Dalton Transactions

Cite this: *Dalton Trans.*, 2012, **41**, 5377

www.rsc.org/dalton

PAPER

Phosphino imidazoles and imidazolium salts for Suzuki C–C coupling reactions†

Bianca Milde, Dieter Schaarschmidt, Tobias Rüffer and Heinrich Lang*

Received 2nd December 2011, Accepted 27th February 2012
DOI: 10.1039/c2dt12322c

The consecutive syntheses of imidazoles 1-(4-X-C_6H_4)-4,5-R_2-$^cC_3HN_2$ (**3a**, X = Br, R = H; **3b**, X = I, R = Me; **3c**, X = H, R = Me; **5**, X = Fc, R = H; **7**, X = C≡CFc, R = H; **9**, X = C_6H_5, R = Me; Fc = Fe(η^5-C_5H_4)(η^5-C_5H_5)), phosphino imidazoles 1-(4-X-C_6H_4)-2-PR'_2-4,5-R_2-$^cC_3N_2$ (**11a–k**; X = Br, I, Fc, FcC≡C, Ph; R = H, Me; R′ = Ph, $^cC_6H_{11}$, $^cC_4H_3O$), imidazolium salts [1-(4-X-C_6H_4)-3-R″-4,5-R_2-$^cC_3HN_2$]I (**16a**; X = Br, R = H, R″ = n-Bu; **16b**, X = Br, R = H, R″ = n-C_8H_{17}; **16c**, X = I, R = Me, R″ = n-C_8H_{17}, **16d**, X = H, R = Me, R″ = n-C_8H_{17}) and phosphino imidazolium salts [1-C_6H_5-2-PR'_2-3-n-C_8H_{17}-4,5-Me_2-$^cC_3N_2$]PF_6 (**17a**, R′ = C_6H_5; **17b**, R′ = $^cC_6H_{11}$) or [1-(4-P(C_6H_5)$_2$-C_6H_4)-3-n-C_8H_{17}-4,5-Me_2-$^cC_3HN_2$]PF_6, (**20**) and their selenium derivatives 1-(4-X-C_6H_4)-2-P(=Se)R'_2-4,5-R_2-$^cC_3N_2$ (**11a-Se–f-Se**; X = Br, I; R = H, Me; R′ = C_6H_5, $^cC_6H_{11}$, $^cC_4H_3O$) are reported. The structures of **11a-Se** and [(1-(4-Br-C_6H_4)-$^cC_3H_2N_2$-3-n-Bu)$_2$$PdI_2$] (**19**) in the solid state were determined. Cyclovoltammetric measurements were performed with the ferrocenyl-containing molecules **5** and **7** showing reversible redox events at E^0 = 0.108 V (ΔE_p = 0.114 V) (**5**) and E^0 = 0.183 V (ΔE_p = 0.102 V) (**7**) indicating that **7** is more difficult to oxidise. Imidazole oxidation does not occur up to 1.3 V in dichloromethane using [(n-Bu)$_4$N][B(C_6F_5)$_4$] as supporting electrolyte, whereas an irreversible reduction is observed between −1.2–−1.5 V. The phosphino imidazoles **11a–k** and the imidazolium salts **17a,b** and **20**, respectively, were applied in the Suzuki C–C cross-coupling of 2-bromo toluene with phenylboronic acid applying [$Pd(OAc)_2$] as palladium source. Depending on the electronic character of **11a–k**, **17a,b** and **20** the catalytic performance of the *in situ* generated catalytic active species can be predicted. As assumed, more electron-rich phosphines with their higher donor capability show higher activity and productivity. Additionally, **11e** was applied in the coupling of 4-chloro toluene with phenylboronic acid showing an excellent catalytic performance when compared to catalysts used by Fu, Beller and Buchwald. Furthermore, **11e** is eligible for the synthesis of sterically hindered biaryls under mild reaction conditions. C–C Coupling reactions with the phosphino imidazolium salts **17b** and **20** in ionic liquids [BMIM][PF_6] and [BDMIM][BF_4] were performed, showing less activity than in common organic solvents.

Introduction

Imidazole- and imidazolium-functionalised phosphines represent an interesting family of molecules because they can act as ambivalent *P,N* donors which allow the coordination of either hard or soft transition metals.[1] These species can be applied, for example, as model systems imitating the catalytically active site in bio-inorganic molecules.[1c,2] In addition, they can be used as easily tuneable ligands with good performance in palladium-catalysed C–C coupling reactions.[1a,d,3] Imidazolium phosphines contain structural elements of an ionic liquid and have been obtained by selective *N*-protonation or *N*-alkylation of the appropriate neutral molecules. Their application in 2-phase catalytic reactions is advantageous since they allow facile recycling and easy separation of the catalyst from the products.[1b,d,e,3a,c,4,6] During the last years, this field of chemistry developed rapidly, however, only little is known about aryl-substituted imidazoles[2b,d,3b,e,5a,e] and imidazolium salts,[3a,d,5] which is attributed to their elaborate multistep preparation procedures. Compared to classical monodentate ligands such as phosphines, phosphino imidazoles and imidazolium salts are advantageous due to their flexible coordination behavior and their ability to reduce metal leaching in homogeneous multiphase catalysis.[1e,6] Recently, it was reported that, for example, dialkylphosphino imidazoles can

Chemnitz University of Technology, Faculty of Science, Institute of Chemistry, Department of Inorganic Chemistry, Straße der Nationen 6209111 Chemnitz, Germany. E-mail: heinrich.lang@chemie.tu-chemnitz.de; Fax: +49 (0)371-531-21210; Tel: +49 (0)371-531-21210

†Electronic supplementary information (ESI) available: Details of the synthesis and experimental data of **11a–k**, **11a-Se–f-Se** and **16a–d** are given in ESI-Experimental section. Reaction profiles for the Suzuki cross-couplings in the presence of phosphines **11**, **17**, **20** and [$Pd(OAc)_2$] are given in ESI-General. In the file ESI–X-ray the restraints used for the refinement of *cis*-**19** are given, together with an indication why they were needed. CCDC **11a-Se** (848041), *trans*-**19** (848043) and *cis*-**19** (848042). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt12322c

be used in the Sonogashira[3e] and Suzuki[3b] C–C as well as Buchwald–Hartwig[3b] C–N coupling.

This prompted us to develop straightforward consecutive synthesis methodologies for the preparation of organic- and organometallic-functionalised aryl phosphino imidazoles which were converted into the appropriate imidazolium salts to study the electronic influence of the *N*-heterocyclic component on the phosphino group. The use of appropriate phosphines in carbon–carbon cross-couplings is reported both in organic solvents and ionic liquids.

Results and discussion

Synthesis

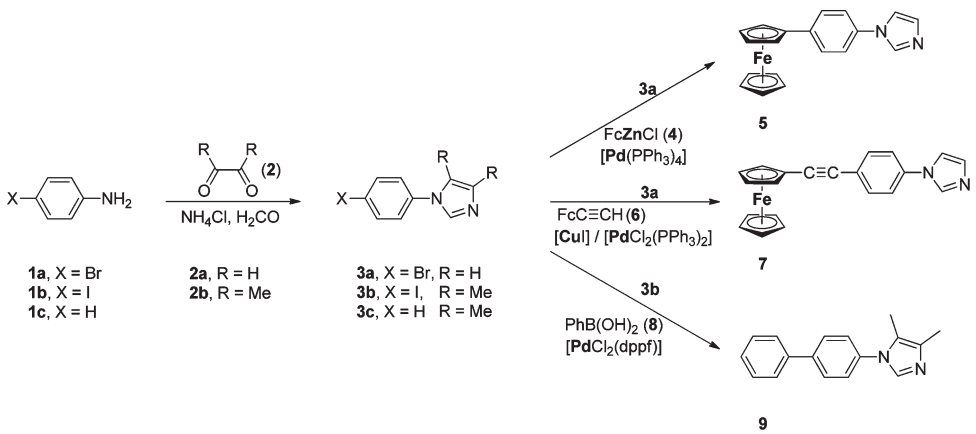
As a starting molecule 1-(4-X-C_6H_4)-4,5-R_2-^{c}C_3HN_2 (**3a**, X = Br, R = H; **3b**, X = I, R = Me, **3c**,[19] X = H, R = Me) was chosen which was synthesised by a modified reaction protocol as described by Zhang and co-workers[2d] (Scheme 1). These species can be further functionalised by applying C–C cross-couplings including the palladium-promoted Negishi, Sonogashira and Suzuki reactions. Compound 1-(4-Fc-C_6H_4)-^{c}$C_3H_3N_2$ (**5**) (Fc = Fe(η^5-C_5H_4)(η^5-C_5H_5)) was accessible by Negishi ferrocenylation of the appropriate bromo-substituted imidazole **3a** with FcZnCl (**4**), available by mono-lithiation of ferrocene according to Mueller-Westerhoff[7] followed by treatment with dry [$ZnCl_2$(thf)$_2$], in presence of catalytic amounts of [Pd(PPh_3)$_4$] (Scheme 1). Imidazole 1-(4-FcC≡C-C_6H_4)-^{c}$C_3H_3N_2$ (**7**) was obtained by the reaction of **3a** with ethynyl ferrocene (**6**) in presence of catalytic amounts of [CuI] and [$PdCl_2$(PPh_3)$_2$] in NEt_3 under Sonogashira cross-coupling conditions. Suzuki C–C coupling of **3b** with phenylboronic acid, potassium carbonate as base and [Pd(dppf)Cl_2] (dppf = 1,1′-bis(diphenylphosphino) ferrocene) as catalyst afforded 1-(4-C_6H_5–C_6H_4)-4,5-Me_2-^{c}C_3HN_2 (**9**) (Scheme 1, Experimental section).

Imidazoles **3**, **5**, **7** and **9** could be converted to the appropriate phosphino imidazoles 1-(4-X-C_6H_4)-2-PR′$_2$-4,5-R_2-^{c}C_3N_2 (**11a–k**; X = Br; I, Fc, FcC≡C, Ph; R = H, Me; R′ = C_6H_5, ^{c}C_6H_{11}, ^{c}C_4H_3O) (Scheme 2, Table 1) by the consecutive reaction of either lithium di-i-propylamide or n-butyl lithium followed by addition of phosphines PR′$_2$Cl (**10**) in tetrahydrofuran (LDA) or diethyl ether solutions (n-BuLi). The reaction of **11a–k** with alkyl iodides R″I (R″ = n-Bu, n-C_8H_{17}) did result in the formation of a mixture of compounds **13–15**, from which desired **13** could not be isolated in pure form, neither by chromatography nor crystallisation (Scheme 2, Experimental section).

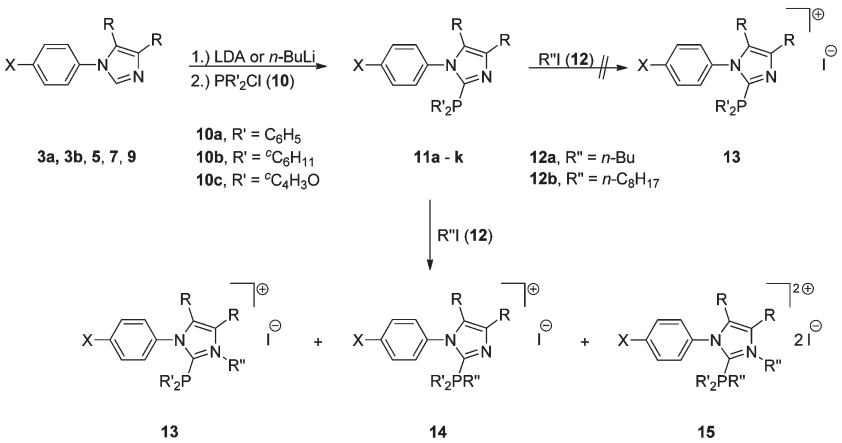
Since no separation of molecules **13–15** from each other was possible, another synthesis procedure had to be developed. The crucial step was the quaternisation of **3a** and **3b** with **12** yielding the imidazolium salts [1-(4-X-C_6H_4)-3-R″-4,5-R_2-^{c}C_3HN_2]I (**16a**; X = Br, R = H, R″ = n-Bu; **16b**, X = Br, R = H, R″ = n-C_8H_{17}; **16c**, X = I, R = Me, R″ = n-C_8H_{17}; **16d**, X = H, R = Me, R″ = n-C_8H_{17}) (Scheme 3). Decreasing the melting point of the imidazolium salts by longer alkyl chains,[6d] results in the formation of ionic liquids. For this reason, we chose **16c** as a starting compound for the synthesis of ionic phosphines. Therefore, **16c** was deprotonated with n-BuLi followed by the reaction of **16c·Li** with PR′$_2$Cl to give after anion exchange with K[PF_6] a mixture of [1-(4-I-C_6H_4)-2-PR′$_2$-3-R″-4,5-Me_2-^{c}C_3N_2]PF_6 (**13a**: R′ = C_6H_5, R″ = n-C_8H_{17}; **13b**: R′ = ^{c}C_6H_{11}, R″ = n-C_8H_{17}) and [1-(C_6H_5)-2-PR′$_2$-3-R″-4,5-Me_2-^{c}C_3N_2]PF_6 (**17a**: R′ = C_6H_5, R″ = n-C_8H_{17}; **17b**: R′ = ^{c}C_6H_{11}, R″ = n-C_8H_{17}), respectively (Scheme 3). However, these mixtures could not be separated like **13–15** (*vide supra*). Nevertheless, a straightforward synthesis procedure to produce pure **17a** and **17b** starts from halide-free 1-(C_6H_5)-4,5-Me_2-^{c}C_3HN_2 (**3c**) applying the same reaction sequence as just described (Scheme 3). Quaternisation of **3c** with **12b** gave **16d**, which on subsequent reaction with LDA, PR′$_2$Cl and K[PF_6] produced **17a** and **17b** (Scheme 3). After appropriate work-up, **17a** and **17b** could be isolated as colourless solids in an overall yield of 66 and 71%, respectively (Experimental section).

On the other hand, a diphenyl phosphino group could be successfully introduced at the phenyl imidazolium building block using a synthesis protocol firstly described by Stelzer *et al.*[8] as demonstrated in reaction (1). After appropriate work-up, the corresponding imidazolium salt [1-(4-PPh_2-C_6H_4)-3-n-C_8H_{17}-4,5-Me_2-^{c}C_3HN_2]PF_6 (**20**) could be isolated as a colourless solid in 63% yield (Experimental section).

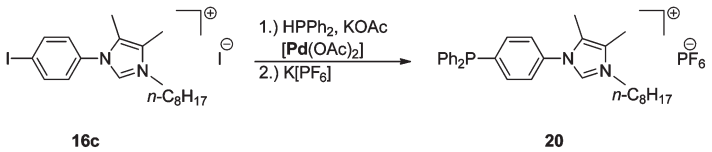
To verify the σ-donor properties of the newly synthesized phosphines **11a–f** we converted them into the appropriate seleno phosphines **11a-Se–f-Se** by addition of a 2-fold excess of elemental selenium in toluene at 100 °C (reaction (2)). In general, the σ-donor ability of phosphines towards selenium



Scheme 1 Synthesis of imidazoles **3a–c**, **5**, **7** and **9** (Fc = (η^5-C_5H_4)(η^5-C_5H_5), dppf = 1,1′-bis(diphenylphosphino)ferrocene).

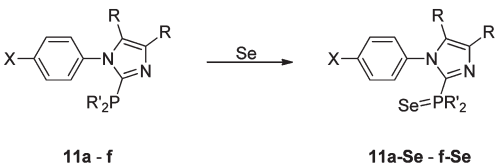


Scheme 2 Synthesis of phosphino imidazoles and imidazolium salts **11a–k** and **13–15**.



(1)

acceptors can be quantified by the phosphorus–selenium coupling constant as indicated by $^{31}P\{^{1}H\}$ NMR spectroscopy.[9] Electron-withdrawing groups increase $^{1}J_{PSe}$, due to the increased s character of the phosphorus orbital involved in the P═Se bonding. This results in shorter bond distances between the phosphorus and the acceptor carbon atoms, which directly affects the steric demand around the P atom resulting in marked changes in the behaviour of the respective transition metal complexes.



(2)

The chemistry of *N*-heterocyclic carbenes developed rapidly during the last years due to their outstanding potential as supporting ligands in homogeneous catalysis.[10] For this reason, we did react the imidazolium salts **16a–c** with $[PdCl_2(cod)]$ (cod = cycloocta-1,5-diene) as palladium source and KO*t*-Bu as deprotonating agent (reaction (3)). Although the reactants were readily consumed only in the case of **16a** we succeeded in isolating a pure palladium carbene complex. By halide exchange the mononuclear palladium carbene complex **19** could be isolated in minor yield (Experimental section). The obtained few crystals were characterised by X-ray diffraction studies indicating that **19** was formed both in the *cis* and *trans* configuration (Fig. 2). Due to the very low yield of **19** no further analytical characterisations could be performed.

It is important to note that all compounds are sensitive towards light and quickly turn yellow. Furthermore, the phosphine-carrying imidazoles are sensitive towards air and the phosphino imidazolium salts are hygroscopic. Therefore, rapid work-up and storage under argon are mandatory.

Table 1 Synthesis of phosphino imidazoles **11a–k**

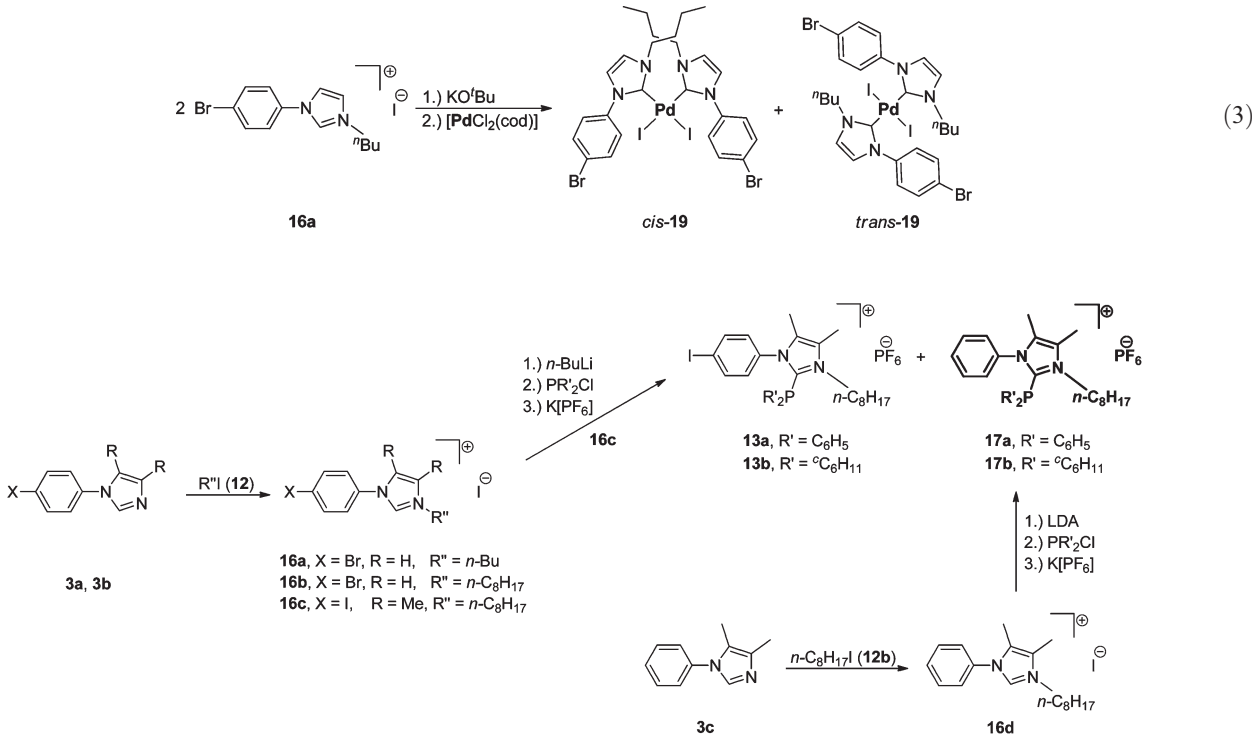
Compd.	X	R	R′	Yield[a] [%]
11a	Br	H	C_6H_5	60
11b	Br	H	$^{c}C_6H_{11}$	49
11c	Br	H	$^{c}C_4H_3O$	52
11d	I	Me	C_6H_5	65
11e	I	Me	$^{c}C_6H_{11}$	55
11f	I	Me	$^{c}C_4H_3O$	55
11g	Fc[b]	H	C_6H_5	63
11h	FcC≡C[b]	H	C_6H_5	44
11i	C_6H_5	Me	C_6H_5	67
11j	C_6H_5	Me	$^{c}C_6H_{11}$	61
11k	C_6H_5	Me	$^{c}C_4H_3O$	72

[a] Based on **3a** and **3b**, respectively. [b] Fc = $Fe(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)$.

Characterisation

The identities of all newly synthesised imidazoles **3b**, **5**, **7** and **9**, phosphino imidazoles **11a–k** and **11a-Se–f-Se** and imidazolium salts **16a–d**, **17a**, **17b** and **20** have been confirmed by elemental analysis, IR and NMR spectroscopy (^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$) as well as high-resolution mass spectrometry (Experimental section). Cyclovoltammetric measurements of **5**, **7** and the halide derivatives **3a** and **3b** were additionally carried out. The structures of **11a-Se** and **19** in the solid state were determined by single crystal X-ray structure analysis.

The IR spectra of the newly prepared molecules are less expressive with exception of the imidazole and imidazolium C═N and C═C vibrations (Experimental section). The



Scheme 3 Synthesis of **13**, **16** and **17**.

introduction of phosphino groups resulted in the visibility of characteristic P–C stretching frequencies and for the appropriate seleno derivatives additional $\tilde{\nu}_{P=Se}$ absorptions are observed. Apparently there is nearly no influence on the C≡C vibration when the imidazole ring is functionalised by a PPh_2 group as given in **7** ($\tilde{\nu}_{C\equiv C}$ = 2206 cm^{-1}) and **11h** ($\tilde{\nu}_{C\equiv C}$ = 2204 cm^{-1}), respectively.

Contrastingly, the NMR spectra of the respective imidazole and imidazolium species are in some extend more meaningful. A striking feature in the ^{1}H NMR spectra is the shift of the $^cC_3HN_2$ core proton in position 2 to a lower field, when changing from the imidazoles to the appropriate imidazolium salts, *i.e.* **3b**, 7.45 ppm and **16c**, 9.82 ppm (Experimental section). For the phenylene C_6H_4 units, as expected, a characteristic AA′XX′ coupling pattern with $^3J_{HH}$ = 8.7 Hz is found, which splits into a more complex pattern, when a phosphorus atom is attached to the heterocyclic core as given in **11a–k** and **11a-Se–f-Se** (Experimental section). For the ferrocenyl-containing molecules **5**, **7** and **11g** and **11h** a singlet as well as two pseudo-triplets are observed between 4.0 (C_5H_5) and 4.7 ppm (C_5H_4), respectively, resulting from the cyclopentadienyl ring protons. For the two methyl groups in **3b**, **9**, **11d–f**, **11d-Se–f-Se**, **16c**, **16d**, **17a**, **17b** and **20** two individual singlets are characteristic due to the asymmetry of the $^cC_3N_2$ core unit.

The interpreting of the ^{13}C{^{1}H} NMR spectra of all imidazoles and imidazolium salts is somewhat more complex due to the presence of *ipso*-carbon atoms. However, when phosphino groups are attached either to the $^cC_3N_2$ or C_6H_4 unit the spectra became more simplified, since characteristic P–C couplings appear (Experimental section). Very distinctive is the signal of the heterocyclic C-2 carbon atom at *ca.* 135 ppm (**3**, **16**) which is shifted to 140–147 ppm in the phosphino-containing species **11** and **17**. Conspicuous in **11a**, **11c**, **11d** and **11f** and the corresponding selenium derivatives **11a-Se–e-Se** is that C-5 shows a $^3J_{CP}$ coupling, while C-4 appears as a singlet. All other molecules of **11** solely show a singlet. Also very characteristic is the *meta*-carbon C_6H_4 atom in **11a–k**, **17** and **20** emerging as a doublet with a $^4J_{CP}$ coupling of 3–6 Hz at *ca.* 130 ppm.

^{31}P{^{1}H} NMR spectroscopy can be used to monitor the progress of the reaction of lithiated **3**, **5**, **7**, **9** and **16** with the respective chloro phosphines PR′$_2$Cl (**10a–c**) since a singlet of the phosphorus atom appears between −73–5 ppm depending on the nature of the organic groups R′ (Experimental section). In addition, the donor properties of the phosphino imidazoles **11a–f** can be quantified by the coupling constant $^1J_{PSe}$ of the appropriate seleno phosphines **11a-Se–f-Se**. An electron-withdrawing group at P increases $^1J_{PSe}$ as a result of the increased s character of the phosphorus orbital involved in the phosphorus–selenium bonding. As a consequence thereof, a shorter bond length between the phosphorus and the acceptor R′ units is observed.[9] This electronic impact has direct influence on the P donor ability. The ^{31}P{^{1}H} NMR data together with the $^1J_{PSe}$ coupling constant for the seleno phosphines **11a-Se–f-Se** are summarised in Table 2.

From Table 2 it can be seen that the seleno phosphines **11a-Se–c-Se** show higher coupling constants than the respective **11d-Se–f-Se** derivatives featuring methyl groups in positions 4 and 5 indicating that the latter three molecules are better σ-donors. The most electron-donating systems are the aliphatic cyclohexyl seleno phosphines **11b-Se** and **11e-Se** with $^1J_{PSe}$ of 718 and

Table 2 Chemical shifts and $^1J_{PSe}$ values of **11a-Se–f-Se**

Compd.	δ/ppm	$^1J_{PSe}$/Hz	Compd.	δ/ppm	$^1J_{PSe}$/Hz
11a-Se	19.1	753	**11d-Se**	17.6	745
11b-Se	41.6	725	**11e-Se**	41.2	718
11c-Se	−20.7	790	**11f-Se**	−21.4	781

Table 3 Cyclovoltammetric data (potentials *vs.* FcH/FcH^+), scan rate 100 mV s^{-1} at a glassy-carbon electrode of 1.0 mmol L^{-1} solutions of **3a**, **3b**, **5**, and **7** in dry dichloromethane containing 0.1 mol L^{-1} of $[(n\text{-}Bu)_4N][B(C_6F_5)_4]$ as supporting electrolyte at 25 °C

Compd.	$E_{red-irrev}$/V	Compd.	E^0 (ΔE_p)/V	$E_{red-irrev}$/V
3a	−1.22	**5**	0.108 (0.114)	−1.48
3b	−1.23	**7**	0.183 (0.102)	−1.52

E^0 = redox potential, ΔE_p = difference between oxidation and reduction potential, $E_{red-irrev}$ = irreversible reduction potential.

725 Hz, respectively (Table 2). In summary, the σ-donor ability decreases in the order **11e** > **11b** > **11d** > **11a** > **11f** > **11c**. The data summarised in Table 2 are indicative of classifying the suitability of the phosphino imidazoles as suitable ligands in palladium-promoted Suzuki C–C cross-couplings (*vide infra*).

Complexes **5** and **7** contain a redox-active ferrocenyl group and hence they have been subjected to cyclovoltammetric measurements in dry dichloromethane solutions utilising $[(n\text{-}Bu)_4N][B(C_6F_5)_4]$ as supporting electrolyte.[11] The cyclovoltammetric studies were carried out at scan rates of 100 mV s^{-1}. All potentials are referenced to the FcH/FcH^+ redox couple as internal standard as recommended by IUPAC.[12] The cyclovoltammetric data are summarised in Table 3 and the cyclovoltammograms (= CV) of **5** and **7** are shown in Fig. S1 in the ESI-General.†

One ferrocenyl-related oxidation half-reaction in the anodic CV sweep and reduction half-reaction in the cathodic CV sweep could be observed. The ferrocenyl substituents showed reversible electrochemical behaviour (ΔE_p = 0.114 (**5**) and 0.102 V (**7**)), while for the imidazole unit one irreversible reduction event is observed at −1.48 V (**5**) and −1.52 V (**7**), respectively. From Table 3 it is obvious that molecule **7** with its alkynyl unit is more difficult to oxidise (**5**, E^0 = 0.108 V; **7**, E^0 = 0.183 V). The imidazole starting compounds **3a** and **3b** show only irreversible reduction events at −1.22 (**3a**) and −1.23 V (**3b**) for the heterocyclic core (ESI-General, Fig. S1,† Table 3).[13] This indicates that, as expected, organometallics **5** and **7** are more electron rich due to the electron donating ferrocenyl groups present.

An advantage of the seleno phosphines is their tendency to crystallise easier than the appropriate phosphino imidazoles or imidazolium salts. Exemplary, the molecular structure of **11a-Se** in the solid state was established by single crystal X-ray structure analysis. Suitable crystals were obtained by slow evaporation of a saturated dichloromethane solution containing **11a-Se** at ambient temperature. The ORTEP diagram, selected bond distances (Å) and angles (°) are shown in Fig. 1. The crystal and structure refinement data are presented in the Experimental section.

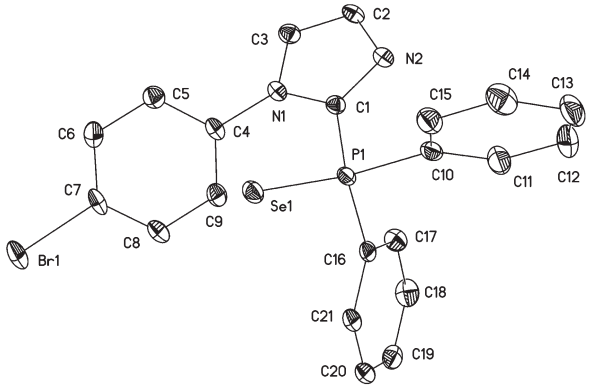


Fig. 1 ORTEP diagram (50% probability level) of the molecular structure of **11a-Se** with the atom numbering scheme. (Hydrogen atoms are omitted for clarity.) Standard uncertainties of the last significant digit(s) are shown in parentheses. Selected bond distances (Å) and angles (°): P1–Se1 = 2.1032(6), P1–C1 = 1.813(2), P1–C10 = 1.813(2), P1–C16 = 1.820(2), N1–C1 = 1.373(3), N1–C3 = 1.371(3), N2–C1 = 1.321(3), N2–C2 = 1.372(3), C2–C3 = 1.368(3); C1–P1–Se1 = 113.56(8), C10–P1–Se1 = 113.18(8), C16–P1–Se1 = 114.43(8), C1–P1–C10 = 103.02 (10), C1–P1–C16 = 105.16(11), C16–P1–C10 = 106.48(11).

Seleno phosphine **11a-Se** crystallises in the monoclinic space group $P2_1/n$. The molecular structure of **11a-Se** is set-up by two phenyl groups, the imidazole unit and one selenium atom which are bound to the phosphorus atom resulting in a tetrahedrally distorted geometry (Fig. 1). The phosphorus–carbon bond separations with 1.813(2) (P1–C1/P1–C10) and 1.820(2) Å (P1–C16) are representative of $P–C_{aryl}$ bond distances.[9c,g,h] Very characteristic is the P–Se bond of 2.1032(6) Å, which is similar to other seleno phosphines, *i.e.* 1-*tert*-butyl-2-(diphenylphosphino selenide)-1*H*-imidzole[1c] and triphenyl seleno phosphine.[14] The C–P–C angles at P1 (Fig. 1) are from 103.02(10)–106.48(11)° in the typical range of tertiary seleno phosphines.[1c,9c,g,h,14] The imidazole core entity with atoms N1, N2 and C1–C3 is planar (r.m.s. deviation 0.0006 Å, highest deviation from planarity observed for C3 with 0.0010 Å). The C_6H_4Br moiety of the imidazole unit is rotated by 58.1° with respect to the imidazole core entity.

As outlined earlier, from the palladium complex **19** single crystals could be separated in a very low yield by slow evaporation of a chloroform solution below 0 °C. Complex *trans*-**19**

Table 4 Reaction of 2-bromo toluene with phenylboronic acid to give 2-methyl biphenyl[a]

Entry	Compd.	Conversion/%	Entry	Compd.	Conversion/%
1	**11a**	7	8	**11h**	60
2	**11b**	80	9	**11i**	24
3	**11c**	0	10	**11j**	100
4	**11d**	20	11	**11k**	5
5	**11e**	100	12	**17a**	55
6	**11f**	5	13	**17b**	97
7	**11g**	32	14	**20**	66

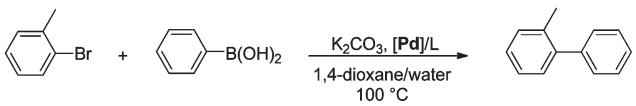
[a] Reaction conditions:[16] 2-bromo toluene (1.0 eq), phenylboronic acid (1.5 eq), K_2CO_3 (3.0 eq), 1,4-dioxane–water (ratio 2.1, v/v) (10 mL $mmol^{-1}$), $[Pd(OAc)_2]$/phosphine (0.25 mol% [Pd], 0.5 mol% phosphine, 100 °C, 1 h. The reaction times were not minimized.

crystallises in the form of pale yellow plates, whereas *cis*-**19** crystallises as colourless needles. For *trans*-**19** the structure determination by X-ray crystallography proceeds unproblematically with the use of Mo K_α radiation. In case of *cis*-**19** the needles were extremely tiny and Cu K_α radiation had to be used with comparatively long exposure times. Due to this, an "icing" of the crystal occurred at higher diffraction angles and the data set obtained so far did not reach full completeness (Table 7, Experimental section). As no further suitable crystals of *cis*-**19** could be selected the incomplete data set has been used for refining. Thus, Fig. 2 displays the molecular structure of *cis*-**19** and selected bond ranges, without further discussion (Experimental section). Fig. 2 presents further the molecular structure of *trans*-**19** (right). Important bond distances (Å) and bond angles (°) for *trans*-**19** are summarised in the caption of this figure. Crystal and structure refinement data are presented in the Experimental section.

Both isomers of complex **19** crystallise in the triclinic space group $P\bar{1}$. The Pd1 atom of *trans*-**19** possesses a planar PdC_2I_2 coordination set-up (r.m.s. deviation 0.0169 Å, highest deviation from planarity observed for I2 with −0.0213 Å) with *trans*-oriented I1–Pd1–I2 and C1–Pd1–C14 angles of 178.963(13) and 178.49(12)°, respectively (Fig. 2). As expected, the imidazole units show planarity (r.m.s. deviation 0.0025 and 0.0020 Å) and are twisted to the C_6H_4Br moieties with angles of 47.1 and 47.3°, respectively. The main structural feature of the imidazole ligands is the slightly decreased N1–C1–N2 angle (104.8(3)°) which is attributed to the extent of electronic delocalisation. A similar behaviour was found for other palladium imidazole species.[15] The Pd–I, Pd–C_{sp2} and the bond distances of the imidazole and phenyl units correspond to the bond lengths of the related molecules, *i.e.* $[(1,3\text{-}Me_2\text{-}^cC_3H_2N_2)_2PdI_2]$.[15a] The formation of both the kinetic and thermodynamic product might be attributed to the isolation method of crystals of **19** (Experimental section).

Catalysis

The application of phosphino imidazoles **11a–k** and phosphino imidazolium salts **17** and **20** in the homogeneous palladium-catalysed Suzuki C–C cross-coupling of 2-bromo toluene with phenylboronic acid was studied as model systems. The catalytic active species was *in situ* generated by applying mixtures of $[Pd(OAc)_2]$ and the respective phosphines **11a–k**, **17** and **20** in the ratio of 1 : 2 (reaction (4)). The catalytic reactions were carried out in 1,4-dioxane–water mixtures of ratio 2 : 1 (v:v) in presence of potassium carbonate at 100 °C using 0.5 mol% of the appropriate phosphine and 0.25 mol% of the palladium source. Acetyl ferrocene as standard was added to the appropriate reaction solution to determine the rate of conversion using ^{1}H NMR spectroscopy.[16] The obtained conversions equal ^{1}H NMR spectroscopic yields and are based on the respective aryl halides.



(4)

As can be seen from Table 4 and Fig. S2–S5 (ESI-General†) all *in situ* generated palladium phosphines are catalytically active, of which the cyclohexyl-substituted phosphines **11b**, **11e**, **11j** and **17b** are significantly more productive and active than the others (Table 4; entries 2, 5, 9 and 13), which originates from the electron-richness and bulkiness of these compounds. Comparing the alkyl- and aryl-functionalised phosphines among each other, the following trend concerning the activity and productivity of their palladium complexes can be seen: **11b** > **11a** > **11c** > and **11e** > **11d** > **11f**. In general, the dimethyl functionalised phosphino imidazole systems (Table 4; entries 4–6), which are also more easily and in better yields accessible (*vide supra*), are by far more productive than the non-substituted derivatives

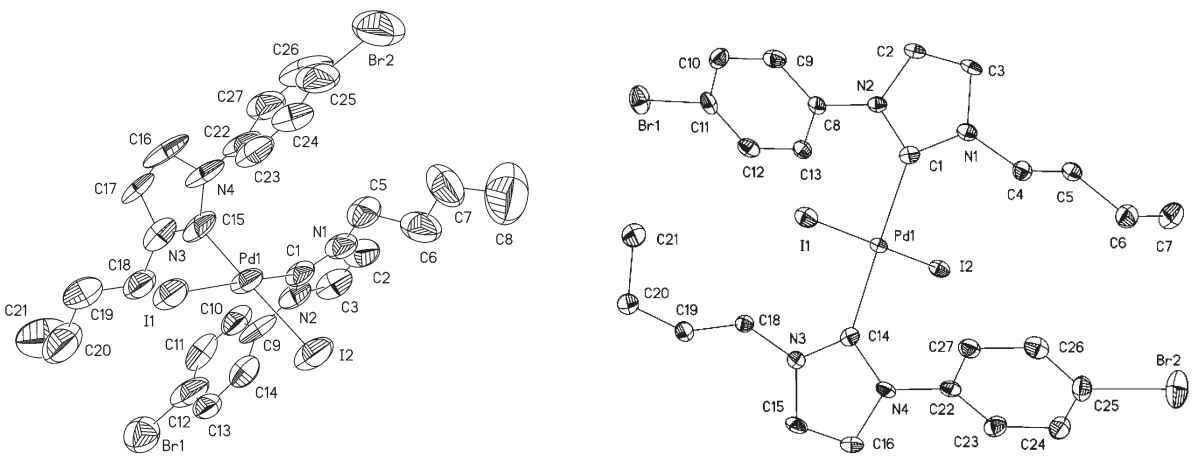
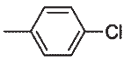
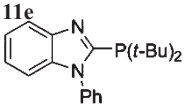
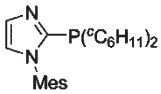
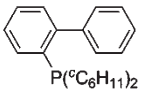
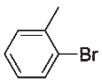
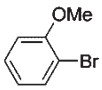
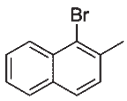
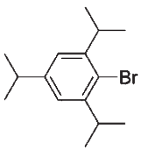
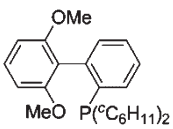


Fig. 2 ORTEP diagram (50% probability level) of the molecular structure of *cis*-**19** (left), showing only one molecule, and *trans*-**19** (right) with the atom-numbering scheme. For *cis*-**19** and *trans*-**19** all hydrogen atoms and one molecule of the packing solvent chloroform (*cis*-**19**) have been omitted for clarity. Selected bond distances (Å), angles (°) and torsion angles (°) for *trans*-**19**: Pd1–I1 = 2.6152(4), Pd1–I2 = 2.6092(4), Pd1–C1 = 2.031(3), Pd1–C14 = 2.032(3), N1–C1 = 1.341(4), N1–C3 = 1.390(4), N1–C4 = 1.463(4), N2–C1 = 1.367(4), N2–C2 = 1.395(4), N2–C8 = 1.422(4), N3–C14 = 1.335(4), N3–C15 = 1.393(4), N3–C18 = 1.463(4), N4–C14 = 1.376(4), N4–C16 = 1.386(4), N4–C22 = 1.422(4), C2–C3 = 1.343(5), C15–C16 = 1.341(5); C1–Pd1–C14 = 178.49(12), I1–Pd1–I2 = 178.963(13), I1–Pd1–C1 = 89.48(9), I1–Pd–C14 = 91.66(9), I2–Pd1–C1 = 90.34(9), I2–Pd1–C14 = 88.54(9), N1–C1–N2 = 104.8(3), N3–C14–N4 = 104.8(3). Range of bond distances for *cis*-**19**: Pd–I = 2.601(4)–2.68(4), Pd–C_{sp2} = 1.91(2)–2.07(2).

Table 5 Suzuki coupling of 4-chloro toluene and sterically hindered aryl bromides

Entry	Aryl halide	Ligand	Catalyst/mol%	Conversion/%	TON
1		**11d**	0.01	28[a]	2800
2		**11e**	0.01	88[a]	8800
3			0.01	86[a,b]	8600
4			0.01	15–66[a,b]	1500–6600
5			0.05	99[c,d]	1860
6			0.01	47[c,d]	4700
7		$P(t\text{-Bu})_3$	0.01	92[c,d]	9200
8		$P(n\text{-Bu})Ad_2$	0.01	94[c,d]	9400
9		**11e**	0.05	100[e]	2000
10		**11e**	0.05	43[e]	860
11		**11e**	0.05	100[e]	2000
12		**11e**	0.05	76[e]	1520
13			0.01	97[e,f]	9700

[a] Reaction conditions:[3b] 4-chloro toluene (3.0 mmol, 1.0 eq), phenylboronic acid (4.5 mmol, 1.5 eq), K_3PO_4 (6.0 mmol, 3.0 eq), toluene (6 mL), $[Pd(OAc)_2]$/phosphine (0.01 mol% [Pd], 0.1 mol% phosphine, 100 °C, 20 h. [b] Ligand from ref. 3*b*. [c] Ligands from ref. 18*b*. [d] Reaction conditions:[18b] 4-chloro toluene (3.0 mmol, 1.0 eq), phenylboronic acid (4.5 mmol, 1.5 eq), K_3PO_4 (6.0 mmol, 3.0 eq), toluene (6 mL), [Pd]:P = 1 : 2, 100 °C, 20 h. [e] Reaction conditions:[19] aryl halide (1.0 mmol, 1.0 eq), phenylboronic acid (1.5 mmol, 1.5 eq), K_3PO_4 (3.0 mmol, 3.0 eq), toluene (2 mL), $[Pd_2(dba)_3]$/phosphine (0.05 mol% [Pd], 0.1 mol% phosphine, 50 °C, 24 h. [f] Ligand from ref. 18*d*, T = 100 °C, 16 h.

11a–c (Table 4; entries 1–3), explainable by the more electron-donating capability of the imidazole rings. Since these compounds possess with the bromo and iodo substituents reactive functionalities, we decided to introduce organic and organometallic catalytic inert groups at the phenylene building block. This led to the derivatives **11i–k**. It was found that the productivities of these species are similar to their halide counter parts (Table 4; entries 4–6 and 9–11). However, their activities are considerably higher (Fig. S3, ESI-General;† Table 4) indicating that the halide carrying phosphines **11a–f** are involved in the catalytic reactions. In addition, the reaction profiles (Fig. S3, ESI-General†) indicate that the influence of the halide is less prominent when electron-deficient phosphino groups are present, explainable by the slower oxidative addition. Comparing the biphenyl- and ferrocenyl-functionalised molecules with each other, it is obvious that the organometallic compounds **11g** and **11h** are superior ligands in the catalysis, however, less active than the respective cyclohexyl phosphines.

From Table 4 it further becomes clear that the neutral as well as the ionic cyclohexyl phosphino systems show the same productivity with a slightly higher activity for **11e**. In the case of the molecules featuring phenyl groups it is obvious that the imidazolium derivative **17a** gives a more active and productive catalyst than **11d** (Table 4; entries 4 and 12; Fig. S5, ESI-General†) most likely attributed to the better solubility of ionic **17a**. The palladium complex carrying the imidazolium salt **20** with the phosphino donating group located at the phenylene unit is, when compared with ligand **17a**, more active and productive, which can be explained with the better σ-donor ability of the triphenylphosphine derivative. Compared with the respective neutral phosphino imidazole molecule,[17] the imidazolium salt **20** is a better ligand for C–C couplings.

We also studied the ability of our systems (i) to couple non-activated 4-chloro toluene using low palladium loadings, and (ii) to convert sterically hindered biaryls at only 50 °C (Table 5). As can be seen from Table 5, the reaction of 4-chloro toluene with phenylboronic acid in the presence of phosphines **11d** and **11e** gave 28 and 88% conversion, respectively, using only 0.01 mol % [$Pd(OAc)_2$] (Table 5; entries 1 and 2). Especially the cyclohexyl derivative **11e** can compete under these reaction conditions with TONs up to 8800 with the di-*t*-butylphosphino-substituted benzimidazole (TON: 8600) and shows excellent results compared to the dicyclohexylphosphino imidazole (TON: 1500–6600) reported by Beller and co-workers[3b] (Table 5; entries 3 and 4). In comparison with the biphenyl ligand first described by Buchwald,[18a,d] significantly higher conversions can be achieved using 0.01 mol% palladium (Table 5, entry 6).[18b] However, comparison with the trialkyl phosphino ligands by Fu *et al.*[18c] and Beller *et al.*[18b] showed a slightly lower conversion under the applied reaction conditions.[18b]

Another challenge in organic synthesis is the preparation of sterically hindered biaryls especially under mild reaction conditions. As can be seen from Table 5 the coupling of aryl bromides with one or two *ortho*-substituents proves the successful use of only 0.05 mol% palladium at 50 °C (Table 5; entries 9–12). Even highly congested 1,3,5-tri-i-propyl-2-bromo benzene can be coupled with good conversions of 76% (Table 5; entry 12). Compared to previously reported catalyst systems suitable for these couplings, *i.e.* $Fe(\eta^5\text{-}(1\text{-}(4\text{-}t\text{-}Bu\text{-}C_6H_4)\text{-}2\text{-}P(2\text{-}CH_3C_6H_4)_2C_5H_3))(\eta^5\text{-}C_5H_5)/[Pd_2(dba)_3]$[19a] (dba = dibenzylideneacetone)[19] only half the amount of palladium is required to achieve good to excellent results. In comparison with the established biphenyl catalyst system by Buchwald *et al.*[18d] (Table 5, entry 13) higher catalyst loadings and longer reaction times are necessary, yet, the catalytic reaction can be performed at considerably lower temperature (50 °C *vs.* 100 °C).

Ionic phosphines **17b** and **20** were additionally tested under similar catalytic conditions (*vide supra*) in the coupling of 2-bromo toluene with phenylboronic acid but exchanging the organic solvent (1,4-dioxane) with the ionic liquid [BMIM][PF_6] (BMIM = 1-butyl-3-methylimidazolium), which should provide excellent solubility due to its structural similarity. It is well-stated that ionic liquids in homogeneous catalysis show some benefits including better solubility, stability under catalytic conditions and easier separation of the organic coupling products from the catalytic active species.[6] The results thereof are shown in Table 6. To our surprise, the conversions in the first run are lower when compared to the reaction in 1,4-dioxane (Table 6; entries 1 and 4). Furthermore, recycling proved unsuccessful and almost no conversion could be detected in further runs (Table 6; entries 2, 3, 5 and 6). These inactivity of our systems might be caused by the formation of 1,3-dialkylimidazole-2-ylidene palladium complexes, which can lead, due to their stability regarding dissociation, to inactive polycarbene palladium complexes.[20] To rule out the possibility of the formation of inactive complexes, we chose 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ([BDMIM][BF_4]) as ionic liquid. However, the Suzuki reaction in [BDMIM][BF_4] resulted in even lower conversions after 1 h when compared to the couplings in [BMIM][PF_6] or 1,4-dioxane (Table 6; entries 7 and 8). Furthermore, precipitation of metallic palladium occurred during the catalytic reaction, which could not be suppressed by carrying out the reaction at 75 °C but with 0.5 mol% of palladium (Table 6; entries 9 and 10). These obtained results show that the catalytic species is only active for a short time leading to rapid decomposition, most probably attributed to the lower σ-donor ability of the ionic phosphines and hence insufficient stabilisation of the active species.

Conclusions

Within this study the synthesis and characterisation (IR, NMR, MS, electrochemistry, elemental analysis) of a series of imidazoles 1-(4-X-C_6H_4)-4,5-R_2-$^cC_3HN_2$ (X = Br, I, Fc, FcC≡C, Ph; R = H; Me; Fc = $Fe(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)$), phosphino imidazoles 1-(4-X-C_6H_4)-2-PR′$_2$-4,5-R_2-$^cC_3N_2$ (X = Br, I, Fc, FcC≡C, Ph; R = H; Me; R′ = Ph, $^cC_6H_{11}$, $^cC_4H_3O$), imidazolium [1-(4-X-C_6H_4)-3-R″-4,5-R_2-$^cC_3HN_2$]I (X = Br, I; R = H, Me; R″ = ^{n}Bu, $^nC_8H_{17}$) and phosphino imidazolium salts [1-C_6H_5-2-PR′$_2$-3-$^nC_8H_{17}$-4,5-Me_2-$^cC_3N_2$]PF_6 (R′ = Ph, $^cC_6H_{11}$) or [1-(4-PPh_2-C_6H_4)-3-$^nC_8H_{17}$-4,5-Me_2-$^cC_3HN_2$]PF_6, and their selenium derivatives 1-(4-X-C_6H_4)-2-P(= Se)R′$_2$-4,5-R_2-$^cC_3N_2$ (X = Br, I; R = H, Me; R′ = Ph, $^cC_6H_{11}$, $^cC_4H_3O$) are reported. They have been prepared by straightforward synthesis methodologies including alkylation, metallation, P–C coupling (Stelzer) and C–C cross-coupling reactions (Suzuki, Negishi, Sonogashira). To verify the σ-donor ability of the phosphino imidazoles the appropriate selenium derivatives have been prepared by addition of selenium in its elemental form to the respective phosphine.

Table 6 Reaction of 2-bromo toluene with phenylboronic acid in ionic liquid

Entry	Run	Compd.	Conversion/%	Entry	Run	Compd.	Conversion/%
1	1	**17b**[a]	65	7	1	**17b**[b]	26
2	2		5	8	2		3
3	3		1				
				9	1	**17b**[c]	36
4	1	**20**[a]	55	10	2		3
5	2		1				
6	3		0				

[a] Reaction conditions: 2-bromo toluene (1.0 eq), phenylboronic acid (1.5 eq), K_2CO_3 (3.0 eq), water (10 mL), [BMIM][PF_6] (7 g, 24.6 mmol), [$Pd(OAc)_2$]/phosphine (0.25 mol% [Pd], 0.5 mol% phosphine, 100 °C, 1 h. [b] Reaction conditions: 2-bromo toluene (1.0 eq), phenylboronic acid (1.5 eq), K_2CO_3 (3.0 eq), water (10 mL), [BDMIM][BF_4] (6 g, 25.0 mmol), [$Pd(OAc)_2$]/phosphine (0.25 mol% [Pd], 0.5 mol% phosphine, 100 °C, 1 h. [c] Reaction conditions: 2-bromo toluene (1.0 eq), phenylboronic acid (1.5 eq), K_2CO_3 (3.0 eq), water (10 mL), [BDMIM][BF_4] (6 g, 25.0 mmol), [$Pd(OAc)_2$]/phosphine (0.5 mol% [Pd], 1.0 mol% phosphine, 75 °C, 1 h.

High $^1J_{PSe}$ values indicate electron-poor phosphines and hence less electron donating σ-donors.[9] The structure of 1-(4-Br-C_6H_4)-2-P(= Se)Ph_2-$^cC_3H_2N_2$ in the solid state was confirmed by single crystal X-ray diffraction studies showing the pseudo-tetrahedral environment about the phosphorus atom. The reaction of [1-(4-Br-C_6H_4)-3-n-Bu-$^cC_3H_3N_2$]I towards [$PdCl_2$(cod)] (cod = cyclo-1,5-octadiene) gave the respective *cis*- and *trans*-palladium carbene complexes [Pd(1-(4-Br-C_6H_4)-3-n-Bu-$^cC_3H_2N_2$)$_2I_2$], which were characterised by single crystal X-ray structure measurements confirming the molecular square-planar coordination about Pd and additionally shows the structural characteristics typical of palladium–carbene complexes.[15] Furthermore, the phosphino imidazoles and imidazolium salts were applied in the palladium-promoted Suzuki C–C cross-coupling. As a model reaction the conversion of 2-bromo toluene and phenylboronic acid as organic substrates and potassium carbonate as base were chosen. All *in situ* generated phosphino palladium species showed catalytic activity towards the formation of 2-methyl biphenyl. It was found that the more electron-rich the phosphines are, the more active and productive the catalytic system is. This was impressively demonstrated by the cyclohexyl-functionalised derivatives. Additionally, the phosphino imidazolium species showed higher activity and productivity than their neutral derivatives. Also it is obvious that the halide ligands at the phenylene units should be replaced by innocent organic or organometallic moieties since otherwise the C–Br or C–I bonds are involved in the catalytic reactions. Compared with, for example, dialkylphosphino-functionalised imidazoles and benzimidazoles applying [$Pd(OAc)_2$][3b] as palladium source, the compounds described within this study show excellent productivities with TONs up to 8800. Furthermore, the cyclohexyl-functionalised phosphino imidazole 1-(4-I-C_6H_4)-2-P($^cC_6H_{11}$)$_2$-4,5-Me_2-$^cC_3N_2$ was used in the synthesis of sterically hindered biphenyls showing good to excellent results at 50 °C and catalyst loadings of only 0.05 mol%. In further studies C–C coupling reactions of the appropriate imidazolium molecules in presence of the ionic liquid [BMIM][PF_6] were carried out. Surprisingly, the conversions were lower when compared to the reaction in 1,4-dioxane, and recycling was not possible. These observations are most likely attributed to deactivation of the catalyst due to the formation of stable, inactive polycarbene palladium complexes.[20] To avoid this type of reaction we carried out the Suzuki catalysis in [BDMIM][BF_4]. Nevertheless, the observed conversions were even lower when compared to [BMIM][PF_6] or 1,4-dioxane. In addition, the formation of "palladium-black" was observed, leading to the assumption that the phosphino imidazolium salts are not suited to stabilise the active species due to their lower σ-donor ability.

Experimental

General procedures

All reactions were carried out under argon atmosphere using standard Schlenk techniques. Toluene and tetrahydrofuran were purified by distillation from sodium–benzophenone; triethylamine was purified by distillation from calcium hydride. Diethyl ether and dichloromethane were received from a MBRAUN (MB-SPS 800) solvent drying and purification system. For filtrations Celite (purified and annealed, Erg. B.6, Riedel de Haen) was used. Column chromatography was carried out using either alumina with a particle size of 90 μm (standard, Merck KGaA) or silica with a particle size of 40–60 μm (230–400 mesh (ASTM), Becker).

NMR spectra were recorded with a Bruker Avance III 500 spectrometer. The ^{1}H NMR spectra were recorded at 500.3 MHz, the $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra at 125.7 MHz and 202.5 MHz, respectively. Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane with the solvent as reference signal (^{1}H NMR: standard internal $CDCl_3$, δ 7.26; $^{13}C\{^1H\}$ NMR: standard internal $CDCl_3$, δ 77.16; $^{31}P\{^1H\}$ NMR: standard external rel. 85% H_3PO_4, δ 0.0; $P(OMe)_3$, δ 139.0, respectively). High resolution mass spectra were recorded with a Bruker Daltonik micrOTOF-QII spectrometer (ESI-TOF). Elemental analyses were carried out with a Thermo FlashAE 1112 series instrument. The melting points of the analytical pure samples were determined using a Gallenkamp MFB 595 010 M melting point apparatus. FT IR spectra were recorded with a Thermo Nicolet IR 200 spectrometer using either KBr pellets or NaCl plates. Cyclovoltammetric measurements of dry degassed dichloromethane solutions (1.0 mmol L^{-1}) of **3a**, **3b**, **5** and **7** containing [(n-Bu)$_4$N][$B(C_6F_5)_4$] (0.1 mol L^{-1}) as supporting electrolyte were conducted under a blanket of purified argon at 25 °C utilising a Radiometer Voltalab PGZ 100 electrochemical workstation interfaced with a personal computer. A three electrode cell, which utilised a Pt auxiliary electrode, a glassy carbon working electrode (surface area 0.031 cm^2) and an Ag/Ag^+ (0.01 mol L^{-1} [$AgNO_3$]) reference electrode mounted on a luggin capillary was used. The working electrode was pre-treated by polishing on a Buehler microcloth first with 1 μ and then with a $\frac{1}{4}$ μ diamond paste. The reference electrode was constructed from a silver wire and inserted into an acetonitrile solution containing [$AgNO_3$] (0.01 mol L^{-1}) and [(n-Bu)$_4$N][$B(C_6F_5)_4$] (0.1 mol L^{-1}), in a luggin capillary with a vycor tip. This luggin capillary was inserted into a second luggin capillary with a vycor tip filled with a 0.1 mol L^{-1} [(n-Bu)$_4$N][$B(C_6F_5)_4$] solution in dichloromethane. Experimental potentials were referenced against an Ag/Ag^+ reference electrode but results are presented referenced against ferrocene as an internal standard as required by IUPAC.[12] Data were manipulated on a Microsoft Excel worksheet to set the formal reduction potentials of the FcH/FcH^+ couple to 0.0 V (FcH = Fe(η^5-C_5H_5)$_2$). Under our conditions the FcH/FcH^+ redox couple was at 320 mV *vs.* Ag/Ag^+.

All starting materials were obtained from commercial suppliers and used without further purification. 1-(4-Bromophenyl)-1*H*-imidazole (**3a**),[5a] 1-phenyl-1*H*-imidazole (**3c**),[21] [$PdCl_2(PPh_3)_2$],[22] [$PdCl_2$(cod)],[23] ethynylferrocene (**6**),[24] diphenylphosphine[25] and the chlorophosphines **10b**[26] and **10c**[27] were prepared according to published procedures.

Synthesis of 1-(4-iodophenyl)-4,5-dimethyl-1*H*-imidazole (3b)

Following the synthesis procedure described by Zhang *et al.*,[2d] 4-iodoaniline (10.95 g, 0.05 mol) dissolved in methanol (300 mL) were reacted with 2,3-butanedione (4.4 mL, 0.05 mol). After stirring for 16 h at ambient temperature, ammonium chloride (5.35 g, 0.1 mol) and 30% aq.

formaldehyde (10 mL, 0.1 mol) were added and the mixture was refluxed for 2 h. Afterwards, phosphoric acid (7 mL) was added in a single portion and the reaction mixture was refluxed for additional 6 h. After cooling down to ambient temperature all volatiles were removed in vacuum and the dark brown residue was poured onto ice and neutralised with potassium hydroxide until pH ≈ 9 was reached. The resulting mixture was extracted with dichloromethane (300 mL) and dried over magnesium sulfate. The solvent was removed in vacuum and the residue was purified on silica (column size: 15 × 5 cm) using diethyl ether as eluent. The product **3b** was obtained as pale yellow solid. Yield: 4.3 g (14.4 mmol, 29% based on 4-iodoaniline). Anal. Calcd for $C_{11}H_{11}IN_2$ (298.12 g mol^{-1}): C, 44.32; H, 3.72; N, 9.40. Found: C, 45.34; H, 3.90; N, 8.75. Mp.: 86 °C. IR (KBr, $\tilde{\nu}$/cm^{-1}): 1495 (m, N═C), 1588 (w, C═C), 2854/2917/2959 (w, C–H), 3060/3105 (w, ═C–H). ^{1}H NMR (500.30 MHz, $CDCl_3$, δ): 2.08 (s, 3 H, CH_3), 2.21 (s, 3 H, CH_3), 7.01 (dpt, $^3J_{HH}$ = 8.7 Hz, 2 H, H^o/C$_6H_4$), 7.45 (s, 1 H, H^2/C$_3H$N$_2$), 7.80 (dpt, $^3J_{HH}$ = 8.7 Hz, 2 H, H^m/C$_6H_4$). ^{13}C{^{1}H} NMR (125.81 MHz, $CDCl_3$, δ): 9.2 (s, *C*H$_3$), 12.9 (s, *C*H$_3$), 93.2 (C^p/*C*$_6$H$_4$), 122.8 (s, C^4/*C*$_3$HN$_2$), 127.4 (s, C^o/*C*$_6$H$_4$), 135.0 (s, C^2/*C*$_3$HN$_2$), 135.1 (s, C^5/*C*$_3$HN$_2$), 136.8 (s, C^i/*C*$_6$H$_4$), 138.8 (s, C^m/*C*$_6$H$_4$). HRMS (ESI-TOF) $C_{11}H_{11}IN_2$ [M + *n*H]$^+$ *m*/*z*: calcd: 299.0050, found: 299.0040. Please, notice that the results of the elemental analysis deviate from the calculated values due to decomposition of **3b** because this compound is highly light sensitive.

Synthesis of 1-(4-ferrocenylphenyl)-1*H*-imidazole (5)

Ferrocene (840 mg, 4.52 mmol) was dissolved in dry tetrahydrofuran (60 mL) and cooled to −78 °C. Then potassium *tert*-butoxide (64 mg, 0.57 mmol, 0.125 eq) was added in a single portion followed by dropwise addition of *t*-BuLi (5.6 mL, 8.96 mmol, 2 eq). After stirring the reaction mixture for 45 min at −78 °C, $[ZnCl_2(thf)_2]$ (1.4 g, 4.99 mmol, 1.1 eq) and **3a** (1.0 g, 4.48 mmol) was added in a single portion at 0 °C. The mixture was stirred for 30 min at this temperature, followed by addition of $[Pd(PPh_3)_4]$ (26 mg, 0.5 mol%). After heating the reaction mixture to 50 °C for 24 h, all volatiles were removed and the residue was purified by column chromatography on silica (column size: 15 × 3.5 cm) using diethyl ether as eluent and then a mixture of diethyl ether–ethyl acetate (ratio 1 : 1, v:v). The product was obtained as an orange solid. Yield: 0.94 g (2.86 mmol, 63% based on **3a**). Anal. Calcd for $C_{19}H_{16}FeN_2$ (328.19 g mol^{-1}): C, 69.53; H, 4.91; N, 8.54. Found: C, 69.06; H, 5.06; N, 8.61. Mp.: 132 °C. IR (KBr, $\tilde{\nu}$/cm^{-1}): 1509/1532 (s, N═C), 1560 (w, C═C), 2868/2931 (w, C–H), 3124 (w,═C–H). ^{1}H NMR (500.30 MHz, CD_2Cl_2, δ): 4.04 (s, 5 H, C$_5H_5$), 4.38 (pt, $^3J_{HH}$ = 1.8 Hz, 2 H, C$_5H_4$), 4.69 (pt, $^3J_{HH}$ = 1.8 Hz, 2 H, C$_5H_4$), 7.35 (dpt, $^3J_{HH}$ = 8.6 Hz, 2 H, H^o/C$_6H_4$), 7.37 (pt, $^3J_{HH}$ = 1.5 Hz, 1 H, H^4/C$_3H_3$N$_2$), 7.43 (pt, $^3J_{HH}$ = 1.5 Hz, 1 H, H^5/C$_3H_3$N$_2$), 7.60 (dpt, $^3J_{HH}$ = 8.6 Hz, 2 H, H^m/C$_6H_4$), 8.33 (m, 1 H, H^2/C$_3H_3$N$_2$). ^{13}C{^{1}H} NMR (125.81 MHz, CD_2Cl_2, δ): 66.8 (s, *C*$_5$H$_4$), 69.8 (s, *C*$_5$H$_4$), 69.9 (s, *C*$_5$H$_5$), 83.2 (s, C^i/*C*$_5$H$_4$), 120.0 (s, C^4/*C*$_3$H$_3$N$_2$), 122.2 (s, C^o/*C*$_6$H$_4$), 127.3 (s, C^m/*C*$_6$H$_4$), 127.9 (s, C^5/*C*$_3$H$_3$N$_2$), 133.6 (s, C^i/*C*$_6$H$_4$), 136.8 (s, C^2/*C*$_3$H$_3$N$_2$), 141.2 (s, C^p/*C*$_6$H$_4$). HRMS (ESI-TOF) $C_{19}H_{16}FeN_2$ [M + *n*H]$^+$ *m*/*z*: calcd: 329.0715, found: 329.0736.

Synthesis of 1-(4-(ethynylferrocenyl)phenyl)-1*H*-imidazole (7)

Ethynylferrocene (**6**, 0.5 g, 2.38 mmol), **3a** (0.53 g, 2.38 mmol), [CuI] (45 mg, 10 mol%) and $[PdCl_2(PPh_3)_2]$ (83 mg, 5 mol%) were dissolved in dry triethylamine (60 mL) and stirred at 60 °C for 16 h. After removal of all volatiles in vacuum, the residue was purified by column chromatography on silica (column size: 15 × 3.5 cm) using diethyl ether and then ethyl acetate as eluents. Product **7** was obtained as yellow solid. Yield: 0.37 g (1.05 mmol, 44% based on **3a**). Anal. Calcd for $C_{21}H_{16}FeN_2$ (352.21 g mol^{-1}): C, 71.61; H, 4.58; N, 7.95. Found: C, 71.45; H, 4.60; N, 7.95. Mp.: 160 °C (dec.). IR (KBr, $\tilde{\nu}$/cm^{-1}): 1490 (w, N═C), 1524 (m, C═C), 2206 (w, C≡C), 2851/2921 (w, C–H), 3108 (w,═C–H). ^{1}H NMR (500.30 MHz, $CDCl_3$, δ): 4.26 (s, 5 H, C$_5H_5$), 4.27 (pt, $^3J_{HH}$ = 1.8 Hz, 2 H, C$_5H_4$), 4.52 (pt, $^3J_{HH}$ = 1.9 Hz, 2 H, C$_5H_4$), 7.24 (m, 1 H, C$_3H_3$N$_2$), 7.32 (m, 1 H, C$_3H_3$N$_2$), 7.35 (dpt, $^3J_{HH}$ = 8.5 Hz, 2 H, C$_6H_4$), 7.59 (dpt, $^3J_{HH}$ = 8.4 Hz, 2 H, C$_6H_4$), 7.89 (m, 1 H, H^2/C$_3H_3$N$_2$). ^{13}C{^{1}H} NMR (125.81 MHz, CD_2Cl_2, δ): 64.8 (s, C^i/C$_5$H$_4$), 69.2 (s. C$_5$H$_4$), 70.1 (s, C$_5$H$_5$), 71.6 (s, C$_5$H$_4$), 84.6 (s, *C*≡C), 90.2 (s, C≡*C*), 121.1 (s, C^4/C$_3$H$_2$N$_2$), 121.3 (s, C^o/C$_6$H$_4$), 123.2 (s, C^p/C$_6$H$_4$), 123.5 (s, C^5/C$_3$H$_2$N$_2$), 133.0 (s, C^m/C$_6$H$_4$), 133.2 (s, C^i/C$_6$H$_4$), 136.5 (s, C^2/C$_3$H$_3$N$_2$). HRMS (ESI-TOF) $C_{21}H_{16}FeN_2$ [M + *n*H]$^+$ *m*/*z*: calcd: 353.0719, found: 353.0736.

Synthesis of 1-(4-(1,1′-biphenyl))-4,5-dimethyl-1*H*-imidazole (9)

Imidazole **3b** (1.29 g, 6.5 mmol), phenylboronic acid (**8**, 0.95 g, 7.81 mmol, 1.2 eq), potassium carbonate (2.69 g, 19.5 mmol, 3 eq) and $[PdCl_2(dppf)]$ (23 mg, 0.5 mol%) were dissolved in a 1,4-dioxane–water mixture (50 mL, ratio 2 : 1, v:v) and stirred at 100 °C for 16 h. After cooling to ambient temperature the organic phase was separated, dried over magnesium sulfate and purified by column chromatography on silica (column size: 18 × 3.5 cm) using diethyl ether as eluent. Biphenyl **9** was obtained as a pale yellow solid. Yield: 1.31 g (5.3 mmol, 82% based on **3b**). Anal. Calcd for $C_{17}H_{16}N_2$ (248.32 g mol^{-1}): C, 82.22; H, 6.49; N, 11.28. Found: C, 81.61; H, 6.60; N, 11.13. Mp.: 103 °C. IR (KBr, $\tilde{\nu}$/cm^{-1}): 1450/1490 (s, N═C), 1595/1605 (w, C═C), 2860/2919 (w, C–H), 3033/3102 (w,═C–H). ^{1}H NMR (500.30 MHz, $CDCl_3$, δ): 2.12 (s, 3 H, CH_3), 2.24 (s, 3 H, CH_3), 7.30 (dpt, $^3J_{HH}$ = 8.4 Hz, 2 H, H^3/C$_6$H$_5$–C$_6H_4$), 7.36 (m, 1 H, H$^{4'}$/C$_6$H$_5$–C$_6$H$_4$), 7.45 (m, 2 H, H$^{3'}$/C$_6$H$_5$–C$_6$H$_4$), 7.51 (s, 1 H, H^2/C$_3H$N$_2$), 7.59 (m, 2 H, H$^{2'}$/C$_6$H$_5$–C$_6$H$_4$), 7.66 (dpt, $^3J_{HH}$ = 8.4 Hz, 2 H, H^2/C$_6$H$_5$–C$_6H_4$). ^{13}C{^{1}H} NMR (125.81 MHz, $CDCl_3$, δ): 9.2 (s, *C*H$_3$), 12.8 (s, *C*H$_3$), 122.9 (s, C^i), 125.7 (s, C^3/C$_6$H$_5$–C$_6$H$_4$), 127.1 (s, C$^{2'}$/C$_6$H$_5$–C$_6$H$_4$), 127.8 (s, C$^{4'}$/C$_6$H$_5$–C$_6$H$_4$), 128.1 (s, C^2/C$_6$H$_5$–C$_6$H$_4$), 128.9 (s, C$^{3'}$/C$_6$H$_5$–C$_6$H$_4$), 134.6 (s, C^i), 135.1 (s, C^2/C$_3$HN$_2$), 136.1 (s, C^i), 139.8 (s, C^i), 141.0 (s, C^i). HRMS (ESI-TOF) $C_{17}H_{16}N_2$ [M + *n*H]$^+$ *m*/*z*: calcd: 249.1386, found: 249.1381; [M + nNa]$^+$ *m*/*z*: calcd: 271.1206, found: 271.1206.

General synthesis procedure for phosphines 11a–f

To 0.5 g of **3a** (2.24 mmol), **3b** (1.68 mmol), **5** (1.52 mmol), **7** (1.42 mmol) or **9** (2.01 mmol) dissolved in dry diethyl ether (**3a**, **5**, **7**, **9**, 40 mL) or tetrahydrofuran (**3b**, 40 mL) one eq of a

2.5 M solution of n-BuLi (**3a**, **5**, **7**, **9**) or a 2.0 M solution of lithium di-i-propylamide (**3b**) was added dropwise at −30 °C. After warming up the solution to ambient temperature, it was again cooled to −30 °C and one eq of the chlorophosphines **10a–c** was added dropwise. The reaction mixture was stirred at ambient temperature for 2 h and the solvent was removed in vacuum. The crude product was purified by column chromatography on silica or alumina and dried in vacuum.

General procedure for the synthesis of seleno phosphines 11a-Se–f-Se

To a toluene solution of **11a–f** (100 mg), 2 eq of elemental selenium was added in a single portion and stirred for 2 h at 100 °C. After cooling to ambient temperature, the solvent was removed in membrane-pump vacuum and the respective seleno phosphines were purified using column chromatography on silica (column size: 2.5 × 8 cm) and dried in membrane-pump vacuum.

General procedure for the synthesis of imidazolium salts 16a–16d

To **3a–c** (0.5 g) dissolved in acetonitrile (50 mL) one eq of n-BuI (**12a**) or n-$C_8H_{17}I$ (**12b**) was added in a single portion and the reaction mixture was stirred at 70 °C for 5 (**12a**) or 14 (**12b**) days. The progress of the reaction was monitored using ^{1}H NMR spectroscopy. After completion of the reaction the solvent was removed in membrane-pump vacuum. The crude product was washed five times with diethyl ether (10 mL portions) and dried in membrane-pump vacuum.

Synthesis of 1-phenyl-2-(diphenylphosphino)-3-*n*-octyl-4,5-dimethyl-1*H*-imidazolium hexafluorophosphate (17a)

To **16d** (0.30 g, 0.73 mmol) in dry dichloromethane (30 mL), n-BuLi (0.30 mL, 0.75 mmol) was added dropwise at −78 °C. The reaction mixture was stirred for 45 min at this temperature, followed by dropwise addition of chlorodiphenylphosphine (0.14 mL, 0.78 mmol). After warming the mixture to ambient temperature, all volatile materials were removed in membrane-pump vacuum and the residue was dissolved in acetone (20 mL). Then a solution of potassium hexafluorophosphate (0.14 g, 0.76 mmol) in water (20 mL) was added in a single portion and the mixture was stirred at ambient temperature for an additional hour. After removal of all volatiles, the residue was purified by column chromatography (column size: 2.5 × 12 cm) on silica using diethyl ether as eluent. Phosphine **17a** was obtained as a colourless solid. Yield: 0.30 g (0.49 mmol, 67% based on **16d**). Anal. Calcd for $C_{31}H_{38}F_6N_2P$ (614.58 g mol^{-1}): C, 60.58; H, 6.23; N, 4.56. Found: C, 60.50; H, 6.53; N, 4.25. Mp.: 92 °C. IR (KBr, $\tilde{\nu}$/cm^{-1}): 1436 (m, P–C), 1499 (m, N═C), 1595/1632 (w, C═C), 2855/2927/2953 (m, C–H), 3058 (w,═C–H). ^{1}H NMR (500.30 MHz, $CDCl_3$, δ): 0.86 (t, $^3J_{HH}$ = 7.2 Hz, 3 H, $CH_2(CH_2)_6CH_3$), 1.07–1.25 (m, 10 H, $CH_2(CH_2)_6CH_3$), 1.35–1.41 (m, 2 H, $CH_2(CH_2)_6CH_3$), 1.97 (s, 3 H, CH_3), 2.41 (s, 3 H, CH_3), 4.15 (m, 2 H, $CH_2(CH_2)_6CH_3$), 6.99 (dpt, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 1.9 Hz, $^5J_{HP}$ = 1.2 Hz, 2 H, H^o/C_6H_4), 7.18–7.23 (m, 6 H, H^{m,p}/C_6H_5–P), 7.33–7.37 (m, 7 H, H^o/C_6H_5–P + H^{m,p}/C_6H_5). ^{13}C{^{1}H} NMR (125.81 MHz, $CDCl_3$, δ): 9.5 (s, CH_3), 9.7 (s, CH_3), 14.2 (s, $CH_2(CH_2)_6CH_3$), 22.7 (s, $CH_2(CH_2)_6CH_3$), 26.6 (s, $CH_2(CH_2)_6CH_3$), 28.9 (s, $CH_2(CH_2)_6CH_3$), 29.0 (s, $CH_2(CH_2)_6CH_3$), 29.7 (s, $CH_2(CH_2)_6CH_3$), 31.7 (s, $CH_2(CH_2)_6CH_3$), 47.9 (d, $^3J_{CP}$ = 10.6 Hz, $CH_2(CH_2)_6CH_3$), 127.7 (s, C^4/C_3N_2), 128.8 (d, $^4J_{CP}$ = 6.6 Hz, C^o/C_6H_5), 129.6 (d, $^3J_{CP}$ = 7.3 Hz, C^m/C_6H_5–P), 129.9 (s, C^p/C_6H_5), 130.4 (s, C^m/C_6H_5), 130.5 (s, C^p/C_6H_5–P), 131.0 (s, C^5/C_3N_2), 132.9 (d, $^2J_{CP}$ = 20.2 Hz, C^o/C_6H_5–P), 133.0 (m, C^i/C_6H_5–P), 133.9 (d, $^3J_{CP}$ = 1.2 Hz, C^i/C_6H_5), 141.1 (d, $^1J_{CP}$ = 54.0 Hz, C^2/C_3N_2). ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, δ): −144.6 (sept, $^1J_{PF}$ = 712.5 Hz, PF_6), −23.5 (s, $P(C_6H_5)_2$). HRMS (ESI-TOF) $[C_{31}H_{38}N_2P]PF_6$ [M]$^+$ *m*/*z*: calcd: 469.2767, found: 469.2767.

Synthesis of 1-phenyl-2-(dicyclohexylphosphino)-3-*n*-octyl-4,5-dimethyl-1*H*-imidazolium hexafluorophosphate (17b)

Compound **16d** (0.50 g, 1.21 mmol) was dissolved in dry dichloromethane (40 mL) and cooled to −78 °C. n-BuLi (0.48 mL, 1.20 mmol) was added dropwise and the reaction mixture was stirred for 45 min at this temperature. After dropwise addition of chlorodicyclohexylphosphine (0.27 mL, 1.22 mmol) the reaction mixture was warmed up to ambient temperature. Then all volatiles were removed in vacuum and the residue was dissolved in acetone (20 mL). A solution of potassium hexafluorophosphate (0.22 g, 1.20 mmol) in water (20 mL) was added dropwise and the mixture was stirred at ambient temperature for 1 h. The solvent was removed in membrane-pump vacuum and the crude product was purified by column chromatography (column size: 2.5 × 12 cm) on silica using diethyl ether as eluent. Phosphine **17b** was obtained as a colourless solid. Yield: 0.54 g (0.86 mmol, 72% based on **16d**). Anal. Calcd for $C_{31}H_{50}F_6N_2P$ (626.68 g mol^{-1}): C, 59.41; H, 8.04; N, 4.47. Found: C, 59.58; H, 8.21; N, 4.32. Mp.: 58 °C. IR (NaCl, $\tilde{\nu}$/cm^{-1}): 1450 (m, P–C), 1500 (m, N═C), 1595/1635 (w, C═C), 2853/2927 (s, C–H), 3067 (w,═C–H). ^{1}H NMR (500.30 MHz, $CDCl_3$, δ): 0.86 (t, $^3J_{HH}$ = 7.1 Hz, 3 H, $CH_2(CH_2)_6CH_3$), 1.05–1.19 (m, 10 H, $CH_2(CH_2)_6CH_3$ + C_6H_{11}), 1.27–1.44 (m, 12 H, $CH_2(CH_2)_6CH_3$ + C_6H_{11}), 1.60–1.65 (m, 8 H, $CH_2(CH_2)_6CH_3$ + C_6H_{11}), 1.74–1.78 (m, 4 H, $CH_2(CH_2)_6CH_3$ + C_6H_{11}), 1.92 (s, 3 H, C_3N_2), 2.34 (s, 3 H, C_3N_2), 4.31 (m, 2 H, $CH_2(CH_2)_6CH_3$), 7.29 (d, $^3J_{HH}$ = 7.4 Hz, 2 H, H^o/C_6H_5), 7.60–7.66 (m, 3 H, H^{m,p}/C_6H_5). ^{13}C{^{1}H} NMR (125.81 MHz, $CDCl_3$, δ): 9.4 (s, CH_3), 9.4 (s, CH_3), 14.1 (s, $CH_2(CH_2)_6CH_3$), 22.6 (s, $CH_2(CH_2)_6CH_3$), 25.6 (s, C_6H_{11}), 26.2 (d, J_{CP} = 1.3 Hz, C_6H_{11}), 26.3 (d, J_{CP} = 6.9 Hz, C_6H_{11}), 26.5 (s, $CH_2(CH_2)_6CH_3$), 28.9 (s, $CH_2(CH_2)_6CH_3$), 29.0 (s, $CH_2(CH_2)_6CH_3$), 30.2 (s, $CH_2(CH_2)_6CH_3$), 31.1 (d, J_{CP} = 9.1 Hz, C_6H_{11}), 31.7 (d, J_{CP} = 23.5 Hz, C_6H_{11}), 31.7 (s, $CH_2(CH_2)_6CH_3$), 35.0 (d, $^1J_{CP}$ = 11.2 Hz, C^1/ C_6H_{11}), 47.4 (d, $^3J_{CP}$ = 17.1 Hz, $CH_2(CH_2)_6CH_3$), 127.4 (m, C^o/C_6H_5), 129.9 (s, C^p/C_6H_5), 130.3 (s, C^m/C_6H_5), 131.6 (m, C^4/C_3N_2), 132.3 (d, $^3J_{CP}$ = 1.7 Hz, C^5/C_3N_2), 134.1 (m, C^i/C_6H_5), 143.3 (d, $^1J_{CP}$ = 61.7 Hz, C^2/C_3N_2). ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, δ): −144.6 (sept, $^1J_{PF}$ = 712.5 Hz, PF_6), −13.8 (s, $P(C_6H_5)_2$). HRMS (ESI-TOF) $[C_{31}H_{50}N_2P]PF_6$ [M]$^+$ *m*/*z*: calcd: 481.3706, found: 481.3679.

Synthesis of [(1-(4-Br-C_6H_4)-^{c}$C_3H_2N_2$-3-n-Bu)$_2$$PdI_2$] (19)

To **16a** (106 mg, 0.26 mmol) dissolved in dry tetrahydrofuran (10 mL) a solution of potassium *tert*-butoxide (58 mg, 0.53 mmol, 2 eq) in dry tetrahydrofuran (5 mL) was added dropwise at ambient temperature. After stirring the solution for 2 h, [$PdCl_2$(cod)] (37 mg, 0.13 mmol) was added in a single portion and the mixture was stirred for additional 16 h. All volatiles were removed in membrane-pump vacuum and the residue was dissolved in chloroform and filtered through a pad of Celite. By slow evaporation in membrane-pump vacuum at 0 °C two different types of crystals (pale yellow plates and colourless needles) suitable for X-ray diffraction analysis could be isolated.

Synthesis of 1-(4-(diphenylphosphino)phenyl)-3-*n*-octyl-4,5-dimethyl-1*H*-imidazolium hexafluorophosphate (20)

Diphenylphosphine (0.18 mL, 1.03 mmol) was added in a single portion to a dimethyl acetamide solution (30 mL) containing **16c** (0.5 g, 0.93 mmol), potassium acetate (109 mg, 1.11 mmol, 1.2 eq) and [$Pd(OAc)_2$] (2.1 mg, 1.0 mol%) and stirred for 2 h at 130 °C. After cooling the reaction mixture to ambient temperature, all volatile materials were removed in vacuum and the residue was dissolved in acetone (10 mL). Then a solution of potassium hexafluorophosphate (172 mg, 0.93 mmol) in water (10 mL) was added in a single portion and the mixture was stirred at ambient temperature for 1 h. The solvent was removed in membrane-pump vacuum and the residue was purified by column chromatography (column size: 2.5 × 12 cm) on silica using a mixture of acetone–diethyl ether (ratio 1 : 1, v:v). Ionic phosphine **20** could be isolated as colourless solid. Yield: 0.36 g (0.59 mmol, 63% based on **16c**). Anal. Calcd for $C_{31}H_{38}F_6N_2P$ (614.58 g mol^{-1}): C, 60.58; H, 6.23; N, 4.56. Found: C, 60.60; H, 6.24; N, 4.31. Mp.: 138 °C. IR (KBr, $\tilde{\nu}$/cm^{-1}): 1434 (m, P–C), 1560 (s, N═C), 1595/1634 (w, C═C), 2855/2925/2951 (s, C–H), 3056/3070/3160 (w,═C–H). ^{1}H NMR (500.30 MHz, $CDCl_3$, δ): 0.86 (t, $^3J_{HH}$ = 7.2 Hz, 3 H, $CH_2(CH_2)_6CH_3$), 1.20–1.38 (m, 10 H, $CH_2(CH_2)_6CH_3$), 1.84 (pent, $^3J_{HH}$ = 7.3 Hz, 2 H, $CH_2(CH_2)_6CH_3$), 2.13 (s, 3 H, CH_3), 2.29 (s, 3 H, CH_3), 4.10 (t, $^3J_{HH}$ = 7.8 Hz, 2 H, $CH_2(CH_2)_6CH_3$), 7.31–7.38 (m, 12 H, $H^{o,m,p}/C_6H_5$+H^m/C_6H_4), 7.40–7.43 (m, 2 H, H^o/C_6H_4). ^{13}C{^{1}H} NMR (125.81 MHz, $CDCl_3$, δ): 8.5 (s, CH_3), 9.1 (s, CH_3), 14.1 (s, $CH_2(CH_2)_6CH_3$), 22.7 (s, $CH_2(CH_2)_6CH_3$), 26.4 (s, $CH_2(CH_2)_6CH_3$), 29.0 (s, $CH_2(CH_2)_6CH_3$), 29.1 (s, $CH_2(CH_2)_6CH_3$), 29.5 (s, $CH_2(CH_2)_6CH_3$), 31.8 (s, $CH_2(CH_2)_6CH_3$), 47.8 (s, $CH_2(CH_2)_6CH_3$), 125.9 (d, $^3J_{CP}$ = 6.3 Hz, C^o/C_6H_4), 127.7 (s, C_3N_2), 128.0 (s, C_3N_2), 129.0 (d, $^3J_{CP}$ = 7.3 Hz, C^m/C_6H_5), 129.5 (s, C^p/C_6H_5), 133.2 (s, C^i/C_6H_4), 133.3 (s, C^2/C_3N_2), 134.1 (d, $^2J_{CP}$ = 20.1 Hz, C^o/C_6H_5), 134.9 (d, $^2J_{CP}$ = 19.2 Hz/C^m/C_6H_4), 135.8 (d, $^1J_{CP}$ = 10.6 Hz, C^i/C_6H_5), 142.3 (d, $^1J_{CP}$ = 16.5 Hz, C^p/C_6H_4). ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, δ): −144.5 (sept, $^1J_{PF}$ = 712.6 Hz, PF_6), −5.4 (s, $P(C_6H_5)_2$). HRMS (ESI-TOF) $[C_{31}H_{38}N_2P]^+$ $[M]^+$ *m*/*z*: calcd: 469.2767, found: 469.2739.

General procedure for the Suzuki reaction

2-Bromo toluene (500 mg, 2.92 mmol), phenylboronic acid (470 mg, 3.85 mmol), potassium carbonate (1.21 g, 8.76 mmol) and acetyl ferrocene (111 mg, 0.49 mmol) were dissolved in a 1,4-dioxane–water mixture (10 mL, ratio 2 : 1, v:v). After addition of 0.25 mol% of [$Pd(OAc)_2$] and 0.5 mol% of the appropriate phosphine (**11**, **17**, **20**), the reaction mixture was stirred for 1 h at 100 °C. Samples of 1 mL were taken after 2.5, 5, 10, 20, 30, and 60 min and chromatographed on silica gel (column size: 6 × 2.5 cm) using diethyl ether as eluent. All volatiles were evaporated under reduced pressure and the conversions were determined by ^{1}H NMR spectroscopy.

General procedure for the Suzuki reaction in ionic liquids

Phenylboronic acid (470 mg, 3.85 mmol), potassium carbonate (1.21 g, 8.76 mmol), acetyl ferrocene (111 mg, 0.49 mmol), 0.25 mol% of [$Pd(OAc)_2$] and 0.5 mol% of the appropriate phosphine (**17b**, **20**) were dissolved in [BMIM][PF_6] (7.0 g, 24.6 mmol) or [BDMIM][BF_4] (6.0 g, 25.0 mmol), followed by the addition of degassed water (5 mL). After stirring of the reaction mixture for 5 min at ambient temperature, 2-bromo toluene (500 mg, 2.92 mmol) was added in a single portion and the mixture was stirred for 60 min at 100 °C. After cooling down to ambient temperature the reaction mixture was continuously extracted with n-pentane until no more colouring of the solution was observable. In the case of [BMIM][PF_6], the water layer was removed and the ionic liquid was washed once with water (10 mL) and then was used in the next run. The [BDMIM][BF_4] solution was used without further purification in the 2nd run. Finally, the n-pentane solution was evaporated in membrane-pump vacuum and the conversion was determined by ^{1}H NMR spectroscopy.

General procedure for the Suzuki coupling of aryl chlorides

4-Chloro toluene (379 mg, 3.0 mmol), phenylboronic acid (550 mg, 4.5 mmol, 1.5 eq), potassium phosphate (1.27 g, 6.0 mmol, 3 eq) and acetyl ferrocene (114 mg, 0.50 mmol) were dissolved in toluene (6 mL). After addition of 0.01 mol% [$Pd(OAc)_2$] and 0.1 mol% of the appropriate phosphine (**11d**, **11e**), the reaction mixture was stirred for 20 h at 100 °C. Afterwards, a sample of 2 mL was taken and filtered through a pad of Celite. After evaporation of all volatiles under reduced pressure, the conversions were determined by ^{1}H NMR spectroscopy.

General procedure for the synthesis of sterically hindered biaryls

Phenylboronic acid (183 mg, 1.5 mmol, 1.5 eq), potassium phosphate (0.64 g, 3.0 mmol, 3.0 eq), acetyl ferrocene (114 mg, 0.50 mmol) 0.05 mol% [$Pd_2(dba)_3$] and 0.1 mol% of **11e** were dissolved in toluene (2 mL). Afterwards, the appropriate aryl bromide (1.0 mmol, 1.0 eq) was added in a single portion and the reaction mixture was stirred for 24 h at 50 °C. Afterwards, the reaction mixture was filtered through a pad of Celite and the solvent was removed in membrane-pump vacuum. The conversions were determined by ^{1}H NMR spectroscopy.

Table 7 Crystal and intensity collection data for **11a-Se**, *trans*-**19** and *cis*-**19**

	11a-Se	*trans*-**19**	*cis*-**19**
Formula weight	486.20	918.56	1037.93
Chemical formula	$C_{21}H_{16}BrN_2PSe$	$C_{26}H_{30}Br_2I_2N_4Pd$	$C_{27}H_{31}Br_2Cl_3I_2N_4Pd$
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	14.6515(2)	8.7047(5)	16.3428(11)
b (Å)	6.86120(10)	12.7269(6)	16.6465(12)
c (Å)	19.3482(3)	14.2494(7)	19.6587(15)
α (°)		78.787(4)	88.435(6)
β (°)	96.639(2)	82.971(4)	79.579(6)
γ (°)		74.495(4)	79.799(6)
V (Å^3)	1931.97(5)	1487.97(13)	5176.7(6)
ρ_{calc} (mg m^{-3})	1.672	2.050	1.998
$F(000)$	960	872	2964
Crystal dimensions (mm)	0.4 × 0.2 × 0.2	0.35 × 0.35 × 0.08	0.10 × 0.03 × 0.02
Z	4	2	6
Max. and min. transmission	1.00000, 0.37259	1.00000, 0.55328	1.00000, 0.25423
Absorption coefficient (λ, mm^{-1})	5.885	5.405	23.419
Scan range (°)	4.60–62.00	3.20–26.12	3.28–62.00
Index ranges	$-16 \le h \le 16$	$-9 \le h \le 10$	$-11 \le h \le 18$
	$-7 \le k \le 7$	$-15 \le k \le 14$	$-12 \le k \le 19$
	$-21 \le l \le 22$	$-11 \le l \le 17$	$-22 \le l \le 22$
Total reflections	7108	9837	23957
Unique reflections	2999	5836	14 330
R_{int}	0.0191	0.0237	0.0603
Data/restraints/para-meters	2999/0/235	5836/0/316	14 330/670/1112
Goodness-of-fit on F^2	1.060	0.927	0.893
R_1 [a], wR_2 [a] [I 2$\sigma(I)$]	0.0253, 0.0659	0.0248, 0.0519	0.0997, 0.2499
R_1 [a], wR_2 [a] (all data)	0.0283, 0.0671	0.0344, 0.0531	0.1714, 0.2796
Largest differences in peak and hole peak in final Fourier map (e Å^{-3})	0.669, −0.620	0.757, −0.668	3.955, −1.841

[a] $R_1 = [\Sigma(||F_o| - |F_c||)/\Sigma|F_o|]$; $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(wF_o^4)]^{1/2}$; $S = [\Sigma w(F_o^2 - F_c^2)^2]/(n - p)^{1/2}$. n = number of reflections, p = parameters used.

Crystal structure determination

The crystal and intensity collection data for **11a-Se**, *trans*-**19** and *cis*-**19** are summarised in Table 7. All data were collected on an Oxford Gemini S diffractometer with graphite monochromatised Mo K_α radiation (λ = 0.71073 Å) at 105 K (*trans*-**19**) and graphite monochromatised Cu K_α radiation (λ = 1.54184 Å) at 100 K (**11a-Se**, *cis*-**19**). The structures were solved by direct methods using SHELXS-91[28] and refined by full-matrix least-square procedures on F^2 using SHELXL-97.[29] All non-hydrogen atoms were refined anisotropically and a riding model was employed in the refinement of the hydrogen atom positions. For *cis*-**19** the crystal available for measuring was comparatively tiny and needed the use of Cu K_α radiation in order to get reasonable results. At higher diffraction angles large exposure times have been used, leading to an 'icing' of the crystal. The measurement was therefore stopped and hence, the ratio between unique to observed reflections is almost poor. As no further crystals were available no re-measurement could be performed. Despite this, all non-hydrogen atoms could be refined anisotropically and a number of fragments could be refined disordered over two positions. Occupation factors: 0.17/0.83 for Pd3, I5, I6/Pd3′, I5′, I6′. 0.49/0.51 for C71–C73/C71′–C73′. 0.75/0.25 for C33, C34/C33′/C34′. 0.48/0.52 for C58–C60/C58′–C60′. 0.39/0.61 for C80, Cl1–Cl3/C80′, Cl1′–Cl3′. Trials to introduce further disordered fragments did not give reliable results, which is attributed to the already poor data-to-parameter ratio.

Acknowledgements

We are grateful to Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous financial support. Furthermore, we would like to thank Sabrina Krauße and Martina Steinert for assistance in the lab.

References

1 (*a*) H. Willms, W. Frank and C. Ganter, *Organometallics*, 2009, **28**, 3049–3058; (*b*) J. Li, J. Peng, Y. Bai, G. Zhang, G. Lai and X. Li, *J. Organomet. Chem.*, 2010, **695**, 431–436; (*c*) S. Sauerbrey, P. K. Majhi, J. Daniels, G. Schnakenburg, G. M. Brändle, K. Scherer and R. Streubel, *Inorg. Chem.*, 2011, **50**, 793–799; (*d*) Q.-X. Wan, Y. Liu and Y.-Q. Cai, *Catal. Lett.*, 2009, **127**, 386–391; (*e*) D. J. Brauer, K. W. Kottsieper, C. Liek, O. Stelzer, H. Waffenschmidt and P. Wasserscheid, *J. Organomet. Chem.*, 2001, **630**, 177–184; (*f*) S. S. Moore and G. M. Whitesides, *J. Org. Chem.*, 1982, **47**, 1489–1493; (*g*) V. Diez, G. Espino, F. A. Jalon, B. R. Manzano and M. Perez-Manrique, *J. Organomet. Chem.*, 2007, **692**, 1482–1495; (*h*) M. A. Jalil, S. Fujinami, T. Honjo and H. Nishikawa, *Polyhedron*, 2001, **20**, 1071–1078.

2 (*a*) T. L. Gilchrist, in *Heterocyclenchemie*, ed. H. Neunhoeffer, Wiley-VCH, Weinheim, 1995, pp. 300–306; (*b*) T. Schulz, C. Torborg, B. Schäffner, J. Huang, A. Zapf, R. Kadyrov, A. Börner and M. Beller, *Angew. Chem., Int. Ed.*, 2009, **48**, 918–921; (*c*) M. R. Grimmett, in *Science of Synthesis – Five Membered Heteroarenes with two Nitrogen or Phosphorus Atoms*, ed. R. Neier, Thieme, Stuttgart, New York, 2002, vol. 12, pp. 325–331; (*d*) J. Liu, J. Chen, J. Zhao, Y. Zhao, L. Li and H. Zhang, *Synthesis*, 2003, 2661–2666.

3 For example: (*a*) A. Dumrath, X.-F. Wu, H. Neumann, A. Spannenberg, R. Jackstell and M. Beller, *Angew. Chem., Int. Ed.*, 2010, **49**, 8988–8992; (*b*) S. Harkal, F. Rataboul, A. Zapf, C. Fuhrmann, T. Riermeier, A. Monsees and M. Beller, *Adv. Synth. Catal.*, 2004, **346**, 1742–1748;

(*c*) J. Sirieix, M. Oßberger, B. Betzemeier and P. Knochel, *Synlett*, 2000, **11**, 1613–1615; (*d*) N. Debono, Y. Canac, C. Duhayon and R. Chauvin, *Eur. J. Inorg. Chem.*, 2008, 2991–2999; (*e*) C. Torborg, J. Huang, T. Schulz, B. Schäffner, A. Zapf, A. Spannenberg, A. Börner and M. Beller, *Chem.–Eur. J.*, 2009, **15**, 1329–1336.

4 S. Saleh, E. Fayad, M. Azouri, J.-C. Hierso, J. Andrieu and M. Picquet, *Adv. Synth. Catal.*, 2009, **351**, 1621–1628.

5 (*a*) S. Ahrens, E. Herdtweck, S. Goutal and T. Strassner, *Eur. J. Inorg. Chem.*, 2006, 1268–1274; (*b*) Y. Canac, N. Debono, L. Vendier and R. Chauvin, *Inorg. Chem.*, 2009, **48**, 5562–5568; (*c*) M. Azouri, J. Andrieu, M. Picquet and H. Cattey, *Inorg. Chem.*, 2009, **48**, 1236–1242; (*d*) J.-C. Shi, P.-Y. Yang, Q. Tong, Y. Wu and Y. Peng, *J. Mol. Catal. A: Chem.*, 2006, **259**, 7–10; (*e*) E. Amigues, C. Hardacre, G. Keane, M. Migaud and M. O'Neill, *Chem. Commun.*, 2006, 72–74.

6 (*a*) C. S. Consorti, G. L. P. Aydos, G. Ebeling and J. Dupont, *Org. Lett.*, 2008, **10**, 237–240; (*b*) J. Andrieu and M. Azouri, *Inorg. Chim. Acta*, 2007, **360**, 131–135; (*c*) P. J. Dyson and T. J. Geldbach, in *Catalysis by Metal Complexes-Metal Catalyzed Reactions in Ionic Liquids*, ed. B. James and P. W. N. M. van Leeuwen, Springer, Dordrecht, 2005, vol. 29; (*d*) P. Wasserscheid and T. Welton, *Ionic Liquids in Synthesis*, Wiley-VCH, Weinheim, 2nd edn, 2008, vol. 1; (*e*) J. Zhang, M. Dakovic, Z. Popovic, H. Wu and Y. Liu, *Catal. Commun.*, 2012, **17**, 160–163.

7 (*a*) R. Sanders and U. T. Müller-Westerhoff, *J. Organomet. Chem.*, 1996, **512**, 219–224; (*b*) U. T. Müller-Westerhoff, Z. Yang and G. Ingram, *J. Organomet. Chem.*, 1993, **463**, 163–167.

8 O. Herd, A. Heßler, M. Hingst, M. Tepper and O. Stelzer, *J. Organomet. Chem.*, 1996, **522**, 69–76.

9 (*a*) R. P. Pinnell, C. A. Megerle, S. L. Manatt and P. A. Kroon, *J. Am. Chem. Soc.*, 1973, **95**, 977–978; (*b*) D. W. Allen and B. F. Taylor, *J. Chem. Soc., Dalton Trans.*, 1982, 51–54; (*c*) D. W. Allen and I. W. Nowell, *J. Chem. Soc., Dalton Trans.*, 1985, 2505–2508; (*d*) A. Suarez, M. A. Mendez-Rojas and A. Pizzano, *Organometallics*, 2002, **21**, 4611–4621; (*e*) D. J. M. Snelders, C. van der Burg, M. Lutz, A. L. Spek, G. van Koten and R. J. M. Klein Gebbink, *ChemCatChem*, 2010, **2**, 1425–1437; (*f*) S. Jeulin, S. Duprat de Paule, V. Ratovelomanana-Vidal, J.-P. Genet, N. Champion and P. Dellis, *Angew. Chem., Int. Ed.*, 2004, **43**, 320–325; (*g*) B. Milde, M. Lohan, C. Schreiner, T. Rüffer and H. Lang, *Eur. J. Inorg. Chem.*, 2011, 5437–5449; (*h*) A. Jakob, B. Milde, P. Ecorchard, C. Schreiner and H. Lang, *J. Organomet. Chem.*, 2008, **693**, 3821–3830; (*i*) B. Milde, D. Schaarschmidt, P. Ecorchard and H. Lang, *J. Organomet. Chem.*, 2012, DOI: 10.1016/j.jorganchem.2012.01.017.

10 For example: (*a*) O. Schuster, L. Yang, H. G. Raubenheimer and M. Albrecht, *Chem. Rev.*, 2009, **109**, 3445–3478; (*b*) S. Diez-Gonzalez, N. Marion and S. P. Nolan, *Chem. Rev.*, 2009, **109**, 3612–3676.

11 F. Barriere, R. U. Kirss and W. E. Geiger, *Organometallics*, 2005, **24**, 48–52.

12 G. Gritzner and J. Kuta, *Pure Appl. Chem.*, 1984, **56**, 461–466.

13 B. Gorodetsky, T. Ramnial, N. R. Branda and J. A. C. Clyburne, *Chem. Commun.*, 2004, 1972–1973.

14 P. W. Kodding and K. A. Kerr, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1979, **35**, 1261–1263.

15 (*a*) W. A. Herrmann, M. Elison, J. Fischer, C. Kocher and G. R. J. Artus, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2371–2374; (*b*) A. Flahaut, K. Toutah, P. Mangeney and S. Roland, *Eur. J. Inorg. Chem.*, 2009, 5422–5432; (*c*) X. Xu, B. Xu, Y. Li and S. H. Hong, *Organometallics*, 2010, **29**, 6343–6349.

16 O. V. Gusev, T. A. Peganova, A. M. Kalsin, N. V. Vologdin, P. V. Petrovskii, K. A. Layssenko, A. V. Tsvetkov and I. P. Beletskaya, *Organometallics*, 2006, **25**, 2750–2760.

17 B. Milde, R. Packheiser, S. Hildebrandt, D. Schaarschmidt, T. Rüffer and H. Lang, *Organometallics*, 2011, submitted.

18 (*a*) J. P. Wolfe, R. A. Singer, B. H. Yang and S. L. Buchwald, *J. Am. Chem. Soc.*, 1999, **121**, 9550–9561; (*b*) A. Zapf, A. Ehrentraut and M. Beller, *Angew. Chem., Int. Ed.*, 2000, **39**, 4153–4155; (*c*) A. F. Littke, C. Dai and G. C. Fu, *J. Am. Chem. Soc.*, 2000, **122**, 4020–4028; (*d*) S. D. Walker, T. E. Barder, J. R. Martinelli and S. L. Buchwald, *Angew. Chem., Int. Ed.*, 2004, **43**, 1871–1876.

19 (*a*) D. Schaarschmidt and H. Lang, *Eur. J. Inorg. Chem.*, 2010, 4811–4821; (*b*) D. Schaarschmidt and H. Lang, *ACS Catal.*, 2011, **1**, 411–416.

20 (*a*) L. Magna, Y. Chauvin, G. P. Niccolai and J.-M. Basset, *Organometallics*, 2003, **22**, 4418–4425; (*b*) V. K. Aggarwal, I. Emme and A. Mereu, *Chem. Commun.*, 2002, 1612–1613; (*c*) C. J. Mathews, P. J. Smith, T. Welton, A. J. P. White and D. J. Williams, *Organometallics*, 2001, **20**, 3848–3850.

21 E. Gelens, F. J. J. De Kanter, R. F. Schmitz, L. A. J. M. Sliedregt, B. J. Van Steen, C. G. Kruse, R. Leurs, M. B. Groen and R. V. A. Orru, *Mol. Diversity*, 2006, **10**, 17–22.

22 H. M. Colquhoun, J. Holton, D. J. Thompson and M. V. Twigg, *New Pathways for Organic Synthesis-Practical Applications of Transition Metals*, Plenum Press, New York, 1983, p. 383.

23 J. Polin and H. Schottenberger, *Org. Synth.*, 1996, **73**, 262–267.

24 D. Drew and J. R. Doyle, *Inorg. Synth.*, 1990, **28**, 348–349.

25 T. Imamoto, T. Oshiki, T. Onozawa, T. Kusumoto and K. Sato, *J. Am. Chem. Soc.*, 1990, **112**, 5244–5252.

26 H. Tomori, J. M. Fox and S. L. Buchwald, *J. Org. Chem.*, 2000, **65**, 5334–5341.

27 N. G. Andersen, R. McDonald and B. A. Keaya, *Tetrahedron:Asymmetry*, 2001, **12**, 263–269.

28 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **46**, 467–473.

29 G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, 1997.

