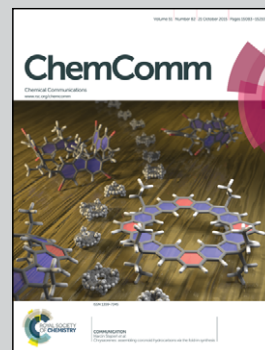


Showcasing work from the catalysis and switchable molecular materials laboratory of Biprajit Sarkar, Institut für Chemie und Biochemie, Freie Universität Berlin, Germany

Triply cyclometalated trinuclear iridium(III) and trinuclear palladium(II) complexes with a tri-mesoionic carbene ligand

A tri-mesoionic carbene platform is presented together with its trinuclear iridium and palladium complexes. The complexes are active catalysts for transfer hydrogenation reactions of aldehydes and ketones, and for alpha-arylation reactions of amides. Cooperative effects have been observed for both kinds of catalysis. The ligand platform thus opens up new avenues for investigating cooperative catalysis.

As featured in:



See Biprajit Sarkar *et al.*,
Chem. Commun., 2015, **51**, 15106.



Cite this: *Chem. Commun.*, 2015, 51, 15106

Received 3rd July 2015,
Accepted 28th July 2015

DOI: 10.1039/c5cc05506g

www.rsc.org/chemcomm

Triply cyclometalated trinuclear iridium(III) and trinuclear palladium(II) complexes with a tri-mesoionic carbene ligand†‡

Ramananda Maity, Amel Mekic, Margarethe van der Meer, Amit Verma and Biprajit Sarkar*

The first example of a triply cyclometalated homopolynuclear tri-Ir^{III} complex with additional carbene donors is presented. Cooperative catalysis and the interplay between homogenous and heterogeneous catalyses are discussed for the tri-Ir^{III} complex and a related non-cyclometalated tri-Pd^{II} complex.

N-Heterocyclic carbenes (NHCs) have emerged as a useful class of ligands in organometallic chemistry.¹ Although the majority of these ligands are based on imidazol-2-ylidenes² or 1,2,4-triazol-5-ylidenes³ (normal NHCs), their mesoionic counterparts, 1,2,3-triazol-5-ylidenes,⁴ are currently gaining immense popularity. Mesoionic carbenes (MIC) have been postulated as even better sigma donors compared to their classical counterparts.^{4a} A number of complexes bearing 1,2,3-triazol-5-ylidenes have emerged in the literature with the complexes being often tested for their potency in various homogeneous catalytic processes.⁵ Recently, we have reported on such types of complexes as catalysts for various organic transformations such as Suzuki–Miyaura cross-coupling reactions,⁶ “click” reactions,⁷ and reduction of aromatic nitro compounds⁸ and for oxidation reactions.⁹ Most of the reported complexes possessing 1,2,3-triazol-5-ylidene ligands are of mononuclear type.^{4,5,10} Only a few dinuclear complexes possessing a MIC donor at each metal center have been reported in the literature recently.¹¹ Even though polynuclear metal complexes have become popular in recent years owing to their augmented catalytic activity¹² compared to their mononuclear counterparts, examples of such complexes with higher nuclearity containing MIC donors remain rare.¹³

Recently, we showed that a di-substituted phenylene bridged bistriazolium salt after deprotonation reacts to yield a dinuclear

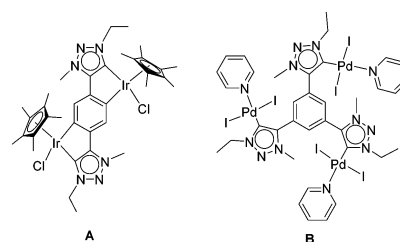


Fig. 1 Dinuclear Ir^{III} and trinuclear Pd^{II} complexes with MIC ligands.¹³

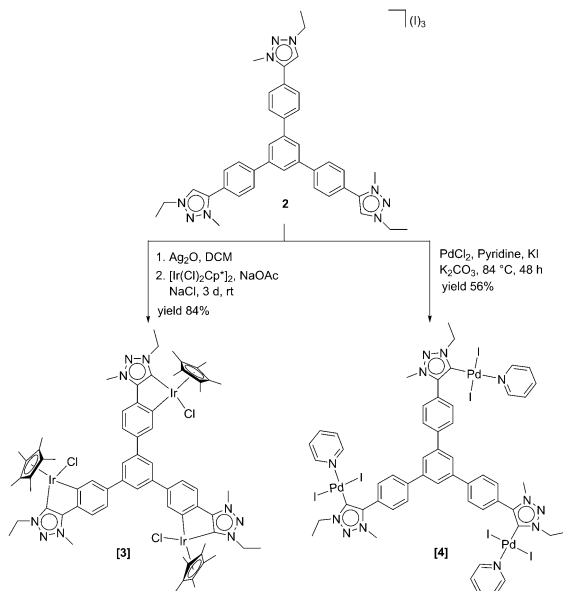
Ir^{III} complex with additional cyclometalation of the central phenyl ring (Fig. 1).^{13a} For Pd^{II} that prefers a square planar coordination geometry, reaction with either di- or 1,3,5-tri-substituted benzene derived triazolium salts in the presence of K₂CO₃ and pyridine yielded PEPPSI type complexes (Fig. 1).^{13b} However, the intended synthesis of a triply cyclometalated Ir^{III} complex with a 1,3,5-tri-substituted benzene derived tris-triazolium salt was unsuccessful.^{13c} We believed that steric effects might render the formation of cyclometalated complexes with this ligand system difficult. Hence, we decided to introduce additional phenyl rings on the ligand backbone to reduce steric crowding and synthesized the tris-triazolium salt **2** (Scheme 1). We present here the synthesis of the first triply cyclometalated trinuclear Ir^{III} complex from a 1,3,5-triphenylbenzene derived tri-MIC ligand, where the coordinated MIC moieties are further removed from each other, and allow the Ir^{III} centers to undergo cyclometalation. In addition, a trinuclear PEPPSI type Pd^{II} complex has also been synthesized using the same tri-MIC ligand platform. Apart from synthetic and structural aspects, we also present catalytic results for transfer hydrogenation and C–C coupling reactions with the Ir^{III} and Pd^{II} complexes, respectively, and also discuss catalytic cooperativity and homogeneous *versus* heterogeneous catalysis.

The reaction of tris-triazolium salt **2** with Ag₂O followed by an addition of [Ir(Cl)₂Cp*]₂ in the presence of sodium acetate resulted in the formation of triply cyclometalated trinuclear Ir^{III} complex [**3**] in 84% yield. Complex [**3**] is stable under air and moisture and well soluble in solvents like chloroform and dichloromethane. This complex is characterized by ¹H, ¹³C{¹H} NMR spectroscopy and

Institut für Chemie und Biochemie, Anorganische Chemie,
Freie Universität Berlin, Fabeckstraße 34-36, D-14195, Berlin, Germany.
E-mail: biprajit.sarkar@fu-berlin.de; Fax: +49-30-838-53310

† Dedicated to Prof. F. E. Hahn on the occasion of his 60th birthday.

‡ Electronic supplementary information (ESI) available: Preparation and spectroscopic properties of complexes [**3**] and [**4**]. Details of the crystal structure determination for [**4**]-2.75CH₂Cl₂. CCDC 1062049. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc05506g



Scheme 1 Preparation of complexes [3] and [4].

ESI mass spectrometry. The formation of complex [3] was easily monitored by ^1H NMR spectroscopy, which shows the disappearance of the triazolium C–H proton signal ($\delta = 9.31$ ppm) for the original tris-triazolium salt 2. Both the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of complex [3] show more than one set of signals in solution which implies the presence of different rotational isomers of the complex in solution. The presence of rotamers are due to the free rotation of the $[\text{Ir}^{\text{III}}(\text{Cl})\text{Cp}^*(\text{C}_{\text{MIC}}^{\wedge}\text{C}_{\text{Ar}})]$ moieties around the $\text{C}_{\text{aryl}}\text{--}\text{C}_{\text{aryl}}$ bonds. Upon heating the sample to 90°C , the signals of the rotamers merge into a single set of signals (Fig. S11, ESI ‡). Resonances for four chemically different aryl C–H protons appeared as four sets in the range of $\delta = 8.17\text{--}8.29$, $7.90\text{--}8.02$, $7.49\text{--}7.52$, $7.27\text{--}7.43$ ppm. The cyclometalation of the aryl ring was confirmed by 2D correlation NMR spectroscopy which shows a resonance (broad) at $\delta = 159.6$ ppm, attributed to the cyclometalated aryl carbon atom. The resonance for the characteristic carbene carbon atoms was observed at $\delta = 153.1$ ppm also as a broad signal. These resonances fall in the range reported for cyclometalated complexes bearing MIC donor ligands.^{13,14} The resonance for the carbene carbon atom in complex [3] is more upfield shifted compared to their corresponding resonances in complexes possessing cyclometalated classical NHC ligands.¹⁵ The ESI mass (positive ions) spectrum of complex [3] shows the peaks at $m/z = 1884.4968$ (calcd for $[[3]\text{--Cl}]^+$ 1884.4863) and 823.7659 (calcd for $[[3]\text{--}2\text{Cl}]^{2+}$ 823.7583) as strongest signals, also confirming the formation of complex [3].

The treatment of tris-triazolium salt 2 with PdCl_2 in the presence of K_2CO_3 as an external base in pyridine yielded a trinuclear PEPPSI type Pd^{II} complex [4]. Complex [4] is stable under air and moisture for long time and also has good solubility in chlorinated solvents like chloroform and dichloromethane. The formation of complex [4] was monitored by ^1H NMR spectroscopy, which shows only one set of signals along with the disappearance of the triazolium C–H proton resonance ($\delta = 9.31$ ppm) for the precursor triazolium salt 2. The resonances for the C–H protons of pyridine rings appeared as

multiplets at $\delta = 8.99$, $7.75\text{--}7.78$ and $7.33\text{--}7.36$ ppm. Upon complexation the resonance for α -hydrogen atoms of the pyridine ring ($\delta = 8.99$ ppm) appeared to be more downfield shifted compared to their corresponding resonance in free pyridine ($\delta = 8.62$). The characteristic resonance for the $\text{C}_{\text{trz}}\text{--Pd}$ carbon atoms was observed at $\delta = 133.1$ ppm in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex [4]. This resonance is slightly downfield shifted from the C5–H resonance of the precursor triazolium salt 2 ($\delta = 129.2$ ppm).

Single crystals suitable for an X-ray diffraction analysis were obtained for complex [4] by slow diffusion of pentane into a saturated dichloromethane solution of complex [4] at ambient temperature. The molecular structure analysis confirmed the formation of a trinuclear palladium complex depicted in Scheme 1. The asymmetric unit contains the $1/3$ formula unit of complex [4] and disordered dichloromethane molecules. The $1/3$ unit is related to the rest of $2/3$ unit by a crystallographic inversion center. In complex [4] each palladium atom is coordinated to a strongly bound MIC donor and a weakly coordinated pyridine donor *trans* to it. The remaining coordination sites of each palladium center are occupied by iodido ligands. The C1–Pd1–N4 (Fig. 2) bond angle measures $177.4(3)^\circ$. This value, like the Pd1–C1 ($1.954(6)$ Å) and Pd1–N4 ($2.096(6)$ Å) bond lengths, falls in the range previously described for palladium MIC complexes.^{13b,16} The MIC donor planes are almost coplanar to the central aryl ring plane; however, they are rotated from the nearest aryl ring plane to coordinate with palladium centers. The torsion angle of the MIC donor plane to the nearest aryl ring plane measures 35.26° . The two central phenyl rings of the tri-mesoionic carbene ligands of neighboring molecules are oriented in a coplanar fashion with a centroid to centroid separation of 3.498 Å indicating $\pi\cdots\pi$ interactions between these rings.

Catalytic transfer hydrogenation is a widely used method for reducing multiple bonds. Conversion of aldehydes and ketones to the corresponding alcohols represents the most prominent examples. Iridium and ruthenium complexes bearing NHC ligands have been widely used as catalysts for transfer hydrogenation.¹⁷ However, similar catalytic conversions using complexes bearing MIC ligands have been rare.^{8,13a,18} In this context, catalytic transfer hydrogenation studies have been carried out with triply cyclometalated Ir^{III} complex [3]. The catalytic conversions for the trinuclear complex have also been compared with a related cyclometalated mononuclear complex C (Fig. 3).

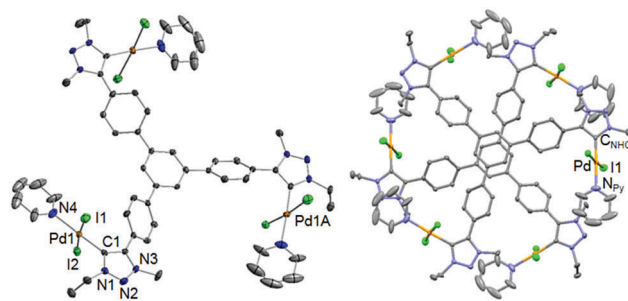


Fig. 2 ORTEP plot of $[\text{4}]\cdot 2.75\text{CH}_2\text{Cl}_2$ (left). Ellipsoids are drawn at 50% probability. Hydrogen atoms and solvent molecules have been omitted for clarity. Intermolecular $\pi\text{--}\pi$ stacking (right).

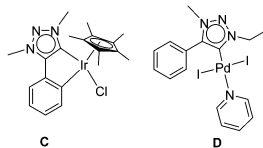


Fig. 3 Mononuclear Ir^{III} and Pd^{II} complexes.

Isopropanol was used as a hydrogen source for transfer hydrogenation reactions. KOH (20 mol%) was used as a base and the reactions were performed at 100 °C. The reaction was carried out with 0.5 mol% of the mononuclear complex or 0.167 mol% (the same amount of iridium for both complexes) of the trinuclear complex. Both the complexes show a full conversion of benzaldehyde and 4-bromo-benzaldehyde to the corresponding benzylalcohol after 3 h. A decrease in reaction time to 1 h shows higher conversion (80 or 50%) for the trinuclear complex compared with the mononuclear Ir^{III} complex (40 or 35%). The trinuclear complex is also a more active precatalyst for more challenging substrates like acetophenone, benzophenone and substituted benzophenone (Table 1).

The palladium-catalyzed C–C bond formation process between an aryl ring and the α -position of a carbonyl compound has been widely used as a mild catalytic method.¹⁹ However, α -arylation of amides (particularly the intermolecular version) is comparatively less common and rarely used with palladium(II) NHC complexes.²⁰ This is an important catalytic reaction for synthesizing valuable chemicals. Trinuclear palladium(II) complex [4] has been tested as a catalyst for both α -arylation and Suzuki–Miyaura cross-coupling reactions. The catalytic efficiency of trinuclear complex [4] has also been compared to the efficiency of a similar mononuclear counterpart **D** (Fig. 3). The α -arylation reactions were typically carried out in toluene in the presence of NaOtBu (2.5 equiv.) as a base at 120 °C for 16 h.

Upon performing the reactions with 5.0 mol% of mononuclear complex **D** or 1.67 mol% (the same amount of palladium for both types of complexes) of trinuclear complex [4], almost 1.5 times more conversion of **5** to **6** (Ar = Ph) was

Table 1 Catalytic transfer hydrogenation of aldehydes and ketones^a

Entry	R ₁	R ₂	Catalyst	Conversion (%) 1 h	Conversion (%) 3 h
1	Ph	H	[3]	80	99
2	Ph	H	C	40	99
3	4-Br(Ph)	H	[3]	50	99
4	4-Br(Ph)	H	C	35	99
5	Ph	CH ₃	[3]	40	65
6	Ph	CH ₃	C	24	40
7	Ph	Ph	[3]	42	80
8	Ph	Ph	C	13	29
9	Ph	4-Br(Ph)	[3]	30	61
10	Ph	4-Br(Ph)	C	11	40
11	4-Me(Ph)	4-Me(Ph)	[3]	20	62
12	4-Me(Ph)	4-Me(Ph)	C	8	38

^a Reaction conditions: 0.5 mol% catalyst (0.167 mol% for the trinuclear complex and 0.5 mol% for the mononuclear complex), 20 mol% KOH, isopropanol, 100 °C.

achieved for the trinuclear complex (Table 2, 71%; isolated yield, see the ESI†) when compared with the mononuclear complex (45%; isolated yield, see the ESI†). The active palladium catalyst was unaffected by the addition of excess Hg(0) to the reaction mixture and leads to a similar yield for the α -arylation product even after addition of Hg(0). This is a strong indication of the homogeneous nature of our catalysts for the α -arylation reaction. We also tested the efficiency of [4] and **D** as catalysts for the Suzuki–Miyaura cross-coupling reaction. For this reaction, no further conversion to the coupling product was observed any more after Hg(0) addition. Addition of mercury after 1 h (13% conversion) inhibited further catalytic coupling and no biaryl aldehyde product (phenylboronic acid and 4-bromobenzaldehyde as substrates) was formed during the subsequent 5 h time period. This observation suggests the possibility that Pd(0) nanoparticles (NP) are the active catalyst in the Suzuki–Miyaura cross-coupling reactions under the mentioned reaction conditions, as has been previously observed for related systems.¹⁰

As expected, for the Suzuki–Miyaura coupling reaction where Pd-NPs are the active species, both **D** and [4] reported similar conversions (Table 3).

In summary, we have presented here the synthesis of a novel tris-triazolium salt **2** based on an extended phenylene platform. **2** was used to synthesize trinuclear complex [3] where each Ir^{III} center is coordinated by a MIC unit and additionally cyclometalates the aryl rings of the ligand. **2** was also used to synthesize trinuclear PEPPSI type complex [4] upon reaction with PdCl₂ in the presence of pyridine and K₂CO₃. Complex [3] is the first example of a triply cyclometalated trinuclear Ir^{III} complex containing additional carbene

Table 2 α -Arylation reaction using Pd^{II} complexes

Entry	Ar	Catalyst	Conversion (%) 16 h	Isolated yield (%)
1	Ph	[4]	80	71
2	Ph	D	60	45
3	4-Me(Ph)	[4]	91	85
4	4-Me(Ph)	D	63	59
5	4-OMe(Ph)	[4]	81	70
6	4-OMe(Ph)	D	65	46

Table 3 Suzuki–Miyaura cross-coupling reaction^a

Entry	Ar	Catalyst	Conversion (%) 5 h	Conversion (%) 12 h
1	Ph	[4]	58	85
2	Ph	D	52	90
3	4-Me(Ph)	[4]	60	87
4	4-Me(Ph)	D	64	92

^a Reactions conditions: 0.5 mol% catalyst (0.167 mol% for the trinuclear complex), 1.4 mol% K₂CO₃, water, rt, 5 h.

donors. The tri-iridium complex [3] is an active pre-catalyst for the conversion of aldehyde and ketones to the corresponding alcohols and shows possible signs of cooperative effects in catalysis. Trinuclear PEPSI type complex [4] is an active catalyst used for both α -arylation of amides and the Suzuki–Miyaura cross-coupling reaction. Complex [4] displays possible signs of cooperative effects for the α -arylation reaction which proceeds homogeneously. The same complex also catalyzes the Suzuki–Miyaura cross-coupling reaction, albeit through the formation of Pd(0)-NPs in a heterogeneous medium, and thus no cooperativity is observed. The new ligand platform presented here opens up new avenues for generating multi-cyclometalated complexes and investigating potentially cooperative catalysis. The results on α -arylation of amides show the potential of Pd–MIC complexes as potent pre-catalysts for that important reaction. Furthermore, our results of the Suzuki–Miyaura cross-coupling reaction shows that for such reactions that are carried out in water even under mild conditions (room temperature), Pd-NPs are often likely to be the real active catalyst.

The authors thank the Fonds der Chemischen Industrie (FCI) and the Freie Universität Berlin for financial support. The ERASMUS-MUNDUS program is acknowledged for providing a post-doctoral fellowship to AV.

Notes and references

- For selected reviews see: (a) P. de Frémont, N. Marion and S. P. Nolan, *Coord. Chem. Rev.*, 2009, **253**, 862; (b) M. Melaimi, M. Soleilhavoup and G. Bertrand, *Angew. Chem., Int. Ed.*, 2010, **49**, 8810; (c) F. E. Hahn and M. C. Jahnke, *Angew. Chem., Int. Ed.*, 2008, **47**, 3122; (d) M. Melaimi, M. Soleilhavoup and G. Bertrand, *Angew. Chem., Int. Ed.*, 2010, **49**, 8810; (e) C. C. Loh and D. Enders, *Chem. – Eur. J.*, 2012, **18**, 10212; (f) J. D. Egbert, C. S. J. Cazin and S. P. Nolan, *Catal. Sci. Technol.*, 2013, **3**, 912.
- (a) M. C. Jahnke and F. E. Hahn, *Top. Organomet. Chem.*, 2010, **30**, 95; (b) W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290.
- (a) A. Zanardi, R. Corberán, J. A. Mata and E. Peris, *Organometallics*, 2008, **27**, 3570; (b) H. Braband, O. Blatt and U. Abram, *Z. Anorg. Allg. Chem.*, 2006, **632**, 2251; (c) D. Enders and T. Balensiefer, *Acc. Chem. Res.*, 2004, **37**, 534; (d) D. Enders, O. Niemeier and A. Henseler, *Chem. Rev.*, 2007, **107**, 5606; (e) M. He and J. W. Bode, *J. Am. Chem. Soc.*, 2008, **130**, 418.
- (a) P. Mathew, A. Neels and M. Albrecht, *J. Am. Chem. Soc.*, 2008, **130**, 13534; (b) K. F. Donnelly, A. Petronilho and M. Albrecht, *Chem. Commun.*, 2013, **49**, 1145; (c) R. H. Crabtree, *Coord. Chem. Rev.*, 2013, **257**, 755; (d) J. M. Aizpurua, R. M. Fratila, Z. Monasterio, N. Perez-Esnaola, E. Andreieff, A. Irastorza and M. Sagartzazu-Aizpurua, *New J. Chem.*, 2014, **38**, 474; (e) D. Schweinfurth, N. Deibel, F. Weisser and B. Sarkar, *Nach. der Chem.*, 2011, **59**, 937; (f) G. Guisado-Barrios, J. Bouffard, B. Donnadieu and G. Bertrand, *Angew. Chem., Int. Ed.*, 2010, **49**, 4759; (g) J. D. Crowley, A. Lee and K. J. Kilpin, *Aust. J. Chem.*, 2011, **64**, 1118.
- For selected examples see: (a) R. Saravanakumar, V. Ramkumar and S. Sankararaman, *Organometallics*, 2011, **30**, 1689; (b) R. Lalrempuia, H. Müller-Bunz, S. Bernhard and M. Albrecht, *Angew. Chem., Int. Ed.*, 2010, **49**, 9765; (c) T. Nakamura, T. Terashima, K. Ogata and S. Fukuzawa, *Org. Lett.*, 2011, **13**, 620; (d) J. R. Wright, P. C. Young, N. T. Lucas, A.-L. Lee and J. D. Crowley, *Organometallics*, 2013, **32**, 7065; (e) J. Huang, J.-T. Hong and S. H. Hong, *Eur. J. Org. Chem.*, 2012, 6630; (f) A. Bolje and J. Kosmrlj, *Org. Lett.*, 2013, **15**, 5084.
- S. Hohloch, W. Frey, C.-Y. Su and B. Sarkar, *Dalton Trans.*, 2013, **42**, 11355.
- (a) S. Hohloch, C.-Y. Su and B. Sarkar, *Eur. J. Inorg. Chem.*, 2011, 3067; (b) S. Hohloch, D. Scheiffele and B. Sarkar, *Eur. J. Inorg. Chem.*, 2013, 3956; (c) S. Hohloch, B. Sarkar, L. Nauton, F. Cisnetti and A. Gautier, *Tetrahedron Lett.*, 2013, **54**, 1808.
- S. Hohloch, L. Suntrup and B. Sarkar, *Organometallics*, 2013, **32**, 7376.
- (a) S. Hohloch, L. Hettmanczyk and B. Sarkar, *Eur. J. Inorg. Chem.*, 2014, 3164; (b) A. Bolje, S. Hohloch, D. Urankar, A. Pevec, M. Gazvoda, B. Sarkar and J. Kosmrlj, *Organometallics*, 2014, **33**, 2588; (c) S. Hohloch, S. Kaiser, F. L. Duecker, Al. Bolje, R. Maity, J. Kosmrlj and B. Sarkar, *Dalton Trans.*, 2015, **44**, 686.
- D. Canseco-Gonzalez, A. Gniewek, M. Szulmanowicz, H. Müller-Bunz, A. M. Trzeciak and M. Albrecht, *Chem. – Eur. J.*, 2012, **18**, 6055.
- (a) M. T. Zamora, M. J. Farguson and M. Cowie, *Organometallics*, 2012, **31**, 5384; (b) J. Cai, X. Yang, K. Arumugam, C. W. Bielawski and J. L. Sessler, *Organometallics*, 2011, **30**, 5033; (c) E. C. Keske, O. V. Zenkina, R. Wang and C. M. Crudden, *Organometallics*, 2012, **31**, 456; (d) K. J. Kilpin, U. S. D. Paul, A.-L. Lee and J. D. Crowley, *Chem. Commun.*, 2011, **47**, 328.
- M. Weiss and R. Peters, *Bimetallic Catalysis: Cooperation of Carbophilic Metal Centers, in Cooperative Catalysis – Designing Efficient Catalysts for Synthesis*, ed. R. Peters, Wiley-VCH, Weinheim, 2015.
- (a) R. Maity, S. Hohloch, M. van der Meer and B. Sarkar, *Chem. – Eur. J.*, 2014, **20**, 9952; (b) R. Maity, M. van der Meer and B. Sarkar, *Dalton Trans.*, 2015, **44**, 46; (c) R. Maity, M. van der Meer, S. Hohloch and B. Sarkar, *Organometallics*, 2015, **34**, 3090.
- K. F. Donnelly, R. Lalrempuia, H. Müller-Bunz and M. Albrecht, *Organometallics*, 2012, **31**, 8414.
- (a) R. Maity, H. Koppetz, A. Hepp and F. E. Hahn, *J. Am. Chem. Soc.*, 2013, **135**, 4966; (b) R. Maity, A. Rit, C. Schulte to Brinke, J. Kösters and F. E. Hahn, *Organometallics*, 2013, **32**, 6174; (c) R. Maity, A. Rit, C. Schulte to Brinke, C. G. Daniliuc and F. E. Hahn, *Chem. Commun.*, 2013, **49**, 1011.
- E. C. Keske, O. V. Zenkina, R. Wang and C. M. Crudden, *Organometallics*, 2012, **31**, 6215.
- For selected examples, see: (a) S. Horn and M. Albrecht, *Chem. Commun.*, 2011, **47**, 8802; (b) D. Gnanamgari, E. L. O. Sauer, N. D. Schley, C. Butler, C. D. Incarvito and R. H. Crabtree, *Organometallics*, 2009, **28**, 321; (c) N. Gürbüz, E. O. Özcan, I. Özdemir, B. Cetinkaya, O. Sahin and O. Büyükgüngör, *Dalton Trans.*, 2012, **41**, 2330; (d) A. C. Hillier, H. M. Lee, E. D. Stevens and S. P. Nolan, *Organometallics*, 2001, **20**, 4246.
- A. Bolje, S. Hohloch, M. van der Meer, J. Kosmrlj and B. Sarkar, *Chem. – Eur. J.*, 2015, **21**, 6756.
- For selected examples see: (a) D. A. Culkin and J. F. Hartwig, *Acc. Chem. Res.*, 2003, **36**, 234; (b) B. C. Hamann and J. F. Hartwig, *J. Am. Chem. Soc.*, 1997, **119**, 12382; (c) A. Verma, N. Prajapati, S. Salecha, R. Giridhar and M. R. Yadav, *Tetrahedron Lett.*, 2013, **54**, 2029.
- For selected examples see: (a) X. Luan, R. Mariz, C. Robert, M. Gatti, S. Blumentritt, A. Linden and R. Dorta, *Org. Lett.*, 2008, **24**, 5569; (b) Y.-X. Jia, D. Katayev, G. Bernardinelli, T. M. Seidel and E. P. Kündig, *Chem. – Eur. J.*, 2010, **16**, 6300; (c) X. Luan, L. Wu, E. Drinkel, R. Mariz, M. Gatti and R. Dorta, *Org. Lett.*, 2010, **12**, 1912; (d) B. Zheng, T. Jia and P. J. Walsh, *Adv. Synth. Catal.*, 2014, **356**, 165; (e) A. M. Taylor, R. A. Altman and S. L. Buchwald, *J. Am. Chem. Soc.*, 2009, **131**, 9900; (f) B. Zheng, T. Jia and P. J. Walsh, *Org. Lett.*, 2013, **15**, 4190; (g) E. Koch, R. Takise, A. Studer, J. Yamaguchi and K. Itami, *Chem. Commun.*, 2015, **51**, 855.