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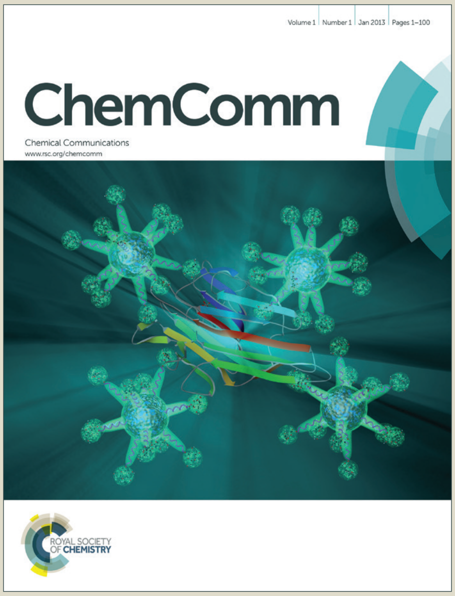

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Triply cyclometalated trinuclear iridium(III) and trinuclea palladium(II) complexes with a tri-mesoionic carbene ligand†

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Received (in XXX, XXX) Xth XXXXXXXXX 2014, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

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 catalysis is 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-ylidenes[2] or 1,2,4-triazol-5-ylidenes[3] (normal NHCs), their mesoionic counterparts 1,2,3-triazol-5-ylidenes[4] are currently gaining immense popularity. The 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 type of complexes as catalysts for various organic transformations such as Suzuki–Miyaura cross-coupling reactions,[6] "click" reactions,[7] reduction of aromatic nitro compounds[8] 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 activity[12] 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 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 K_2CO_3 and pyridine yielded the PEPPSI type complexes (Fig. 1).[13b] However, the intended synthesis of triply cyclometalated Ir^{III} complex with 1,3,5-tri substituted benzene derived tristriazolium salt was unsuccessful.[13c] We believed that steric effects might render th formation of cyclometalated complexes with this ligand system difficult. Hence, we decided to introduce additional phenyl ri on the ligand backbone to reduce steric crowding and synthesized the tris-triazolium salt **2** (Scheme 1). We present here the f triply cyclometalated trinuclear Ir^{III} complex from a 1,3,5-triphenylbenzene derived tri-MIC ligand, where the coordinat MIC moieties are further removed from each other and allow th Ir^{III} centers to undergo cyclometalation. In addition, a trinuclear PEPPSI type Pd^{II} complex has also been synthesized using th same tri-MIC ligand platform. Apart from synthetic and structural aspects, we also present catalytic results for transfe hydrogenation and C–C coupling reactions with the Ir^{III} and Pd complexes, respectively, discussing catalytic cooperativity an homogeneous versus heterogeneous catalysis.

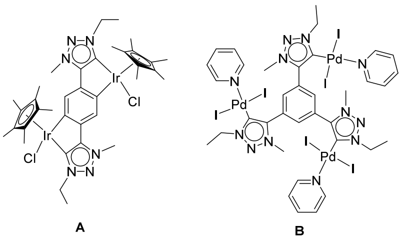

Fig. 1 Dinuclear Ir^{III} and trinuclear Pd^{II} Complexes with MIC ligands.[13]

The reaction of the tris-triazolium salt **2** with Ag_2O followe by the addition of $[Ir(Cl)_2Cp^*]_2$ in the presence of sodium acetate resulted in the formation of a triply cyclometalated trinuclear Ir complex [**3**] in 84% yield. The complex [**3**] is stable under air an moisture and well soluble in solvents like chloroform and dichloromethane. The complex [**3**] is characterized by ^{1}H $^{13}C\{^1H\}$ NMR spectroscopy and ESI mass spectrometry. The formation of complex [**3**] was easily monitored by the ^{1}H NMR spectroscopy, which shows the disappearance of the triazoliu C–H protons signal ($\delta = 9.31$ ppm) for the original tris-triazolium salt **2**. Both the ^{1}H and $^{13}C\{^1H\}$ NMR spectra of complex [**3** show more than one set of signals in solution which implies th presence of different rotational isomers of the complex in solution. The rotamers are caused due to the free rotation of th $[Ir^{III}(Cl)Cp^*(C_{MIC}\text{^}C_{Ar})]$ moieties around the C_{aryl}–C_{aryl} bonds. On

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† Electronic supplementary information (ESI) available: Preparation and spectroscopic properties of complexes [**3**] and [**4**]. Details of the crystal structure determinations for [**4**]·$2.75CH_2Cl_2$ (CCDC 1062049). See http://www.rsc.org/suppdata/xx/b0/b00000x/

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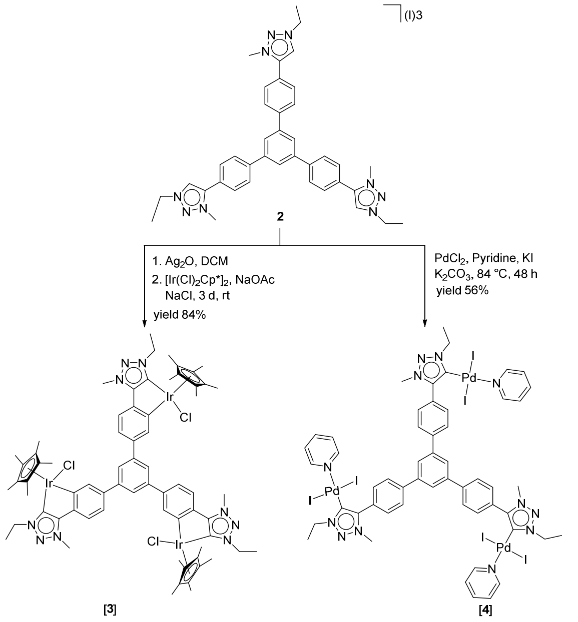
heating the sample to 90°C, the signals of the rotamers merge to a single set of signal (Fig. S11). The resonances for four chemically different aryl C–H protons appeared as four sets in the range of δ = 8.17–8.29, 7.90–8.02, 7.49–7.52, 7.27–7.43 ppm. The cyclometalation of the aryl ring was confirmed by 2D correlation NMR spectroscopy which shows a resonance (broad) at δ = 159.6 ppm, attributed to the cyclometalated aryl carbon atom. The resonance for the characteristic carbene carbon atoms was observesd at δ = 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 resonance 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 $[[\mathbf{3}]-\mathrm{Cl}]^+$ 1884.4863) and 823.7659 (calcd for $[[\mathbf{3}]-2\mathrm{Cl}]^{2+}$ 823.7583) as strongest signals, also confirming the formation of complex [**3**].



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

The treatment of the tristriazolium 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**]. The complex [**4**] is stable under air and moisture for long time and also has a good solubility in chlorinated solvents like chloroform and dichloromethane. The formation of complex [**4**] was monitored by ^{1}H NMR spectroscopy, which shows only one set of signals along with the disappearance of the triazolium C–H proton resonance (δ = 9.31 ppm) for the precursor triazolium salt **2**. The resonances for the C–H protons of pyridine rings appeared as multiplets at δ = 8.99, 7.75–7.78 and 7.33–7.36 ppm. Upon complexation the resonance for α-hydrogen atoms of the pyridine ring (δ = 8.99 ppm) appeared more downfield shifted compared to their corresponding resonance in free pyridine (δ = 8.62). The characteristic resonance for the C_{trz}–Pd carbon atoms was observed at δ = 133.1 ppm in the $^{13}C\{^1H\}$ NMR spectrum of complex [**4**]. This resonance is slightly downfield shifted from the C5–H resonance of the precursor triazolium salt **2** (δ = 129.2 ppm).

Single crystals suitable for an X-ray diffraction analysis were obtained for complex [**4**] by slow diffussion of pentane into a saturated dichloromethane solution of complex [**4**] at ambient temperature. The molecular structure analysis confirmed the formation of trinuclear palladium complex depicted in Scheme 1. The asymmetric unit contains ⅓ formula unit of the complex [**4**] and disordered dichloromethane molecules. The ⅓ unit is related to the rest ⅔ unit by a crystallographic inversion center. In complex [**4**] each palladium atom is coordinated to one 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)°. This value, like the Pd1–C1 (1.954(6) Å) and Pd1–N4 (2.096(6) Å) bond lengths, fall 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 out of 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 π···π interactions between these rings.

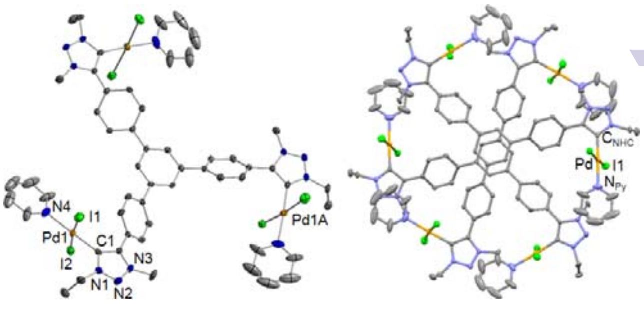


Fig. 2 ORTEP plot of [**4**]·2.75CH_2Cl_2 (left). Ellipsoids are drawn at 50 % probability. Hydrogen atoms and solvent molecules have been omitted for clarity. Intermolecular π-π stacking (right).

The 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 the 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).

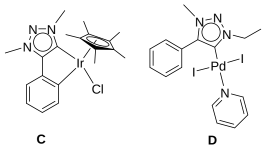
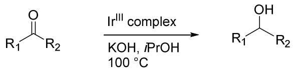


Fig. 3 Mononuclear Ir^{III} and Pd^{II} Complexes.

Table 1 Catalytic transfer hydrogenation of aldehyde and ketones.[a]



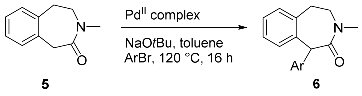
Entry	R_1	R_2	Catalyst	Conversion (%) 1 h	Conversion (%) 3 h
1	Ph	H	[**3**]	80	99
2	Ph	H	**C**	40	99
3	4-Br(Ph)	H	[**3**]	50	99
4	4-Br(Ph)	H	**C**	35	99
5	Ph	CH_3	[**3**]	40	65
6	Ph	CH_3	**C**	24	40
7	Ph	Ph	[**3**]	42	80
8	Ph	Ph	**C**	13	29
9	Ph	4-Br(Ph)	[**3**]	30	61
10	Ph	4-Br(Ph)	**C**	11	40
11	4-Me(Ph)	4-Me(Ph)	[**3**]	20	62
12	4-Me(Ph)	4-Me(Ph)	**C**	8	38

[a] Reactions 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.

Isopropanol was used as a hydrogen source for the 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% (same amount of iridium for both complexes) of the trinuclear complex. Both complexes show a full conversion of benzaldehyde 4-bromo-benzaldehyde to the corresponding benzylalcohol after 3 h. Decrease in reaction time to 1 h shows a higher conversion (80 or 50%) for the trinuclear complex compared with 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 explored as a mild catalytic method.[19] However, *α*-arylation of amides (particularly the intermolecular version) is comparatively less common and rarely explored with palladium(II) NHC complexes.[20] This is an important catalytic reaction for synthesizing valuable chemicals. The 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 the 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 NaO*t*Bu (2.5 equiv.) as a base and the reactions were performed at 120 °C for 16 h.

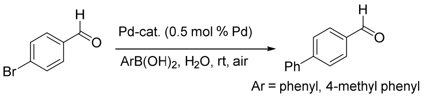
Table 2 *α*-Arylation reaction using Pd^{II} complexes.



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

On performing the reactions with 5.0 mol% of the mononuclear complex **D** or 1.67 mol% (same amount of palladium for both types of complexes) of the trinuclear complex [**4**], almost 1.5 times more conversion of **5** to **6** was achieved for the trinuclear complex (Table 2, 71%; isolated yield, see ESI) when compared with the mononuclear complex (45%; isolated yield, see ESI). The active palladium catalyst was unaffected by the addition of excess Hg(0) to the reaction mixture and leads to similar yield for the *α*-arylation product even after addition of Hg(0). This is strong indication of the homogeneous nature of the 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 that 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. This observation suggests the possibility that Pd(0) nanoparticles (NP) are the active catalyst in Suzuki–Miyaura cross-coupling reactions under the mentioned reaction conditions, as has been previously observed for related systems.[19]

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% K_2CO_3, water, rt, 5 h.

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

Summarizing, we have presented here the synthesis of a novel tris-triazolium salt **2** based on an extended phenylene platform. **2** was used to synthesize a 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 the trinuclear PEPPSI type complex [**4**] upon reaction with $PdCl_2$ in the presence of pyridine and K_2CO_3. The complex

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[**3**] is the first example of a triply cyclometalated trinuclear Ir^{III} complex containing additional carbene 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. The trinuclear PEPPSI type complex [**4**] is an active catalyst for both α-arylation of amides and the Suzuki–Miyaura cross-coupling reaction. [**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 heterogenous 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 shows the potential of Pd-MIC complexes as potent pre-catalysts for that important reaction. Furthermore, our results on 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

1 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; (c) M. Melaimi, M. Soleilhavoup and G. Bertrand, *Angew. Chem., Int. Ed.*, 2010, **49**, 8810; (*d*) C. C. Loh and D. Enders, *Chem. –Eur. J.* 2012, **18**, 10212; (*e*) J. D. Egbert, C. S. J. Cazin and S. P. Nolan, *Catal. Sci. Technol.*, 2013, **3**, 912.

2 (*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.

3 (*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.

4 (*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.

5 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.

6 S. Hohloch, W. Frey, C.-Y. Su and B. Sarkar, *Dalton Trans.*, 2013, **42**, 11355.

7 (*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.

8 (a) S. Hohloch, L. Suntrup and B. Sarkar, *Organometallics*, 2013, **32**, 7376.

9 (*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. Košmrlj, *Organometallics*, 2014, **33**, 2588; (*c*) S. Hohloch, S. Kaiser, F. L. Duecker, Al. Bolje, R. Maity, J. Košmrljb and B. Sarkar, *Dalton Trans.*, 2015, **44**, 686.

10 D. Canseco-Gonzalez, A. Gniewek, M. Szulmanowicz, H. Müller-Bunz, A. M. Trzeciak and M. Albrecht, *Chem. –Eur. J.,* 2012, **18**, 6055.

11 (*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.

12 M. Weiss and R. Peters, Bimetallic Catalysis: Cooperation o Carbophilic Metal Centers in: *Cooperative Catalysis – Designing Efficient Catalysts for Synthesis*, R. Peters (Ed.), Wiley-VCH Weinheim, 2015.

13 (*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.

14 K. F. Donnelly, R. Lalrempuia, H. Müller-Bunz and M. Albrecht, *Organometallics*, 2012, **31**, 8414.

15 (*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.

16 E. C. Keske, O. V. Zenkina, R. Wang and C. M. Crudden, *Organometallics*, 2012, **31**, 6215.

17 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, 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.

18 A. Bolje, S. Hohloch, M. van der Meer, J. Košmrlj and B. Sarkar, *Chem. −Eur. J.,* 2015, **21**, 6756.

19 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.

20 for selected examples see: (*a*) X. Luan, R. Mariz, C. Robert, M. Gatti, S. Blumentritt, A. Linden and Reto 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. Cat.* 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. Wlash, *Org. Lett* 2013, **15**, 4190; (g) E. Koch, R. Takise, A. Studer, J. Yamaguchi and K. Itami, *Chem. Commun*, 2015, **51**, 855.

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DOI: 10.1039/C5CC05506G

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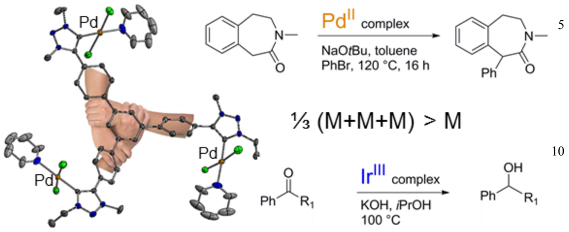

A tri-cyclometalated Ir^{III} MIC complex and a tri-Pd^{II} MIC complex are presented. The complexes show potential cooperative catalytic behavior.