2+}$ as peak of highest intensity. Only one multiplet was observed in the $^{31}P\{^1H\}$ NMR spectrum at $\delta = 30.9$ ppm for the two chemically different phosphorus atoms.

[*] M. Schmidtendorf, T. Pape, Prof. Dr. F. E. Hahn
Institut für Anorganische und Analytische Chemie
Westfälische Wilhelms-Universität Münster
Corrensstrasse 30, 48149 Münster (Germany)
E-mail: fehahn@uni-muenster.de

[**] We thank the Deutsche Forschungsgemeinschaft (IRTG 1444 and SFB 858) for financial support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201107227.



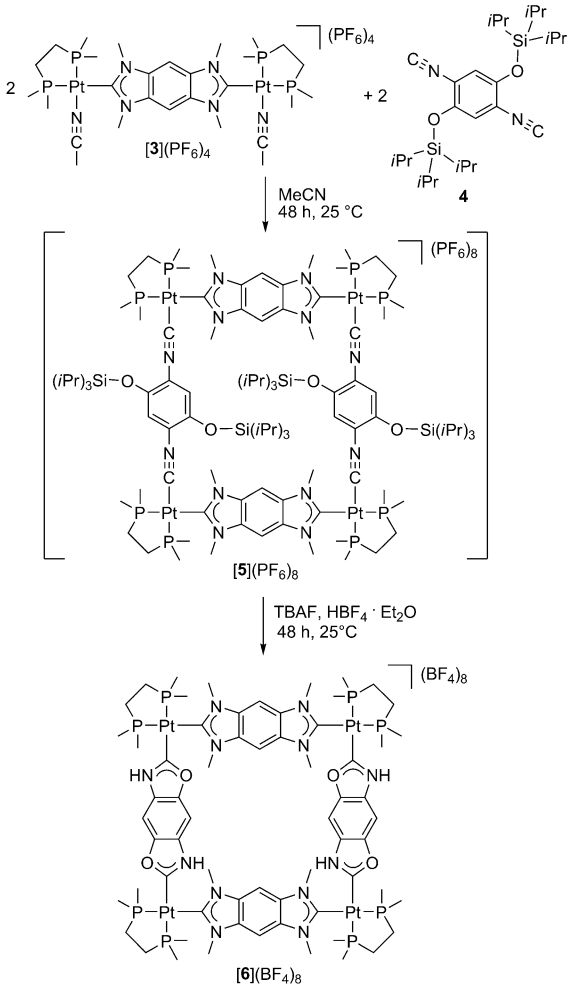
Scheme 2. Preparation of the dinuclear platinum(II) complexes $[\mathbf{2}]I_2$ and $[\mathbf{3}](PF_6)_4$.

Although the reaction of $\mathbf{1}I_2$ with $[PtCl_2(dmpe)]$ may also yield a mixture of *syn*- (depicted in Scheme 2) and *anti*-$[\mathbf{2}]I_2$, the *anti* isomer can and does rearrange (see below) into the *syn* isomer for subsequent reactions. An expansion of the steric demand of the substituents at the nitrogen atoms of the carbene ligand (*N*,*N*′,*N*″,*N*‴-tetrabutyl substitution) leads to the preferred formation of the *anti* complex, which was characterized by X-ray crystallography (see the Supporting Information). In addition, the $^{31}P\{^1H\}$ NMR spectrum of this complex features two resonances for the chemically different phosphorus atoms ($\delta = 34.7$ and 27.2 ppm), indicating that the *anti* isomer does not convert into the *syn* isomer.

For subsequent reactions, the iodo ligands and counterions in $[\mathbf{2}]I_2$ were exchanged for acetonitrile ligands and PF_6^- counterions, respectively, leading to the tetracationic complex $[\mathbf{3}]^{4+}$. Compound $[\mathbf{3}](PF_6)_4$ was obtained by reaction of $[\mathbf{2}]I_2$ with $AgPF_6$ in acetonitrile in quantitative yield (Scheme 2; see Supporting Information). The $^{13}C\{^1H\}$ NMR spectrum showed the resonance for the carbene carbon atom shifted slightly upfield relative to $[\mathbf{2}]I_2$ as a doublet of doublets ($\delta =$ 179.4 ppm, $^2J_{C,P\,trans} = 119.9$ Hz, $^2J_{C,P\,cis} = 9.1$ Hz).

We have previously shown that β-hydroxyphenyl isocyanides can be converted into NH,O-NHCs by using suitable metal templates. This reaction is reversible and the outcome is controlled by the electronic situation at the template metal center and in particular by the capability of the metal atom to engage in $M \rightarrow C_{isocyanide}$ backbonding.[18] We now used this cyclization reaction for the generation of the molecular square $[\mathbf{6}](BF_4)_8$, which features two different bridging dicarbene ligands (Scheme 3). Treatment of compound $[\mathbf{3}](PF_6)_4$ with β,β′-bis(triisopropylsiloxy)phenyl-1,4-diisocyanide (**4**) yielded the molecular rectangle $[\mathbf{5}](PF_6)_8$ as an intermediate, which was not isolated. Further treatment of the reaction mixture with tetrabutylammonium fluoride and tetrafluoroboric acid diethyl ether adduct led to cleavage of the four O–Si(*i*Pr)$_3$ bonds in $[\mathbf{5}](PF_6)_8$ and the subsequent intramolecular nucleophilic attack of the liberated hydroxy groups at the isocyanide groups in their β positions. This yielded the molecular square $[\mathbf{6}](BF_4)_8$, which features two bridging di(NR,NR-NHC) and two di(NH,O-NHC) ligands, in an excellent yield of 95% (Scheme 3).

Owing to the limited solubility of complex $[\mathbf{6}](BF_4)_8$ and the expected multiplicity of the resonance arising from



Scheme 3. Synthesis of the molecular rectangle $[\mathbf{5}](PF_6)_8$ and its conversion into the molecular square $[\mathbf{6}](BF_4)_8$. TBAF = tetra-*n*-butylammonium fluoride.

coupling with the two phosphorus atoms, we were not able to detect the resonance signal for the carbene carbon atoms in the $^{13}C\{^1H\}$ NMR spectrum. The $^{31}P\{^1H\}$ NMR spectrum exhibits two resonances at $\delta = 30.6$ ppm ($^1J_{P,Pt} = 2140$ Hz, $^2J_{P,P} = 7.5$ Hz) and at $\delta = 28.3$ ppm ($^1J_{P,Pt} = 2175$ Hz, $^2J_{P,P} =$ 7.5 Hz). The coupling constants $^1J_{P,Pt} \approx 2150$ Hz recorded for $[\mathbf{6}]^{8+}$ indicate that each of the phosphorus atoms has a carbene carbon atom in its *trans* position. High-resolution mass spectrometry (ESI, positive ions) shows the cationic complex ion $[\mathbf{6}^{8+} - 4H^+ + BF_4^-]^{3+}$ as the peak of highest intensity with the correct isotopic pattern.

Single crystals of $[\mathbf{6}](BF_4)_8 \cdot 8H_2O \cdot CH_2Cl_2$ were analyzed by X-ray diffraction (Figure 1). The compound crystallized in the triclinic space group $P\bar{1}$ with the complex cation residing on a crystallographic inversion center.[19] The metric parameters in $[\mathbf{6}]^{8+}$ fall in the typical range observed for platinum(II) complexes bearing NR,NR-[20] or NH,O-NHC[21] ligands. The Pt1–Pt2 and Pt2–Pt1* distances are 10.534 Å and 10.671 Å, respectively. The minor difference in these two values of about 1% justifies the description of $[\mathbf{6}]^{8+}$ as a molecular square and demonstrates the similarity of the geometrical properties of the bridging di(NR,NR)- and

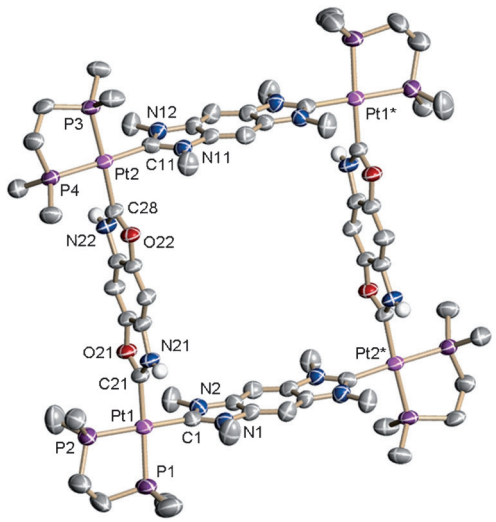


Figure 1. Molecular structure of $[\mathbf{6}]^{8+}$ in $[\mathbf{6}](BF_4)_8 \cdot 8\,H_2O \cdot CH_2Cl_2$. Ellipsoids set at 50% probability; solvent molecules and hydrogen atoms, except for the N–H hydrogen atoms, omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt1–P1 2.284(2), Pt1–P2 2.292(2), Pt1–C1 2.042(7), Pt1–C21 2.011(7), Pt2–P3 2.285(2), Pt2–P4 2.291(2), Pt2–C11 2.053(8), Pt2–C28 2.021(7), N1–C1 1.332(10), N2–C1 1.380(10), O21–C21 1.352(9), N21–C21 1.329(10), N11–C11 1.349(10), N12–C11 1.332(10), O22–C28 1.352(9), N22–C28 1.314(10); P1-Pt1-P2 85.05(7), P1-Pt1-C1 92.9(2), P1-Pt1-C21 177.2(2), P2-Pt1-C1 177.9(2), P2-Pt1-C21 92.4(2), C1-Pt1-C21 89.7(3), P3-Pt2-P4 85.30(8), P3-Pt2-C11 93.8(2), P3-Pt2-C28 173.9(2), P4-Pt2-C11 175.4(2), P4-Pt2-C28 91.5(2), C11-Pt2-C28 89.8(3), N1-C1-N2 106.7(6), O21-C21-N21 107.9(6), N11-C11-N12 106.9(7), O22-C28-N22 109.0(6).

di(NH,O)-NHC ligands. The Pt–$C_{NH,O\text{-}NHC}$ bonds (2.011(7) and 2.021(7) Å) are slightly shorter than the Pt–$C_{NR,NR\text{-}NHC}$ separations (2.042(7) and 2.053(8) Å), thus reflecting the different nature of the bridging dicarbene ligands. This situation, however, does not lead to a significant difference in the Pt–P bond distances.

Complexes featuring two different NHC ligands coordinated to the same metal center are extremely rare. Some complexes simultaneously bearing different NHCs derived from benzimidazole and imidazole have been described, but essentially no differences in the M–C_{NHC} distances were detected in these derivatives.[22] Cation $[\mathbf{6}]^{8+}$ is the first example for a complex simultaneously bearing an NR,NR- and an NH,O-NHC ligand.

We have demonstrated that *N*,*N*′,*N*″,*N*‴-tetramethyl substituted rigid ditopic dicarbene ligands and β,β′-bis(triisopropylsiloxy)phenyl-1,4-diisocyanide ligands together with end-capped platinum(II) metal components can be used for the preparation of a novel molecular square featuring two different bridging dicarbene ligands. The structural parameters of the bridging di(NR,NR) and the di(NH,O) carbene ligands are quite similar.

Previously it has been shown that the transformation of β-hydroxyphenyl isocyanides into NH,O-NHCs is a reversible reaction that is controlled by the backbonding capability of the metal center to which these ligands are coordinated.[18] This property should also in principle allow the retransformation of the di(NH,O)-NHCs in complexes of type $[\mathbf{6}]^{8+}$ into bridging β,β′-dihydroxphenyl-1,4-diisocyanide ligands, thereby leading to a complex similar to $[\mathbf{5}]^{8+}$. In such a molecular assembly, the M···M separation of the diisocyanide edges is larger than the M···M separation of the dicarbene edges. The conversion dicarbene→diisocyanide can be initiated by a change of the oxidation state of the metal centers and would thus convert a tetrakis(dicarbene) bridged molecular square of type $[\mathbf{6}]^{8+}$ into a bis(dicarbene)/bis(diisocyanide) bridged molecular rectangle. This type of conversion is however not feasible with platinum complexes, which are electron-poor and always yield the NH,O-carbene complex from the 2-hydroxyphenyl isocyanide complex.[21] We are currently studying derivatives of $[\mathbf{6}]^{8+}$ with iron or rhenium atoms in different oxidation states (Fe^{II}/Fe^{III} or Re^{I}/Re^{III}) at the vertices. Such complexes could possibly give access to molecular squares and rectangles that interconvert depending on the oxidation state of the metal atoms at the vertices.

Received: October 12, 2011
Revised: November 23, 2011
Published online: January 27, 2012

Keywords: carbene ligands · organometallic chemistry · platinum · self-assembly · supramolecular chemistry

[1] J.-M. Lehn, A. Rigault, J. Siegel, J. Harrowfield, B. Chevrier, D. Moras, *Proc. Natl. Acad. Sci. USA* **1987**, *84*, 2565–2569.
[2] a) S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853–908; b) G. F. Swiegers, T. J. Malefetse, *Chem. Rev.* **2000**, *100*, 3483–3537; c) R. W. Saalfrank, H. Maid, A. Scheurer, *Angew. Chem.* **2008**, *120*, 8924–8956; *Angew. Chem. Int. Ed.* **2008**, *47*, 8794–8824; d) D. L. Caulder, K. N. Raymond, *Acc. Chem. Res.* **1999**, *32*, 975–982; e) C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* **1997**, *97*, 2005–2062; f) M. Albrecht, *Chem. Rev.* **2001**, *101*, 3457–3497; g) T. Kreickmann, F. E. Hahn, *Chem. Commun.* **2007**, 1111–1120; h) S. R. Seidel, P. J. Stang, *Acc. Chem. Res.* **2002**, *35*, 972–983.
[3] a) K. Kumazawa, K. Biradha, T. Kusukawa, T. Okano, M. Fujita, *Angew. Chem.* **2003**, *115*, 4039–4043; *Angew. Chem. Int. Ed.* **2003**, *42*, 3909–3913; b) S. Sato, J. Iida, K. Suzuki, M. Kawano, T. Ozeki, M. Fujita, *Science* **2006**, *313*, 1273–1276; c) J. Mattsson, P. Govindaswamy, J. Furrer, Y. Sei, K. Yamaguchi, G. Süss-Fink, B. Therrien, *Organometallics* **2008**, *27*, 4346–4356; d) Y.-F. Han, W.-G. Jia, Y.-J. Lin, G.-X. Jin, *Angew. Chem.* **2009**, *121*, 6352–6356; *Angew. Chem. Int. Ed.* **2009**, *48*, 6234–6238; e) B. Birkmann, R. Fröhlich, F. E. Hahn, *Chem. Eur. J.* **2009**, *15*, 9325–9329; f) G. Steinfeld, V. Lozan, H.-J. Krüger, B. Kersting, *Angew. Chem.* **2009**, *121*, 1988–1991; *Angew. Chem. Int. Ed.* **2009**, *48*, 1954–1957; g) M. D. Pluth, R. G. Bergman, K. N. Raymond, *Science* **2007**, *316*, 85–88; h) M. D. Pluth, R. G. Bergman, K. N. Raymond, *Angew. Chem.* **2007**, *119*, 8741–8743; *Angew. Chem. Int. Ed.* **2007**, *46*, 8587–8589; i) C. J. Hastings, M. D. Pluth, R. G. Bergman, K. N. Raymond, *J. Am. Chem. Soc.* **2010**, *132*, 6938–6940; j) M. Yoshizawa, M. Tamura, M. Fujita, *Science* **2006**, *312*, 251–254; k) P. Mal, B. Breiner, K. Rissanen, J. R. Nitschke, *Science* **2009**, *324*, 1697–1699.
[4] a) M. Fujita, J. Yazaki, K. Ogura, *J. Am. Chem. Soc.* **1990**, *112*, 5645–5647; b) M. Fujita, M. Tominaga, A. Hori, B. Therrien, *Acc. Chem. Res.* **2005**, *38*, 371–380.
[5] P. J. Stang, B. Olenyuk, *Acc. Chem. Res.* **1997**, *30*, 502–518.
[6] a) C. H. M. Amijs, G. P. M. van Klink, G. van Koten, *Dalton Trans.* **2006**, 308–327; b) S. Bélanger, J. T. Hupp, C. L. Stern,

R. V. Slone, D. F. Watson, T. G. Carell, *J. Am. Chem. Soc.* **1999**, *121*, 557 – 563; c) V. C. Lau, L. A. Berben, J. R. Long, *J. Am. Chem. Soc.* **2002**, *124*, 9042 – 9043; d) S. Shanmugaraju, A. K. Bar, K.-W. Chi, P. S. Mukherjee, *Organometallics* **2010**, *29*, 2971 – 2980; e) F. Würthner, C.-C. You, C. R. Saha-Möller, *Chem. Soc. Rev.* **2004**, *33*, 133 – 146.

[7] Y. Yamamotoa, H. Suzuki, N. Tajima, K. Tatsumi, *Chem. Eur. J.* **2002**, *8*, 372 – 379.

[8] S.-W. Lai, K.-K. Cheung, M. C.-W. Chan, C.-M. Che, *Angew. Chem.* **1998**, *110*, 193 – 195; *Angew. Chem. Int. Ed.* **1998**, *37*, 182 – 184.

[9] Y. Han, L. J. Lee, H. V. Huynh, *Chem. Eur. J.* **2010**, *16*, 771 – 773.

[10] a) S. Yamago, Y. Watanabe, T. Iwamoto, *Angew. Chem.* **2010**, *122*, 769 – 771; *Angew. Chem. Int. Ed.* **2010**, *49*, 757 – 759; b) S. J. Lee, C. R. Luman, F. N. Castellano, W. Lin, *Chem. Commun.* **2003**, 2124 – 2125; c) H. Jiang, A. Hu, W. Lin, *Chem. Commun.* **2003**, 96 – 97.

[11] a) F. E. Hahn, C. Radloff, T. Pape, A. Hepp, *Organometallics* **2008**, *27*, 6408 – 6410; b) C. Radloff, J. J. Weigand, F. E. Hahn, *Dalton Trans.* **2009**, 9392 – 9394.

[12] a) D. M. Khramov, A. J. Boydston, C. W. Bielawski, *Angew. Chem.* **2006**, *118*, 6332 – 6335; *Angew. Chem. Int. Ed.* **2006**, *45*, 6186 – 6189; b) A. J. Boydston, C. W. Bielawski, *Dalton Trans.* **2006**, 4073 – 4077; c) L. Mercs, A. Neels, M. Albrecht, *Dalton Trans.* **2008**, 5570 – 5576.

[13] a) F. E. Hahn, C. Radloff, T. Pape, A. Hepp, *Chem. Eur. J.* **2008**, *14*, 10900 – 10904; b) C. Radloff, H.-Y. Gong, C. Schulte to Brinke, T. Pape, V. M. Lynch, J. L. Sessler, F. E. Hahn, *Chem. Eur. J.* **2010**, *16*, 13077 – 13081; c) D. Wang, B. Zhang, C. He, P. Wu, C. Duan, *Chem. Commun.* **2010**, *46*, 4728 – 4730.

[14] a) A. Rit, T. Pape, F. E. Hahn, *J. Am. Chem. Soc.* **2010**, *132*, 4572 – 4573; b) A. Rit, T. Pape, A. Hepp, F. E. Hahn, *Organometallics* **2011**, *30*, 334 – 347; c) A. Rit, T. Pape, A. Hepp, F. E. Hahn, *Organometallics* **2011**, *30*, 6393 – 6401.

[15] a) M. Melaimi, M. Soleilhavoup, G. Bertrand, *Angew. Chem.* **2010**, *122*, 8992 – 9032; *Angew. Chem. Int. Ed.* **2010**, *49*, 8810 – 8849; b) L. Mercs, M. Albrecht, *Chem. Soc. Rev.* **2010**, *39*, 1903 – 1912; c) P. de Frémont, N. Marion, S. P. Nolan, *Coord. Chem. Rev.* **2009**, *253*, 862 – 892; d) F. E. Hahn, M. C. Jahnke, *Angew. Chem.* **2008**, *120*, 3166 – 3216; *Angew. Chem. Int. Ed.* **2008**, *47*, 3122 – 3172.

[16] C. Radloff, F. E. Hahn, T. Pape, R. Fröhlich, *Dalton Trans.* **2009**, 7215 – 7222.

[17] M. Heckenroth, E. Kluser, A. Neels, M. Albrecht, *Dalton Trans.* **2008**, 6242 – 6249.

[18] a) F. E. Hahn, M. Tamm, *J. Organomet. Chem.* **1993**, *456*, C11 – C14; b) F. E. Hahn, M. Tamm, *J. Chem. Soc. Chem. Commun.* **1993**, 842 – 844; c) F. E. Hahn, M. Tamm, T. Lügger, *Angew. Chem.* **1994**, *106*, 1419 – 1421; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1356 – 1359; d) F. E. Hahn, M. Tamm, *J. Chem. Soc. Chem. Commun.* **1995**, 569 – 570; e) F. E. Hahn, M. Tamm, *Organometallics* **1995**, *14*, 2597 – 2600; f) M. Tamm, T. Lügger, F. E. Hahn, *Organometallics* **1996**, *15*, 1251 – 1256; g) F. E. Hahn, L. Imhof, *Organometallics* **1997**, *16*, 763 – 769; h) M. Tamm, F. E. Hahn, *Coord. Chem. Rev.* **1999**, *182*, 175 – 209.

[19] CCDC 847925 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[20] a) M. V. Baker, D. H. Brown, P. V. Simpson, B. W. Skelton, A. H. White, C. C. Williams, *J. Organomet. Chem.* **2006**, *691*, 5845 – 5855; b) M. C. Jahnke, T. Pape, F. E. Hahn, *Z. Naturforsch. B* **2010**, *65*, 341 – 346; for complexes with NH,NR-NHC ligands, see: c) T. Kösterke, T. Pape, F. E. Hahn, *J. Am. Chem. Soc.* **2011**, *133*, 2112 – 2115; d) T. Kösterke, T. Pape, F. E. Hahn, *Chem. Commun.* **2011**, *47*, 10773 – 10775.

[21] F. E. Hahn, D. Klusmann, T. Pape, *Eur. J. Inorg. Chem.* **2008**, 4420 – 4424.

[22] a) H. V. Huynh, Y. Han, R. Jothibasu, J. A. Yang, *Organometallics* **2009**, *28*, 5395 – 5404; b) H. V. Huynh, R. Jothibasu, *J. Organomet. Chem.* **2011**, *696*, 3369 – 3375.

