Showcasing research from the Professor Janez Košmrlj's laboratory, Faculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia.

A mesoionic bis(Py-*tz*NHC) palladium(II) complex catalyses "green" Sonogashira reaction through an unprecedented mechanism

Bis-carbene palladium reactive species are likely involved in two connected palladium catalytic cycles. The system works like a waterproof Swiss watch.

As featured in:

See Janez Košmrlj *et al.*, *Chem. Commun.*, 2016, **52**, 1571.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

Registered charity number: 207890

ChemComm

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Chem. Commun.*, 2016, 52, 1571

Received 20th October 2015,
Accepted 4th November 2015

DOI: 10.1039/c5cc08717a

www.rsc.org/chemcomm

A mesoionic bis(Py-*tz*NHC) palladium(II) complex catalyses "green" Sonogashira reaction through an unprecedented mechanism†‡

Martin Gazvoda, Miha Virant, Andrej Pevec, Damijana Urankar, Aljoša Bolje, Marijan Kočevar and Janez Košmrlj*

A novel *bis*(pyridyl-functionalized 1,2,3-triazol-5-ylidene)-palladium(II) complex $[Pd(Py\text{-}tzNHC)_2]^{2+}$ catalyses the copper-, amine-, phosphine-, and additive-free aerobic Sonogashira alkynylation of (hetero)aryl bromides in water as the only reaction solvent. The catalysis proceeds along two connected Pd-cycles with homogeneous bis-carbene Pd^0 and Pd^{II} species, as demonstrated by electrospray ionization mass spectrometry.

Initiated by the report of Arduengo *et al.* in 1991 on the first isolation of N-heterocyclic carbene (NHC),[1] this class of compounds has become one of the most important ligands in transition-metal catalysis. NHCs have been introduced as ligands in palladium complexes[2–9] to support and activate palladium in various cross-coupling reactions, in particular the Heck and Suzuki reactions.[10] In this context, pyridine functionalized imidazolin-2-ylidene NHCs as chelating ligands for palladium have been developed (Fig. 1),[11–13] followed by Pd-NHCs from a PEPPSI (pyridine-enhanced precatalyst preparation, stabilization, and initiation) series with a further improved stability and activity profile.[14] The success of normal NHC ligands is greatly attributed to their superior σ-donating capabilities as compared to phosphines, which is even greater in abnormal NHC counterparts.[15,16] Interesting examples are based on the mesoionic 1,2,3-triazol-5-ylidene (*tz*NHC) structure[8] including those of the PEPPSI type reported recently.[17,18]

Appropriate balancing of the stability of the palladium species is essential in designing better catalysts. We surmised that the bis-bidentate palladium complex of chelating pyridine-functionalized *tz*NHC featuring a highly stabilizing mesoionic carbenic structure and a donor pyridine substituent should possess unique properties in terms of stability and catalytic activity (Fig. 1). We aimed at developing a palladium catalyst for Sonogashira cross-coupling that would enable copper- and amine-free alkynylation of aryl halogenides that operate in water, in the presence of air, and in the absence of any additive. The Sonogashira reaction[19] has witnessed a tremendous success in both academia and industry, being used as the key step in the synthesis of many natural products, bio-active compounds and pharmaceuticals.[20–22] It should be noted, however, that protocols allowing the presence of air and employing water as the only reaction solvent are scarce[23] and no such example is reported for Pd-NHCs as catalysts.[10,15,16,23,24] Herein, we report a highly efficient novel palladium bis(Py-*tz*NHC) complex (Fig. 1) that catalyses Sonogashira reaction under green reaction conditions, operating through an unprecedented mechanism.

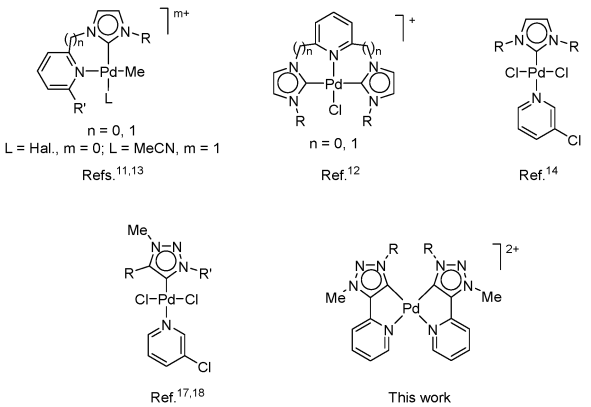


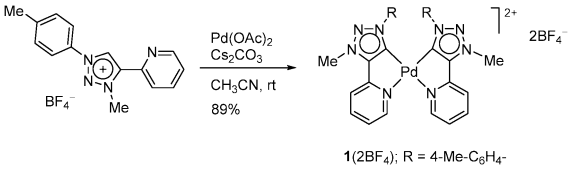
Fig. 1 Selection of pyridine-NHC–Pd complexes.

Cationic complex **1**$(2BF_4)$ was easily prepared in air by a one-step route through direct metalation of the appropriate triazolium cation[25] with $Pd(OAc)_2$ in the presence of a weak base, without requiring preactivation with Ag_2O (Scheme 1). A water soluble air-stable product was isolated in pure form in 89% yield by a simple workup. The carbene signal in the ^{13}C NMR spectrum of **1** appears at 143.6 ppm, which is indicative of a *tz*NHC-Pd-complex having pyridine and carbene in the *trans* position.[26] In the ^1H NMR spectra a small up-field shift of the $Py^{H\text{-}6}$ resonance upon

Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna pot 113, SI-1000 Ljubljana, Slovenia. E-mail: janez.kosmrlj@fkkt.uni-lj.si

† Dedicated to Dr Maja Osmak on the occasion of her 65th birthday.

‡ Electronic supplementary information (ESI) available: Experimental procedures, spectra, crystallographic details, and CIF files. CCDC 1405057 and 1430207. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc08717a



1(2BF$_4$); R = 4-Me-C$_6$H$_4$-

Scheme 1 The synthesis of complex **1**(2BF$_4$).

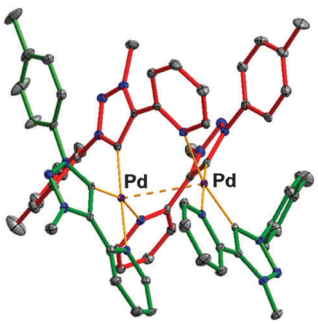


Fig. 2 Ortep drawing (30% probability ellipsoids) of cation **1′** (blue = N, gray = C, and violet = Pd) with bidentate (green) and bridging coordination (red). Anions, solvents and hydrogen atoms are omitted for clarity (ESI‡).

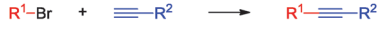
formation of **1** from the triazolium cation ($\Delta\delta \approx 0.1$ ppm; DMSO-d_6, DMF-d_7, CD_3CN) suggested weak interactions between the two pyridine wingtips and palladium, which are essential to stabilize the complex, yet to provide an open coordination site for catalysis to occur (ESI‡). Interestingly, in the solid state, complex **1**(2BF$_4$) forms a bi-metallic structure **1′** with a short Pd–Pd intermetallic distance of 3.0232(4) Å (Fig. 2). Upon dissolution **1′** instantly transforms into **1** as evident from ^{1}H NMR and ESI-HRMS analyses.

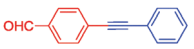
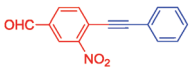
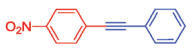
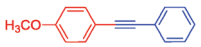
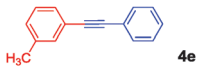
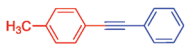
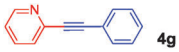
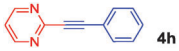
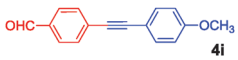
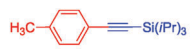
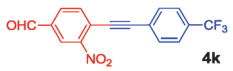
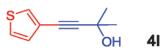
Complex **1**(2BF$_4$) was evaluated as a precatalyst for the Sonogashira reaction. An initial screening revealed that it effectively cross-coupled acetylenes with aryl iodides and bromides in the presence of air and in water as the only solvent (ESI‡).

To identify the optimal reaction conditions for Sonogashira cross-coupling with **1**(2BF$_4$), the effect of the catalyst loading, reaction temperature and base was screened (ESI‡). Excellent results were obtained with 1 mol% of **1**(2BF$_4$) at 100–140 °C for 1–4 h, with carbonate (K_2CO_3 or Cs_2CO_3) base.

The results of the substrate scope screening are shown in Table 1. In general, 1 mol% of **1**(2BF$_4$) effectively catalysed the alkynylation of electron-poor and electron-rich aryl bromides. For coupling of those substrates that are sparingly soluble in hot water, *i.e.* 4-bromonitrobenzene (**2c**), the addition of DMF to the reaction mixture proved to be beneficial. Although the highly deactivated 4-methoxybromobenzene (**2d**) was coupled with **3a** in only 36%, *m*- and *p*-bromotoluene **2e** and **2f** reacted quantitatively. Both electron-rich and electron-poor heterocyclic substrates including 2-bromopyridine (**2g**), 2-bromopyrimidine (**2h**) and 3-bromothiophene (**2i**) reacted with acetylenes in good to excellent yields. The general applicability of **1**(2BF$_4$) was also confirmed through the selection of electron-rich and deficient acetylenes as coupling partners including 4-ethynylanisole (**3b**), (triisopropylsilyl)acetylene (**3c**), 4-ethynyl-α,α,α-trifluorotoluene (**3d**) and dimethyl ethynyl carbinol (**3e**), reacting smoothly with

Table 1 Substrate scope screening for the Sonogashira reaction with **1**(2BF$_4$)



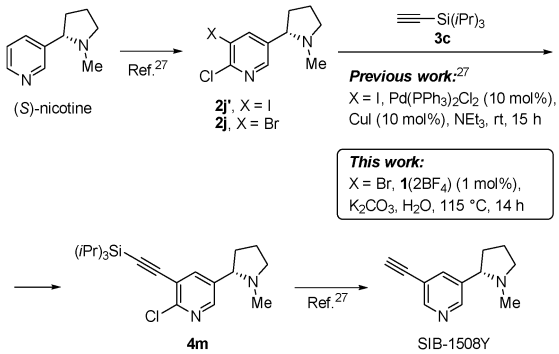
Entry	2	3	Cond.[a]	4	Conv.[b] (Yield)[c]
1	**2a**	**3a**	A[d]	 **4a**	100
2			B		82 (75)
3	**2b**	**3a**	A	 **4b**	100
4			B		100 (92)
5	**2c**	**3a**	B	 **4c**	68 (65)
6			A[d]		100 (91)
7	**2d**	**3a**	B[d]	 **4d**	36
8	**2e**	**3a**	B	 **4e**	100 (95)
9	**2f**	**3a**	A	 **4f**	60 (58)
10			A[d]		100 (86)
11	**2g**	**3a**	B	 **4g**	100 (97)
12	**2h**	**3a**	B	 **4h**	66
13	**2a**	**3b**	B	 **4i**	100 (91)
14	**2f**	**3c**	B	 **4j**	100 (95)
15	**2b**	**3d**	B	 **4k**	100 (89)
16	**2i**	**3e**	A	 **4l**	90 (87)

[a] Conditions A: bromide **2** (0.25 mmol), acetylene **3** (0.5 mmol), Cs_2CO_3 (0.5 mmol), complex **1**(2BF$_4$) (0.0025 mmol, 1.0 mol%), water (2 mL), 100 °C in an ACE tube, 1 h. Conditions B: as for conditions A but with K_2CO_3 (0.5 mmol) as a base, at 140 °C for 4 h. [b] Conversion determined from at least two consecutive runs by ^{1}H NMR. [c] Percent yield of the isolated pure product. [d] DMF/H_2O (2/1) as the reaction solvent.

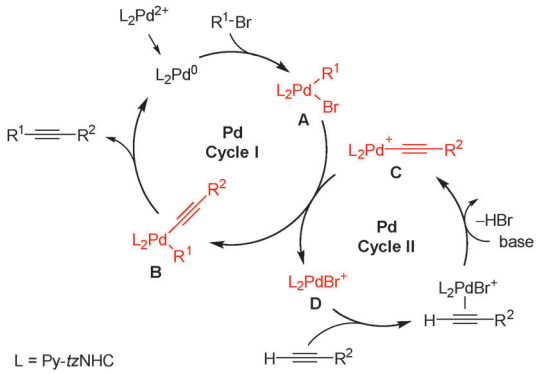
excellent yields of **4**(**i**–**l**). These results clearly demonstrate the robustness and general superior catalytic activity of **1**(2BF$_4$) over the monodentate *tz*NHC palladium complexes.[16]

To get a feel of the potency of the catalyst under typical Sonogashira reaction conditions that are normally applied, we selected the alkynylation of **2a** with **3a** at 100 °C in DMF and in the presence of DABCO as a base.[21] By using **1**(2BF$_4$) in 0.1 mol% loading the formation of **4a** was quantitative within 1 h. With 0.01 mol%, the transformation was 98% in 8 h (ESI‡).

We have been interested in the synthesis of SIB-1508Y (Altinicline), a potential drug for neurodegenerative diseases.[22] An expedient five-step preparation of SIB-1508Y with selective halogenation of natural (*S*)-nicotine to iodide **2j′** and a subsequent "classical" Sonogashira reaction with **3c** to the intermediate product **4m** has been reported (Scheme 2).[27] To demonstrate the robustness of **1**(2BF$_4$) and render it practicable, we tested it under green reaction conditions for the synthesis of **4m** from bromide **2j**, instead of iodide **2j′**. Bromide **2j** was let to react with **3c** in the presence of 1 mol% of **1**(2BF$_4$) to afford **4m** in 82% yield in optically pure form, without racemization (Scheme 2).



Scheme 2 Synthesis of SIB-1508Y involving the Sonogashira reaction.



Scheme 3 Proposed mechanism and reactive intermediates drawn in red colour as identified by ESI-HRMS.

It is known that some Pd-*tz*NHCs used in the cross-coupling reactions give under very mild conditions palladium nanoparticles as the catalytically active phase.[17] In an independent representative experiment by using **1**($2BF_4$) for the cross-coupling of **2a** with **3a** under the conditions B from Table 1 (vigorous stirring) a large excess of Hg(0) was added (mercury poisoning experiment)[17,28,29] into the reaction mixture after 30 min (36% conversion). This addition had no effect on the conversion into **4a**, reaching 76% after 4 h; a parallel Hg-free reaction reached 75% over the same period (qNMR assay). A similar observation was made when Hg(0) was added to the reaction mixture at the onset (ESI‡). The thermal stability of complex **1**($2BF_4$) was ascertained in the solid state at 150 °C and in solution (DMF-d_7, D_2O) at 140 °C (the highest reaction temperatures used herein for the Sonogashira reaction). No decomposition could be detected by qNMR (ESI‡) indicating its remarkable stability over some related PEPPSI-type Pd-*tz*NHC complexes.[17] These results suggest that the catalysis with **1**($2BF_4$) occurs by *in situ* generated homogeneous catalytically active molecular Pd^0 species.

To get an insight into the mechanism of this process, the coupling of **2a** with **3a** in the presence of Cs_2CO_3 in DMF was monitored by high-resolution electrospray ionization mass spectrometry (ESI-HRMS).[29,30] All peaks from the mass spectra have been identified. As evident from the characteristic isotopic pattern, only mono-palladium bis-carbene cationic species could be found in the spectra. These include ions at *m*/*z* 711.1849 (calcd for $C_{37}H_{33}N_8OPd^+$ ([**A** − Br]$^+$): 711.1807), *m*/*z* 813.2299 (calcd for $C_{45}H_{39}N_8OPd^+$ ([**B** + H]$^+$): 813.2276), *m*/*z* 707.1856 (calcd for $C_{38}H_{33}N_8Pd^+$ ([**C**]$^+$): 707.1858) and *m*/*z* 685.0642 (calcd for $C_{30}H_{28}{}^{79}BrN_8Pd^+$ ([**D**]$^+$): 685.0650) (Scheme 3). Peaks for **C** and **D** were the most intensive in the ESI-MS spectra. In contrast to some Pd–NHC complexes,[17,29] neither clusters of the type [Pd_n(Py-*tz*NHC)$_{2m}$] ($n > m$), nor mono-carbene-Pd species, or negatively charged Pd containing ions (ESI−) could be found in the spectra.

The proposed plausible mechanism is shown in Scheme 3 and contains two connected Pd-cycles (**I** and **II**). Much research work has been devoted to address the question whether mono-ligated Pd^0(NHC) or bis-ligated $Pd^0(NHC)_2$ is involved in the catalytic cycle.[31–33] In our case, the fact that no mono-carbene Pd(Py-*tz*NHC) species could be found in the ESI-HRMS spectra suggest Pd^0(Py-*tz*NHC)$_2$ to be the catalytically active species. The latter undergoes oxidative addition with aryl bromide to form intermediate **A** *via* an associative mechanism without dissociation of the Py-*tz*NHC ligand.

The Pd^0(Py-*tz*NHC)$_2$ species may be generated by reductive elimination (alkyne homocoupling) from [Pd^{II}(Py-*tz*NHC)$_2$(C≡CR^2)$_2$].[34] The species [Pd^{II}(Py-*tz*NHC)$_2$(C≡CR^2)$_2$] was identified by ESI-HRMS as the [M + H]$^+$ ion (*m*/*z* 809.2318, calcd for $C_{46}H_{39}N_8Pd^+$ 809.2327, ESI‡).

The acetylene η^2-coordination to the bromido-Pd species **D** and a subsequent base mediated deprotonation produce the alkynylpalladium intermediate **C**, which then undergoes transmetalation with **A** to form intermediate **B**. This was confirmed by an independent ESI-HRMS experiment, where premixing either **1**($2BF_4$) or **D**, acetylene **3a** and Cs_2CO_3 in DMF at 100 °C resulted in the accumulation of **C**. Intermediate **C** completely disappeared from the spectra after the addition of an excess of aryl bromide **2a** with the concomitant product **4a** formation (ESI‡).

Cation **D** can be formed independently by reacting **1**($2BF_4$) with KBr. Although we were unable to support the structure of **D** by single crystal X-ray analysis, this was possible for the closely related cation **5**, formed by treating **1**($2BF_4$) with potassium acetate (Fig. 3) (ESI‡).

In conclusion, a novel type of water soluble and thermally stable Pd-NHC complex **1**($2BF_4$) based on a bidentate pyridyl-1,2,3-triazol-5-ylidene ligand that requires only low synthetic investment has been identified as a highly efficient precatalyst for Sonogashira cross-coupling. We know of no such efficient aryl bromide–terminal acetylene cross-coupling that proceeds

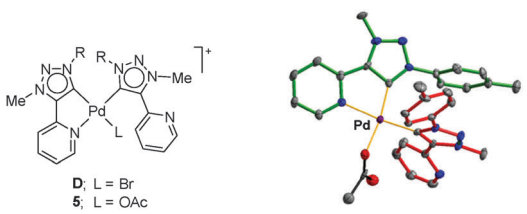


Fig. 3 Structures of **D** and **5** (R = 4-Me-C_6H_4–), and Ortep drawing of **5** (ESI‡).

in air and in pure water, and in the complete absence of amine, copper, phosphine and other additives, as reported herein for complex **1**($2BF_4$). To our knowledge, this is the first report on the Sonogashira catalysis with a cationic Pd-complex. Preliminary mechanistic investigation indicates that bis-carbene palladium reactive species are involved in two connected palladium catalytic cycles.

Financial support from the Ministry of Education, Science and Sport, Republic of Slovenia, the Slovenian Research Agency (Grant P1-0230; Postdoctoral Grant to M.G. (430-168/2013/114), and Grant P1-0175) is acknowledged. This work was partially supported through the infrastructure of the EN-FIST Centre of Excellence, Ljubljana, Slovenia.

Notes and references

1 A. J. Arduengo, R. L. Harlow and M. J. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 361.
2 W. A. Herrmann, M. Elison, J. Fischer, C. Köcher and G. R. J. Artus, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2371.
3 R. Jackstell, M. G. Andreu, A. Frisch, K. Selvakumar, A. Zapf, H. Klein, A. Spannenberg, D. Röttger, O. Briel, R. Karch and M. Beller, *Angew. Chem., Int. Ed.*, 2002, **41**, 986.
4 L. R. Titcomb, S. Caddick, F. G. N. Cloke, D. J. Wilson and D. McKerrecher, *Chem. Commun.*, 2001, 1388.
5 M. S. Viciu, R. F. Germaneau, O. Navarro-Fernandez, E. D. Stevens and S. P. Nolan, *Organometallics*, 2002, **21**, 5470.
6 V. César, S. Bellemin-Laponnaz and L. H. Gade, *Organometallics*, 2002, **21**, 5204.
7 D. R. Jensen, M. J. Schultz, J. A. Mueller and M. S. Sigman, *Angew. Chem., Int. Ed.*, 2003, **42**, 3810.
8 P. Mathew, A. Neels and M. Albrecht, *J. Am. Chem. Soc.*, 2008, **130**, 13534.
9 (*a*) T. Karthikeyan and S. Sankararaman, *Tetrahedron Lett.*, 2009, **50**, 5834; (*b*) T. Nakamura, K. Ogata and S. Fukuzawa, *Chem. Lett.*, 2010, **39**, 920; (*c*) S. Hohloch, W. Frey, C.-Y. Suc and B. Sarkar, *Dalton Trans.*, 2013, **42**, 11355; (*d*) M. Górna, M. S. Szulmanowicz, A. Gniewek, W. Tylus and A. M. Trzeciak, *J. Organomet. Chem.*, 2015, **785**, 92.
10 Selected reviews on N-heterocyclic carbenes: (*a*) J. C. Garrison and W. J. Youngs, *Chem. Rev.*, 2005, **105**, 3978; (*b*) N. Marion, S. Díez-González and S. P. Nolan, *Angew. Chem., Int. Ed.*, 2007, **46**, 2988; (*c*) F. A. Glorius, *Top. Organomet. Chem.*, 2007, **21**, 1; (*d*) E. A. B. Kantchev, C. J. O'Brien and M. G. Organ, *Angew. Chem., Int. Ed.*, 2007, **46**, 2768; (*e*) O. Kühl, *Coord. Chem. Rev.*, 2009, **253**, 2481; (*f*) M. C. Jahnke and F. E. Hahn, *Top. Organomet. Chem.*, 2010, **30**, 95; (*g*) S. Budagumpi, R. A. Haque and A. W. Salman, *Coord. Chem. Rev.*, 2012, **256**, 1787; (*h*) M. Fèvre, J. Pinaud, Y. Gnanou, J. Vignolle and D. Taton, *Chem. Soc. Rev.*, 2013, **42**, 2142; (*i*) *N-Heterocyclic Carbenes. Effective Tools for Organometallic Synthesis*, ed. S. P. Nolan, Wiley-VCH, Weinheim, 2014; (*j*) T. A. Schaub and M. Kivala, in *Metal-Catalyzed Cross-Coupling Reactions and More*, ed. A. de Meijere, S. Bräse and M. Oestreich, Wiley-VCH, Weinheim, 2014, pp. 665–762; (*k*) D. M. Flanigan, F. Romanov-Michailidis, N. A. White and T. Rovis, *Chem. Rev.*, 2015, **115**, 9307.
11 (*a*) A. A. D. Tulloch, A. A. Danopoulos, R. P. Tooze, S. M. Cafferkey, S. Kleinhenz and M. B. Hursthouse, *Chem. Commun.*, 2000, 1247–1248; (*b*) D. S. McGuinness and K. J. Cavell, *Organometallics*, 2000, **19**, 741.
12 A. A. D. Tulloch, A. A. Danopoulos, G. J. Tizzard, S. J. Coles, M. B. Hursthouse, R. S. Hay-Motherwell and W. B. Motherwell, *Chem. Commun.*, 2001, 1270.
13 V. Khlebnikov, A. Meduri, H. Mueller-Bunz, T. Montini, P. Fornasiero, E. Zangrando, B. Milani and M. Albrecht, *Organometallics*, 2012, **31**, 976.
14 C. J. O'Brien, E. A. B. Kantchev, C. Valente, N. Hadei, G. A. Chass, A. Lough, A. Hopkinson and M. G. Organ, *Chem. – Eur. J.*, 2006, **12**, 4743.
15 Selected reviews on *tz*NHCs: (*a*) O. Schuster, L. Yang, H. G. Raubenheimer and M. Albrecht, *Chem. Rev.*, 2009, **109**, 3445; (*b*) J. D. Crowley, A. Lee and K. J. Kilpin, *Aust. J. Chem.*, 2011, **64**, 1118; (*c*) D. J. Nelson and S. P. Nolan, *Chem. Soc. Rev.*, 2013, **42**, 6723; (*d*) R. H. Crabtree, *Coord. Chem. Rev.*, 2013, **257**, 755; (*e*) B. Schulze and U. S. Schubert, *Chem. Soc. Rev.*, 2014, **43**, 2522.
16 (*a*) W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290; (*b*) M. Melaimi, M. Soleilhavoup and G. Bertrand, *Angew. Chem., Int. Ed.*, 2010, **49**, 8810; (*c*) X.-F. Wu, H. Neumann and M. Beller, *Chem. Soc. Rev.*, 2011, **40**, 4986; (*d*) S. Inomata, H. Hiroki, T. Terashima, K. Ogata and S. Fukuzawa, *Tetrahedron*, 2011, **67**, 7263; (*e*) K. F. Donnelly, A. Petronilho and M. Albrecht, *Chem. Commun.*, 2013, **49**, 1145.
17 D. Canseco-Gonzalez, A. Gniewek, M. Szulmanowicz, H. Müller-Bunz, A. M. Trzeciak and M. Albrecht, *Chem. – Eur. J.*, 2012, **18**, 6055.
18 J. Huang, J.-T. Hong and S. H. Hong, *Eur. J. Org. Chem.*, 2012, 6630.
19 (*a*) K. Sonogashira, Y. Tohda and N. Hagihara, *Tetrahedron Lett.*, 1975, **16**, 4467; (*b*) K. Sonogashira, in *Metal Catalyzed Cross-Coupling Reactions*, ed. F. Diederich and P. J. Stang, Wiley-VCH, Weinheim, 1998, pp. 203–229; (*c*) H. Doucet and J.-C. Hierso, *Angew. Chem., Int. Ed.*, 2007, **46**, 834; (*d*) M. Lamblin, L. Nassar-Hardy, J.-C. Hierso, E. Fouquet and F.-X. Felpin, *Adv. Synth. Catal.*, 2010, **352**, 33; (*e*) M. Bakherad, *Appl. Organomet. Chem.*, 2013, **27**, 125; (*f*) A. M. Thomas, A. Sujatha and G. Anilkumar, *RSC Adv.*, 2014, **4**, 21688; (*g*) R. A. D. Arancon, C. S. K. Lin, C. Vargas and R. Luque, *Org. Biomol. Chem.*, 2014, **12**, 10.
20 D. Wang and S. Gao, *Org. Chem. Front.*, 2014, **1**, 556.
21 R. Chinchilla and C. Nájera, *Chem. Rev.*, 2007, **107**, 874.
22 (*a*) A. O. King and N. Yasuda, *Top. Organomet. Chem.*, 2004, **6**, 205; (*b*) C. Torborg and M. Beller, *Adv. Synth. Catal.*, 2009, **351**, 3027.
23 (*a*) H. D. Velazquez and F. Verpoort, *Chem. Soc. Rev.*, 2012, **41**, 7032; (*b*) *Metal-Catalyzed Reactions in Water*, ed. P. Dixneuf and V. Cadierno, Wiley-VCH, Weinheim, 2013; (*c*) E. Levin, E. Ivry, C. E. Diesendruck and N. G. Lemcoff, *Chem. Rev.*, 2015, **115**, 4607.
24 (*a*) L. Yang, P. Guan, P. He, Q. Chen, C. Cao, Y. Peng, Z. Shi, G. Pang and Y. Shi, *Dalton Trans.*, 2012, **41**, 5020; (*b*) A. Kumar and P. Ghosh, *Eur. J. Inorg. Chem.*, 2012, 3955 and references therein; (*c*) C. W. D. Gallop, M.-T. Chen and O. Navarro, *Org. Lett.*, 2014, **16**, 3724.
25 A. Bolje and J. Košmrlj, *Org. Lett.*, 2013, **15**, 5084.
26 E. C. Keske, O. V. Zenkina, R. Wang and C. M. Crudden, *Organometallics*, 2012, **31**, 6215.
27 F. F. Wagner and D. L. Comins, *J. Org. Chem.*, 2006, **71**, 8673.
28 R. H. Crabtree, *Chem. Rev.*, 2012, **112**, 1536.
29 M. S. Szulmanowicz, A. Gniewek, W. Gil and A. M. Trzeciak, *ChemCatChem*, 2013, **5**, 1152.
30 (*a*) D. Schröder, *Acc. Chem. Res.*, 2012, **45**, 1521; (*b*) K. L. Vikse, Z. Ahmadi and J. S. McIndoe, *Coord. Chem. Rev.*, 2014, **279**, 96.
31 J. Pytkowicz, S. Roland, P. Mangeney, G. Meyer and A. Jutand, *J. Organomet. Chem.*, 2003, **678**, 166.
32 A. K. K. Lewis, S. Caddick, F. G. N. Cloke, N. C. Billingham, P. B. Hitchcock and J. Leonard, *J. Am. Chem. Soc.*, 2003, **125**, 10066.
33 (*a*) U. Christmann and R. Vilar, *Angew. Chem., Int. Ed.*, 2005, **44**, 366; (*b*) A. Jutand, *Chem. Rev.*, 2008, **108**, 2300; (*c*) A. Jutand, J. Pytkowicz, S. Roland and P. Mangeney, *Pure Appl. Chem.*, 2010, **82**, 1393.
34 G. P. McGlacken and I. J. S. Fairlamb, *Eur. J. Org. Chem.*, 2009, 4011.

