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Structural variation, dynamics, and catalytic application of palladium(II) complexes of di-N-heterocyclic carbene-amine ligands

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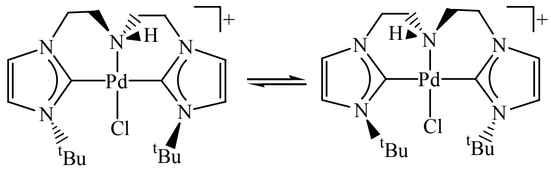
A series of palladium(II) complexes incorporating di-NHC amine ligands has been prepared and their structural, dynamic and catalytic behaviour investigated. The complexes [*trans*-(κ^2-^{tBu}*C*N(Bn)*C*^{tBu})$PdCl_2$] (**12**) and [*trans*-(κ^2-^{Mes}*C*N(H)*C*^{Mes})$PdCl_2$] (**13**) do not exhibit interaction between the amine nitrogen and palladium atom respectively. NMR spectroscopy between –40 and 25 °C shows that the di-NHC amine ligand is flexible expressing C_s symmetry and for **13** rotation of the mesityl groups is prevented. In the related C_1 complex [(κ^3-^{tBu}*CN*(H)*C*^{tBu})PdCl][Cl] (**14**) coordination of NHC moieties and amine nitrogen atom is observed between –40 and 25 °C. Reaction between **12**–**14** and two equivalents $AgBF_4$ in acetonitrile gives the analogous complexes [*trans*-(κ^2-^{tBu}*C*N(Bn)*C*^{tBu})$Pd(MeCN)_2$][BF_4]$_2$ (**15**), [*trans*-(κ^2-^{Mes}*C*N(H)*C*^{Mes})$Pd(MeCN)_2$][BF_4]$_2$ (**16**) and [(κ^3-^{tBu}*CN*(H)*C*^{tBu})Pd(MeCN)][BF_4]$_2$ (**17**) indicating that ligand structure determines amine coordination. The single crystal X-ray structures of **12**, **17** and two ligand imidazolium salt precursors ^{tBu}C(H)N(Bn)C(H)^{tBu}][Cl]$_2$ (**2**) and [^{tBu}C(H)N(H)C(H)^{tBu}][BPh_4]$_2$ (**4**) have been determined. Complexes **12-14** and **15-17** have been shown to be active precatalysts for Heck and hydroamination reactions respectively.

The chemistry of N-heterocyclic carbenes (NHC) and their functionalised derivatives has developed significantly over the last ten years with perhaps the greatest emphasis on catalytic applications. Interest has partly arisen from the electronic properties of NHC as ligands, and catalytic performance of NHC metal complexes has been discussed mainly in the context of comparison to tertiary phosphines.[1] NHC also exhibit structural diversity via modification of substituents particularly at the N-atoms and consequently steric factors can also play an equally critical role in controlling reactivity most obviously in asymmetric reactions.[2] Several studies have also examined the dynamic behaviour of NHC ligand metal complexes elucidating rotation about the M-C_{NHC} bond[3] and ligand conformations of chelating NHC derivatives.[4]

This paper describes the synthesis, coordination chemistry, and some limited dynamics and catalytic applications of di-NHC-amine ligands. Previous reports describing di-NHC-N donor hybrid ligands predominantly incorporate pyridyl derivatives as the N-donor and several transition metal complexes have been prepared that exhibit good catalytic activity and long lifetimes, most notably for C-C coupling,[4b, 5, 6] and alkene oligomerisation.[7]

Several studies have also addressed the coordination chemistry and dynamic properties of di-NHC ligands that contain hydrocarbyl and N-donor containing linking groups. It has been shown that as the length of the linker increases trans coordination is generally preferred and bridging between two metal atoms can occur.[8] Dynamic studies include cationic complexes of di-NHC ligands incorporating a 2,6-lutidinyl linker that exhibit fluxional behaviour between atopisomers where the rate is dependent on the size of NHC-N-substitutents and the counter anion.[4b, 4d, 9] Linker length has also been shown to have a significant effect on the reaction rate and selectivity of elimination from dialkyl complexes.[10]

In a previous study we communicated the synthesis of a palladium(II) complex (**14**) (eqn 1) of a di-NHC ligand that incorporates an amine linker and examined the mechanism and rate of atropisomerism *vide infra*.[11] Complex **14** could also be converted to an NHC-amido transition metal complex, via deprotonation of the palladium coordinated amine. Described here are subsequent complementary studies to expanded this chemistry via substitution at the amine nitrogen and NHC-N substituents, to compare coordination, dynamic and ultimately catalytic performance between di-NHC-amine ligand complexes.



(**14**) (eqn 1)

Results and Discussion

Ligands and metal complex synthesis. The synthetic routes to imidazolium salt precursors **2-5** used to prepare the complexes described in this paper are shown in scheme 1. Reaction between **1** and ^{t}Bu- or mesityl imidazole gave the corresponding diimidazolium salts **2** and **3** respectively that

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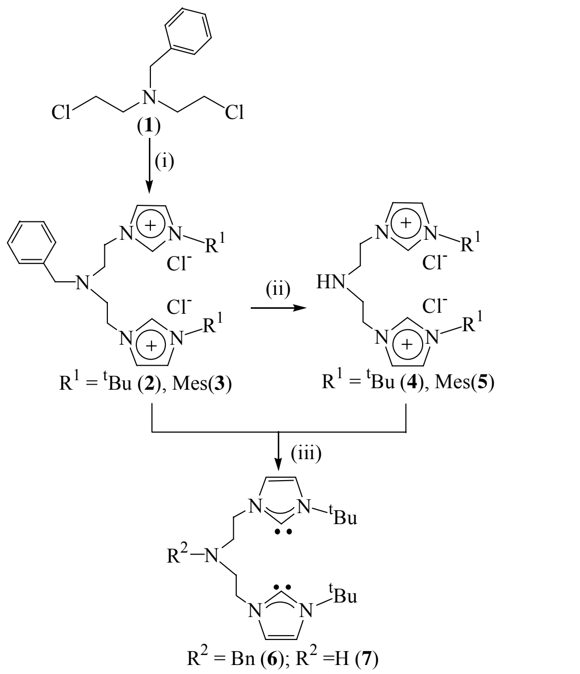
can be converted to the secondary amine derivatives **4** and **5** via hydrogenation. Compound **5** can also be prepared from reaction between mesityl imidazole and bis(2-dichloroethyl)amine hydrochloride,[12] however this route is not successful for the ^{t}Bu analogue. ^{1}H and ^{13}C NMR spectroscopic data for **2**-**5** obtained in D_2O show spectra consistent with C_s symmetry and in the ^{1}H NMR spectra, characteristic signals for the imidazolium salt NC(*H*)N protons are observed in the region δ 8.56-9.09 ppm. To corroborate the proposed structures, single crystal diffraction studies of **2** and a $[BPh_4]^-$ derivative of **4** were obtained. Unfortunately single crystal structures of **3** or **5** could not be grown and generally it was found that compounds containing mesityl substituents were obtained in lower yield, and their purification was more problematic, particularly so for the benzyl amine derivative **3**.

Molecular structures of the cations of **2** and **4** are shown in figure 1. The dications of both **2** and **4** exhibit conformations where the imidazolium moieties are eclipsed with respect to each other, but intra- and intermolecular distances are not indicative of directional bonding, and bond lengths and angles are considered unexceptional.†

Reaction between salts **2** or **4** and KO^{t}Bu showed that di-



Scheme 1. i) 2 equiv. R-imidazole, dioxane, 130 °C; ii) 10% Pd/C, H_2 (1 bar), ethanol, 65 °C; iii) 2 equiv. KO^{t}Bu, THF, 25 °C.

NHC-amines **6** and **7** could be prepared, however work-up gave sensitive viscous oils that were problematic to handle and therefore intermediate silver complexes were prepared for use as ligand transfer agents.[13]

Imidazolium salts **2**-**5** can cleanly be converted to the corresponding silver(I) chloride complexes via reaction with silver(I) oxide to give complexes **8**-**11**, that can subsequently act as ligand transfer agents to palladium as shown in scheme 2. ^{1}H and ^{13}C NMR spectroscopy of **8**-**11** are again consistent with C_s symmetry, for example in the ^{1}H NMR spectra the

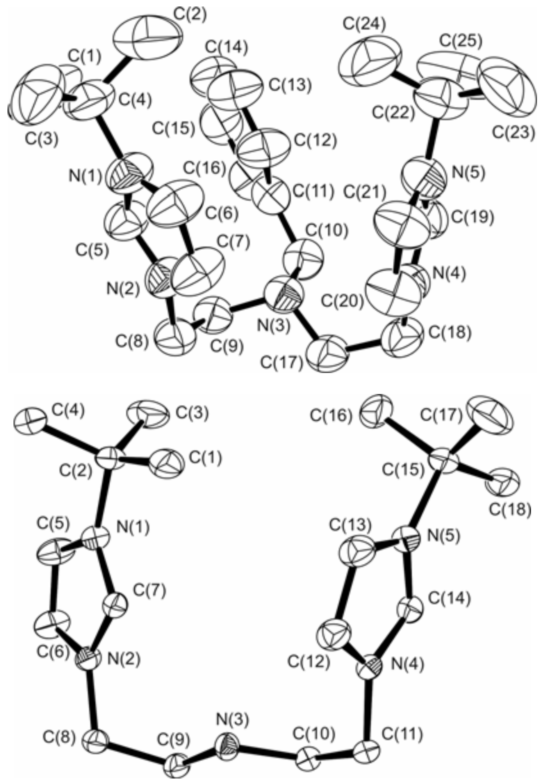
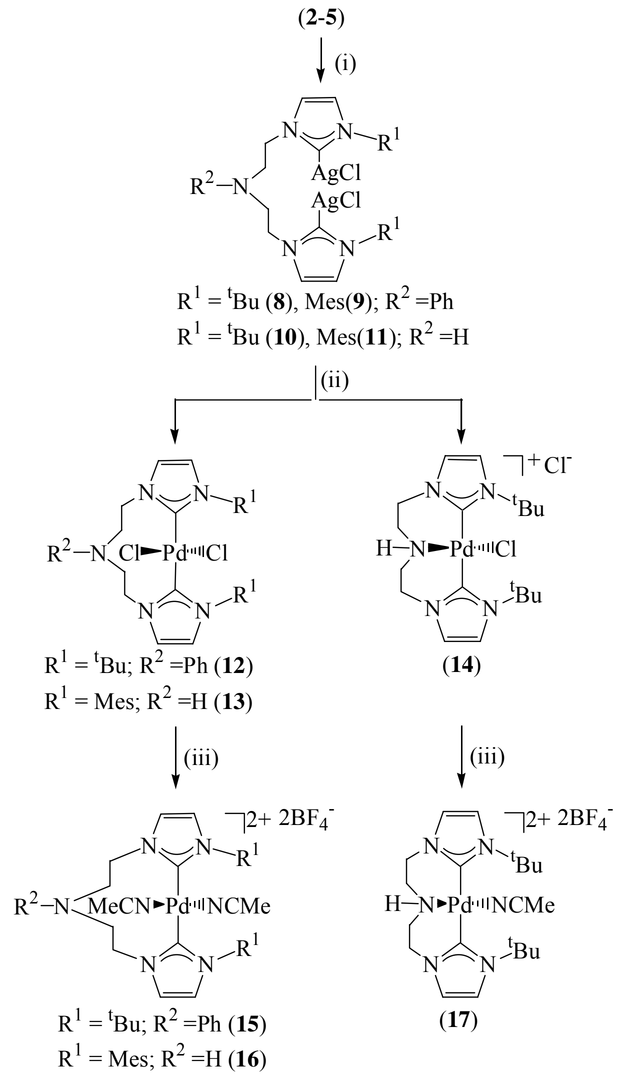


Fig. 1. Molecular structure of the cations of compounds **2** and **4**. Ellipsoids are shown at 50 % probability. Hydrogen atoms have been removed for clarity.

eight NCH_2CH_2N protons are observed as two triplets, and ^{t}Bu and mesityl derivatives give one and two signals respectively for N-substituent methyl groups.

Interest in the catalytic applications of ligands derived from **2**-**5** prompted us to prepare palladium complexes **12**-**14** (scheme 2) from reaction between **8**, **10** and **11** and $PdCl_2(MeCN)_2$. Reactions between **9** and $PdCl_2(MeCN)_2$ result in the immediate characteristic precipitation of AgCl, however a single complex could not be satisfactorily purified. ^{1}H NMR spectroscopy indicated possible formation of oligomers via coordiantionof ligand NHC moieties to two metals as judged by the presence of triplet signals attributable to ethylene CH_2 groups. Subsequent chemistry was therefore restricted to complexes derived from **2**, **4** and **5**.



Scheme 2. i) Ag_2O, CH_2Cl_2, 25 °C; ii) $PdCl_2(MeCN)_2$, CH_2Cl_2, 25 °C; iii) 2 equiv. $AgBF_4$, MeCN, 25 °C.

We have previously reported the single crystal structure determination and dynamic NMR behaviour of complex **14**, which showed that the ligand coordinates via NHC carbon and amine nitrogen atoms respectively, and interconversion between atropisomers occurs above –30 °C as shown in equation 1.[11] Below –30 °C the ^{1}H NMR spectrum displays signals consistent with C_1 symmetry including eight signals for the diastereotopic CH_2 protons, whereas at 25 °C signals consistent with C_s symmetry are observed including four very broad signals for the CH_2 protons.

In contrast, it was clear from the ^{1}H and ^{13}C NMR spectra that complexes **12** and **13** exhibit different dynamic behaviour to **14**. For **12** which differs in composition from **14** by containing a benzyl substituted tertiary nitrogen atom, the ^{1}H NMR spectrum shows signals between 25 and –40 °C consistent with C_s symmetry, including four broad signals for the non-benzylic CH_2 protons at 25 °C that on cooling to –40 °C resolve into four complex multiplet signals. The ^{13}C NMR spectrum contains two signals corresponding to the non-benzylic CH_2 carbons between 25 and -40 °C again consistent with C_s symmetry that correlate to the four NCH_2CH_2N ^{1}H signals in ^{13}C-^{1}H correlation spectra. Furthermore, the remaining ^{13}C NMR signals also reflect a mirror element parallel with the N-Pd-Cl vector that is perpendicular to the square plane. However, in contrast to all other NMR signals, the ^{1}H NMR spectrum at 25 °C, clearly shows diastereotopic benzylic CH_2 protons observed as an AB pair of doublets at δ 3.77 and 3.95 ppm indicative of **12** exhibiting C_1 symmetry.

Fortunately, single crystals of complex **12** allowed an X-ray structure determination, aiding interpretation of the NMR data. The molecular structure of complex **12** is shown in figure 2 and select data are given in table 1. A square planar geometry about the palladium atom is observed with bond lengths and angles typical of other trans-di-NHC complexes derived from chelating di-NHC ligands.[14] However, clearly in contrast to **14**, complex **12** is neutral, contains a ten-atom palladocycle and exhibits no bond between the palladium and amine nitrogen atoms. The ^{1}H and ^{13}C NMR data of **12** are rationalised as arising from limited flexibility within the palladocycle but that inversion at the amine nitrogen atom does not occur rapidly on the NMR timescale. Slow inversion and limited flexibility could render benzylic CH_2 protons diastereotopic and reflective of C_1 symmetry, whereas pairs of non-benzylic CH_2 protons are not sufficiently differentiated in chemical shift and appear as a single, though complex, signal indicative of C_s symmetry.

Unfortunately crystals suitable for a single crystal diffraction study of the N-mesityl substituted derivative **13** have yet to be grown to confirm the structure. Nevertheless **13** exhibits NMR spectra distinct from complex **14** and again indicative of a structure analogous to complex **12**. Distinctive features in the NMR spectra of complex **13** are signals attributable to the ethylene CH_2 and mesityl methyl groups respectively. For the ethylene CH_2 groups, **13** exhibits four signals in the ^{1}H NMR spectrum between 25 and – 40 °C each of which correlate to the two NCH_2CH_2N signals present in the ^{13}C NMR spectrum as observed for complex **12**. At all temperatures the mesityl methyl groups are observed as three

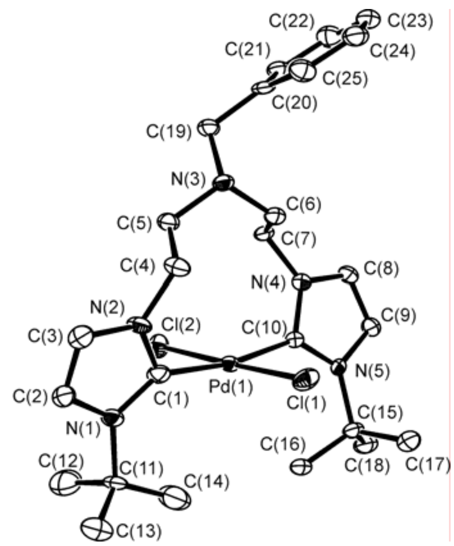


Fig. 2. Molecular structure of complex **12**. Ellipsoids are shown at 50 % probability. Hydrogen atoms have been removed for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for complexes **14** and **17.**

$[(^{tBu}CN(Bn)C^{tBu})PdCl_2]$ **14**	
Pd(1)-C(1)	2.032(4)
Pd(1)-C(10)	2.034(4)
Pd(1)-Cl(1)	2.3189(12)
Pd(1)-Cl(2)	2.3187(12)
C(1)-Pd(1)-C(10)	170.48(17)
Cl(2)-Pd(1)-Cl(1)	178.08(5)
C(1)-Pd(1)-Cl(2)	87.67(13)
C(10)-Pd(1)-Cl(2)	89.96(12)
$NHC_{(1)} – NHC_{(10)}$ twist	28.1(3)

$[(^{tBu}CN(H)C^{tBu})Pd(NCMe)_2][BF_2]_2$ **17**	
Pd(1)-C(1)	2.058(4)
Pd(1)-C(10)	2.043(4)
N(3)-Pd(1)	2.049(4)
N(6)-Pd(1)	2.014(4)
C(10)-Pd(1)-C(1)	171.66(16)
N(6)-Pd(1)-N(3)	174.44(16)
C(10)-Pd(1)-N(3)	82.12(17)
N(3)-Pd(1)-C(1)	89.95(17)
$NHC_{(1)} – NHC_{(10)}$ twist	81.0(3)

signals in the ^{13}C and ^{1}H NMR spectra with each ^{1}H NMR signal integrating for six hydrogen atoms. All the NMR data is consistent with **13** exhibiting C_s symmetry. The three methyl signals can be interpreted as arising from the restricted rotation of a mesityl substituent about the N-C_{mes} bond and restricted inversion at the amine nitrogen atom respectively on the NMR timescale. If N-C_{mes} bond rotation or amine inversion occurred at an appreciable rate on the NMR timescale the methyl groups in the 2, 6 positions would be magnetically equivalent.

Clearly there is a diversity of coordination and resulting dynamic NMR behaviour that is dependent on the amine and NHC N-substituent. For catalytic applications the preparation of acetonitrile solvates of complexes **12** – **14** would be beneficial for rapid substrate coordination in comparison to chloride analogues. We were also interested to determine if the amine moiety in analogues of complexes **12** and **13** would coordinate to the palladium atom if the chlorine atom was removed. Reaction between complexes **12** – **14** and two equivalents of $AgBF_4$ in acetonitrile gave the acetonitrile complexes **15** – **17** shown in scheme 2. NMR spectroscopy of **15** -**17** indicated that the constitution of the ligand and dynamic behaviour was essentially analogous to that of the precursor chloride complexes **12** – **14**. The ^{1}H NMR spectra of **15** and **16** showed signals consistent with C_s symmetry at all temperatures between 25 and – 40 °C and in the case of the benzyl derivative **15** the benzyl CH_2 signals appear as a singlet signal in contrast to **12**. At – 30 °C the ^{1}H NMR spectrum of complex **17** shows signals consistent with C_1 symmetry including eight resolved signals for the ethylene CH_2 hydrogen atoms. Although we did not determine the thermodynamic parameters for atropisomerism of **17**, comparison between variable temperature ^{1}H NMR spectra of **17** and previously reported **14** indicate very similar values ($\Delta G^{\ddagger}_{281K}$ = 57.44 (0.37), $\Delta H^{\ddagger}$ 32.5 (4.9) $kJmol^{-1}$, $\Delta S^{\ddagger}$ -88 (18) $JK^{-1}mol^{-1}$) reflective of congruent dynamic behaviour. One unexplained feature is that comparison of the ^{1}H NMR chemical shift of the N*H* atom of complexes **13** (7.58), **14** (8.33),[11] **16** (5.72) and **17** (5.27) indicate that as the charge on the metal complex increases the signal shifts upfield, but the chemical shift is not as sensitive to coordination of the N atom.

Single crystals of **17** could be grown that were suitable for a single crystal diffraction study. The structure of the metal dication is shown in figure 3 and selected data are given in table 1. With respect to the metal-carbene ligand moiety, the cations of complexes **14** and **17** are essentially isostructural. For example, the Pd-N_{amine} bond lengths are 2.058(12) and 2.049(4) Å for **14** and **17** respectively and each complex contains NHC groups with a twist about the C-Pd-C vector of *ca.* 53 and 47 ° relative to the square plane. The Pd-C_{NHC} bond lengths for the dication of **17** (Pd(1)-C(1) = 2.057(15) and Pd(1)-C(10) = 2.087(15) Å) are on average marginally longer than for the monocation of **14** (Pd(1)-C(1) = 2.058(4) and Pd(1)-C(10) = 2.043(4) Å) which is in contrast to what may be expected on electrostatic grounds and is probably reflective of the comparative bulk of Cl and MeCN ligands.

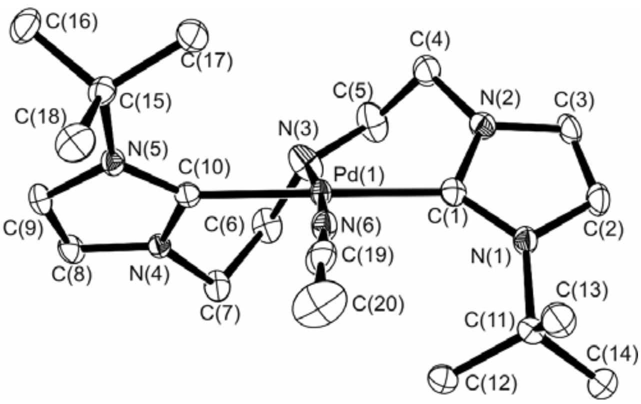


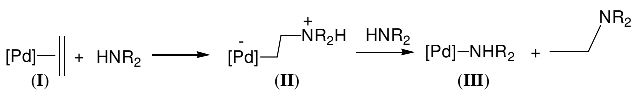
Fig. 3. Molecular structure of the dication moiety of complex **17**. Ellipsoids are shown at 50 % probability. Anions and hydrogen atoms have been removed for clarity.

Catalysis. We were interested in the application of complexes **12** – **17** as potential catalysts for both Heck and hydroamination of alkenes respectively. Numerous palladium NHC catalysts have been investigated for Heck-type coupling[4b, 6a-c, 9, 15] including tridentate di-NHC-pyridine complexes where presumably either an NHC or the pyridine functionality must dissociate in order for two coordination sites to be available for catalysis. Given the structural diversity in complexes **12** – **14** with respect to amine coordination, we wished to investigate any potential structure-property relationships. Representative data using complexes **12** - **14** as precatalysts for reaction between tert-butylacrylate or styrene and aryl bromides and chlorides are shown in table 2.

Conditions were chosen to observe differentiation between the catalyst precursors and although none of the activities shown in table 2 can be considered spectacular, collectively the TOF's are comparable and in some cases marginally better than those reported for palladium NHC complexes incorporating pyridine moieties.[6] Perhaps the only clear structural trend is that the mesityl substituted complex **13** generally gives lower activities than the ^{t}Bu derivatives **12** and **14** that can be attributed to the out of square plane steric bulk preventing associative substitution processes. However, given the increase in turnover frequency at lower catalyst loading it is more likely the data is reflective of the participation of colloidal palladium catalysis[16] where catalyst decomposition and aggregation processes are ligand dependent. Control experiments showed $Pd(OAc)_2$ was inferior in all cases, particularly for 4-chloroacetophenone, clearly showing that the ligands do enhance catalytic rate. The generation of catalysts in situ using $Pd(OAc)_2$ and one equivalent of salts **2**-**5** gave activities approximately two thirds that of the analogous complexes and the use of two ligand equivalents reduced activities significantly, indicating that the use of preformed precatalysts is beneficial.

The hydroamination of alkenes using NHC based ligands has not been intensively investigated, with select examples reported of intra- and intermolecular reactions using rhodium di-NHC[17] and rhodium and palladium phosphine-NHC hybrid precatalysts.[18] The most active and versatile late metal catalysts use phosphine ligands including chelating bis phosphines and tridentate PCP, PNP, and PPP ligand types.[19]

The reported NHC rhodium and palladium complexes exhibit reasonable activity but interpretation with respect to the NHC moiety is complicated by the probability that catalysis proceeds through different mechanisms.[20] For group 9 metals, oxidative addition and reductive elimination of N-H and C-H bonds respectively are implicated.[21] whereas for group 10, mechanistic and computational data using phosphine ligands indicates catalysis proceeds via nucleophilic addition of precursor amine to a palladium coordinated alkene (I, scheme 3) with subsequent protonation of the resulting palladium 2-amino alkyl intermediate (II).[22] Protonation is commonly the rate limiting step and acid cocatalysts such as CF_3SO_2H can be used, however clearly the actual acid cocatalyst will be an ammonium salt due to the relative excess of precursor and product amines. In the absence of additional acid, protonation occurs via an ammonium salt from reaction between II and a precursor (or product) amine effectively using the amine as a proton shuttle.



Scheme 3.

Table 2. Catalytic data for reaction between tert-butylacrylate and arylhalides using complexes **12-14**.

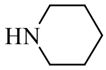
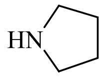
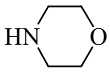
cat:mol%	aryl[a]	t(hr)	yield(%)	TOF[b]
12: 0.01	BAP	5	>99	1980
13: 0.01	BAP	5	>99	1980
14: 0.01	BAP	5	>99	1980
12: 0.001	BAP	24	93	3870
13: 0.001	BAP	24	40	1680
14: 0.001	BAP	24	56	2350
14: $7x10^{-5}$	BAP	24	58	34700
12: 0.1	BT	5	85	170
13: 0.1	BT	5	71	142
14: 0.1	BT	5	85	170
12: 0.1	CAP	24	78	33
13: 0.1	CAP	24	39	16
14: 0.1	CAP	24	81	34
12: 0.01	CAP	5	28	560
13: 0.01	CAP	5	12	240
14: 0.01	CAP	5	17	340
12: 0.01	CAP[c]	24	48[d]	20
13: 0.01	CAP[c]	24	69[d]	29
14: 0.01	CAP[c]	24	66[d]	27

[1]BAP = 4-bromoacetophenone, BT = 4-bromotoluene, CAP = 4-chloroacetophenone; [b]Turnover Frequency (TOF) = [mol product/(mol Pd x h)]; [c]styrene used instead of tert-butylacrylate; [d]only the trans isomer detected; Conditions: NaOAc (0.46 mmol), tetra-n-butyl ammonium bromide (0.041 mmol), aryl halide (0.41 mmol), n-butyl acrylate (0.57 mmol), dimethylacetamide (2 mL), 140 ^oC.

The presence of an amine group and differing coordination in complexes **15**-**17** prompted use to consider if any effect could be observed via protonation/coordination that could be attributable to the ligand amine moiety. Results of some hydroamination reactions using complexes **15**-**17** are given in table 3. Complexes **15**-**17** do catalyse reaction between the activated alkene methyacrylonitrile and cyclic secondary alkenes, but much lower activity was observed for styrene where only trace quantities of hydroamination products were detected. One general complication is the poor solubility of **15**-**17** in aromatic and ether solvents that are commonly used for this class of reaction. However, on initiation of catalysis at temperatures above 40 ^oC metal complex solubility increased significantly.

In the absence of acid cocatalyst complex **17** gives the greatest yield, with **16** performing particularly poorly (table 3, entries 1-3). Increasing the temperature from 40 to 90 ^oC increased the yield (entry 4) but by far the greatest effect was on addition of acid cocatalyst (entry 5) where the yield using **16** increased to 93%. Mass spectrometry of a solution containing **16**, piperidine, CF_3SO_3H heated to 90 ^oC showed a fragment attributable to $[\mathbf{16}\text{-2Cl}]^+$ indicating that the ligand remains coordinated to palladium during reaction. Subsequent reactions using pyrrolidine, morpholine, and N-methyl piperazine were restricted to complexes **16** and **17** to directly compare uncoordinated (**16**) and coordinated (**17**) secondary amine of the ligand. Pyrrolidine (entries 6-8) again showed that complex **17** did not require acid cocatalyst (entry 7) to achieve good yield (97%) whereas **16** only gave reasonable

Table 3. Hydroamination of methylacrylonitrile using precatalysts **15** – **17**.

entry	catalyst	amine	yield (%)[c]
1	15[a]		28
2	16[a]		9
3	17[a]		79
4	17		88
5	16[b]		93
6	16[b]		69
7	17		97
8	17[b]		> 99
9	16[b]		77
10	17		17
11	17[b]		55
12	16[b]		82
13	17		16

[a] 40 °C, 24 h; [b]added CF_3SO_3H (5.5 µL, 60µmol); [c]determined using GC; Conditions: methacrylonitrile (105 µL,1.25 mmol), amine (0.31 mmol), palladium complex (2 mol%), toluene (0.25 mL), 90 °C, 24 h.

yield (69%) with acid cocatalyst. Comparing entries 1-8 it is tempting to suggest that perhaps the coordinated secondary amine of **17** could potentially aid in protonation of an intermediate palladium 2-alkylamino complex via proton transfer to the metal. Exchange of N-H for N-D in complex **17** was achieved from reaction between **14** and D_2O at 40 °C. Subsequent reaction between **14**-D and 2 equivalents of $AgBF_4$ in CH_3CN gave **17**-D, and ^{2}D NMR showed a single resonance at δ 5.65ppm corresponding to selective exchange of the N*H* atom. To obtain sufficient solubility for NMR analysis, a catalytic reaction was conducted in CH_3CN in an NMR tube at 40 °C using a palladium: piperidine: methacrylonitrile ratio of 1:5:10. After 24 hr ^{2}D NMR showed the absence of a peak at δ 5.65 ppm and several new signals between δ 0.7 and 3.0 ppm indicative of several exchange processes. Given the absence of outstanding catalytic activity, substrate limitation to activated alkenes, and the significant amount of work required to unravel the exchange process further work was considered unwarranted. Furthermore using morpholine (entries 9-11) and *N*-methyl piperazine (entries 1-14) showed that complex **16** was more active than **17** for these substrates and acid cocatalyst is required to give reasonable yields, complicating a collective interpretation of all the catalytic data.

Conclusions

Comparison of complexes **12–17** indicates that non-covalent ligand interactions are primarily responsible for the observed constitution. Supporting this view, synthesis of chloride **12-14** and analogous complexes **15-17** containing the more weakly coordinating acetonitrile ligand exhibit similar structures, including structurally characterised cations of **14**[11] and **17**. With respect to the ligand composition, amine coordination is modified by substitution at the amine nitrogen atom (cf. **12** and **15** vs **14** and **17**) or substitution at the NHC *N*-substituents (cf. **13** and **16** vs **14** and **17**). As a consequence of differing coordination, complexes **12-17** exhibit a variety of dynamic behaviour that is reflective of ligand bulk, including the lack of mesityl rotation in complexes **13** and **16**.

Catalytic activity has been demonstrated for Heck and hydroamination reactions using precatalysts **12-14** and **15-17** respectively. For Heck reactions increased activity is observed for decreasing concentration that is indicative of reaction mediated by colloidal palladium generated via complex decomposition, a process that is also likely for other NHC complexes. Hydroamination reaction is limited to activated alkenes and rates can be increased by addition of acid cocatalyst.

Experimental

General procedures. All manipulations were performed under argon using standard Schlenk techniques unless stated otherwise. All solvents were dried over the appropriate drying agent and distilled under dinitrogen according to literature methods.[23] Reagents were purchased from Aldrich, Acros or Lancaster and used as supplied. $[PdCl_2(NCMe)_2]$ was prepared using a literature procedure.[24] The synthesis of compounds **1**, **2**, **4**, **10** and **14** has been reported previously.[11] NMR spectra were recorded at probe temperature on a JEOL 270 (^{1}H, 270 MHz; ^{13}C, 67.9 MHz), Brüker AV-300 (^{1}H, 300 MHz; ^{13}C, 75.5 MHz), or Brüker AMX-400 (^{1}H, 400 MHz; ^{13}C, 100.5 MHz) respectively. Chemical shifts are described in parts per million downfield shift from $SiMe_4$ and are reported consecutively as position (δ_H or δ_C), relative integral, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, br = broad), coupling constant (*J*/Hz) and assignment. Proton NMR spectra were referenced to the chemical shift of residual proton signals ($CHCl_3$ δ 7.27, C_6D_5H δ 7.16, and CD_2HCN δ 1.94). Carbon spectra were referenced to a ^{13}C resonance of the solvent ($CDCl_3$ δ 77.16, C_6D_6 δ 128.06, and CD_3CN δ 118.26). ^{13}C HSQC, PENDANT and Gradient HMBC experiments were performed using standard Brüker pulse sequences. NMR experiments on each of the palladium halide NHC complexes were performed with a 1 min relaxation delay in order to detect the carbon atom bound to the palladium atom. Mass spectra were recorded on VG 70-250E or Kratos MS-50 spectrometers. Electrospray (ES) was recorded using methanol or acetonitrile as the mobile phase. Major fragments were given as percentages of the base peak intensity (100%). Elemental analyses were performed at the University of North London. Complexes **9**, **13** and **16** did not give reproducible bulk analysis.

[^{Mes}C(H)N(Bn)C(H)^{Mes}][Cl]$_2$ (3) An ampoule charged with mesityl imidazole (2.75 g, 0.015 mol), benzyl-bis-(2-chloroethyl)amine (1.56 g, 6.72 mmoL), and 1, 4-dioxane (44 mL) was heated with stirring at 130 ˚C under argon. Over a period of 5 days the initial pale yellow solution precipitated a beige coloured solid, that was isolated by decanting the supernatant and washing with 1, 4-dioxane (2 x 20 mL). The beige solid was then dissolved in ethanol and the volatiles removed under reduced pressure to give **3** as an off white solid. Yield = 1.89 g, 47%. ^{1}H NMR (270 MHz, D_2O), 1.93 (12 H, s, C*H*$_3$), 2.33 (6 H, s, C*H*$_3$), 3.19 (4 H, t, $^3J_{H-H}$ = 5.4, C*H*$_2$CH$_2$), 3.73 (2 H, s, C*H*$_2$Ph), 4.43 (4 H, t, $^3J_{H-H}$ = 5.4, CH$_2$C*H*$_2$), 7.12 (4 H, s, C$_6$*H*$_2$(CH$_3$)$_3$), 7.24 (5 H, m, C$_6$*H*$_5$), 7.49 (2 H, s, CH=C*H*), 7.63 (2 H, s, C*H*=CH), 8.56 (2 H, s, NC*H*N). ^{13}C NMR (67.9 MHz, D_2O), 16.6 (*C*H$_3$), 20.3 (*C*H$_3$), 47.7 (*C*H$_2$CH$_2$), 53.0 (CH$_2$*C*H$_2$), 57.6 (*C*H$_2$Ph), 123.2 (*C*H=CH), 124.2 (CH=*C*H), 128.9 (*C*H$_{aryl}$), 129.3 (*C*H$_{aryl}$), 129.4 (N*C*HN), 129.6 (*C*H$_{aryl}$), 130.6 (*C*H$_{aryl}$), 130.7 ($^{ipso}C_{aryl}$), 134.6 ($^{ipso}C_{aryl}$), 136.3 ($^{ipso}C_{aryl}$), 141.7 ($^{ipso}C_{aryl}$). MS (ESI) m/z 568.1 ([M-Cl]$^+$, 95%), 532.1 ([M-2Cl]$^+$, 100).

[^{Mes}C(H)N(H)C(H)^{Mes}][Cl]$_2$ (5): An ampoule was charged with ethanol (50 mL), **3** (2.000 g, 3.3 mmol) and 10 % Pd/C (0.520 g) and the mixture stirred at 65 °C under one bar of hydrogen for 18 hr. The mixture was filtered and the filtrate concentrated under reduced pressure to give compound **5** as a white solid. Yield = 1.50 g, 88 %. ^{1}H NMR (270 MHz, D_2O) 1.98 (12 H, s, C*H*$_3$), 2.31 (6 H, s, C*H*$_3$), 3.31 (4 H, $^3J_{H-H}$ = 5.6, CH$_2$C*H*$_2$), 4.49 (4 H, t, $^3J_{H-H}$ = 5.6, C*H*$_2$CH$_2$), 7.11 (4 H, s, C*H*$_{aryl}$), 7.53 (2 H, s, CH=C*H*), 7.80 (2 H, s, C*H*=CH), 9.09 (2 H, s, NC*H*N); ^{13}C{^{1}H} NMR (67.9 MHz, D_2O) 16.6 (*C*H$_3$), 20.3 (*C*H$_3$), 46.0 (CH$_2$*C*H$_2$), 47.0 (*C*H$_2$CH$_2$), 123.3 (CH=*C*H), 125.1 (*C*H=CH), 129.4 (*C*H$_{aryl}$), 129.4 ($^{ipso}C_{aryl}$), 134.7 ($^{ipso}C_{aryl}$), 137.4 (N*C*HN), 141.7 ($^{ipso}C_{aryl}$); MS (TOF ES$^+$) *m/z* 478 ([M-Cl]$^+$, 35 %), 442 ([M-2Cl-H]$^+$, 50 %); HRMS calc. for $C_{28}H_{37}N_5Cl$; 478.2737, found 478.2737.

[^{tBu}CN(Bz)C^{tBu}] (**6**): A mixture of **2** (300 mg, 0.62 mmol) and sodium hydride (42 mg, 1.75 mmol) in THF (10 ml) was stirred for 5 min. Potassium *tert*-butoxide (104 mg, 0.93 mmol) was added and the mixture stirred for a further 30 min. The mixture was filtered, the volatiles removed under reduced pressure and the resulting yellow oil extracted with toluene (15 ml). The volatiles were removed from the extract to give **6** as an orange oil. Yield = 170 mg, 67 %. ^{1}H NMR (270 MHz, C_6D_6) 1.51 (18 H, s, C*H*$_3$), 2.79 (4 H, t, $^3J_{H-H}$ = 6.5, CH$_2$C*H*$_2$), 3.42 (2 H, s, PhC*H*$_2$), 3.99 (4 H, t, $^3J_{H-H}$ = 6.5, C*H*$_2$CH$_2$), 6.54 (2 H, s, CH=C*H*), 6.72 (2 H, s, C*H*=CH), 7.16 – 7.17 (5H, m, C$_6$*H*$_5$); ^{13}C{^{1}H} NMR (67.9 MHz, C_6D_6), 31.3 (*C*H$_3$), 49.7 (CH$_2$*C*H$_2$), 55.8 (Ph*C*H$_2$), 55.9 (*C*H$_2$CH$_2$), 59.3 (*C*(CH$_3$)), 115.1 (CH=*C*H), 119.0 (*C*H=CH), 127.0 (*C*$_6$H$_5$), 128.3 (*C*$_6$H$_5$), 129.0 (*C*$_6$H$_5$), 140.0 (*ipso*-*C*$_6$H$_5$), 213.3 (N*C*N).

[^{tBu}CN(H)C^{tBu}] (**7**): A potassium *tert*-butoxide (74 mg, 0.67 mmol) solution in THF (7 mL) was added dropwise to a suspension of **4** (130 mg, 0.33 mmol) in THF (7 mL) over a period of 10 mins. The mixture was stirred for a further 30 min, and the volatiles removed under reduced pressure. The resulting yellow solid was extracted with diethyl ether (15 mL), and the volatiles removed from the extract to give **7** as an orange oil. Yield = 78 mg, 74 %. ^{1}H NMR (270 MHz, C_6D_6) 1.46 (18H, s, C*H*$_3$), 2.81 (4H, t, $^3J_{H-H}$ = 5.94, C*H*$_2$CH$_2$), 3.95 (4H, t, $^3J_{H-H}$ = 5.94, CH$_2$C*H*$_2$), 6.65 (2H, s, C*H*=CH), 6.71 (2H, s, CH=C*H*); ^{13}C{^{1}H} NMR (67.9 MHz, C_6D_6) 31.4 (*C*H$_3$), 50.9 (CH$_2$*C*H$_2$), 51.4 (*C*H$_2$CH$_2$), 55.7 (*C*(CH$_3$)$_3$), 115.2 (CH=*C*H), 119.0 (*C*H=CH), 212.9 (N*C*N).

[^{tBu}C(AgCl)N(Bn)C(AgCl)^{tBu}] (**8**): To a dichloromethane solution (60 mL) of **2** (1.04 g, 2.2 mmol) was added Ag_2O (0.61 g, 2.6 mmol) and the mixture stirred in the dark for 18 hr. The solution was then filtered and solvents removed from the filtrate under reduced pressure to afford compound **8** as an off-white solid. Yield = 1.09 g, 72 %. ^{1}H NMR (300 MHz, CDCl$_3$) 1.71 (18 H, s, C*H*$_3$) 2.99 (4 H, t, $^3J_{H-H}$ = 6.8, CH$_2$C*H*$_2$), 3.71 (2 H, s, PhC*H*$_2$), 4.19 (4H, t, $^3J_{H-H}$ = 6.8, C*H*$_2$CH$_2$), 7.06 (2 H, d, $^3J_{HH}$ = 1.8, CH=C*H*), 7.14 – 7.30 (7H, m, C$_6$*H*$_5$, C*H*=CH); ^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$) 38.9 (*C*H$_3$), 49.8 (*C*H$_2$CH$_2$), 55.2 (CH$_2$*C*H$_2$), 56.4 (Ph*C*H$_2$), 59.4 (*C*(CH$_3$)$_3$), 121.8 (*C*H=CH), 122.0 (CH=*C*H), 128.5 (*C*$_6$H$_5$), 128.8 (*C*$_6$H$_5$), 129.1 (*C*$_6$H$_5$), 138.0 ($^{ipso}C_6H_5$), 181.1 (*C*Ag); MS (TOF ES$^+$) *m/z* 694.3 ([M] 5 %), 514.2 (100, [M-Ag-2Cl]$^+$). Anal. [found(calc.)] $C_{25}H_{39}Ag_2Cl_2N_5$: C 43.19 (43.19), H 5.69 (5.36), N 9.87 (10.07).

[^{Mes}C(AgCl)N(Bn)C(AgCl)^{Mes}] (**9**): Compound **9** was prepared as a light brown solid following an analogous procedure as for **8** using dichloromethane (15 mL), **3** (488 mg, 0.81 mmol) and Ag_2O (0.21 g, 0.88 mmol). Yield = 415 mg, 67 %. ^{1}H NMR (270 MHz, CDCl$_3$) δ 1.96 (12 H, s, C*H*$_3$), 2.30 (6 H, s, CH$_3$), 3.07 (4 H, t, $^3J_{H-H}$ = 6.7, CH$_2$C*H*$_2$), 3.78 (2 H, s, PhC*H*$_2$), 4.25 (4 H, t, $^3J_{H-H}$ = 6.7, C*H*$_2$CH$_2$), 6.89 (2 H, d, $^3J_{H-H}$ = 1.5, CH=C*H*), 6.92 (2 H, s, C*H*$_{mes}$), 7.25 (5H, m, C$_6$*H*$_5$), 7.33 (2 H, d, ^3J = 1.5 Hz, CH=C*H*); ^{13}C{^{1}H} NMR (67.9 MHz, CD$_3$CN) δ 17.8 (*C*H$_3$), 21.6 (*C*H$_3$), 51.0 (*C*H$_2$CH$_2$), 56.0 (CH$_2$*C*H$_2$), 60.2 (Ph*C*H$_2$), 123.5 (*C*H=CH), 124.0 (CH=*C*H), 128.6 (*C*H$_{aryl}$), 129.0 (*C*H$_{aryl}$), 129.8 (*C*H$_{aryl}$), 130.4 (*C*H$_{aryl}$), 136.4 ($^{ipso}C_{aryl}$), 137.3 ($^{ipso}C_{aryl}$), 139.5 ($^{ipso}C_{aryl}$), 140.7 ($^{ipso}C_{aryl}$) (*C*Ag) not detected; MS (TOF ES$^+$) *m/z* 638 (100, [M-Ag-2Cl]$^+$).

[^{tBu}C(AgCl)N(H)C(AgCl)^{tBu}] (**10**): Compound **10** was prepared as a light brown solid following an analogous procedure as for **8** using dichloromethane (60 mL), **4** (2.15 g, 5.5 mmol) and Ag_2O (1.53 g, 6.6 mmol). Yield = 2.57 g, 64%. ^{1}H NMR (300 MHz, CDCl$_3$) 1.71 (18 H, s, C*H*$_3$), 3.02 (4 H, t, $^3J_{H-H}$ = 5.9, CH$_2$C*H*$_2$), 4.23 (4 H, t, $^3J_{H-H}$ = 5.9, C*H*$_2$CH$_2$), 7.18 (2 H, d, $^3J_{H-H}$ = 6.0, CH=C*H*), 7.19 (2 H, d, $^3J_{H-H}$ = 6.0, C*H*=CH); ^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$), 32.2 (*C*H$_3$), 50.6 (CH$_2$*C*H$_2$), 53.5 (*C*H$_2$CH$_2$), 58.1 (*C*(CH$_3$)$_3$), 119.3 (CH=*C*H), 120.8 (*C*H=CH), 178.0 (*C*Ag); MS (TOF ES$^+$) *m/z* 644.5 ([M+K]$^+$, 7 %), 318.2 (M-2Cl-2Ag-H]$^+$, 76 %), 354.2 (100, [M-Cl-2Ag-H]$^+$). Anal. [found (Calc.)] for $C_{18}H_{33}Ag_2Cl_2N_5$: C 35.76 (35.79), H 5.32 (5.17), N 11.42 (11.59).

[^{Mes}C(AgCl)N(H)C(AgCl)^{Mes}] (**11**): Compound **11** was prepared as a white powder solid following an analogous procedure as for **8** using dichloromethane (15 mL), **5** (157 mg, 0.31 mmol) and Ag_2O (156 mg, 0.67 mmol). Yield = 155 mg, 70 %. ^{1}H NMR (270 MHz, CDCl$_3$) δ 1.93 (12 H, s, C*H*$_3$), 2.31 (6 H, s, C*H*$_3$), 3.13 (4 H, t, $^3J_{H-H}$ = 6.3, CH$_2$C*H*$_2$), 4.29 (4 H, t, $^3J_{H-H}$ = 6.3, C*H*$_2$CH$_2$), 6.92 (4 H, s, C*H*$_{aryl}$), 7.24 (2 H, d, $^3J_{H-H}$ = 1.5, CH=C*H*), 7.45 (2 H, d, $^3J_{H-H}$ = 1.5, C*H*=CH); ^{13}C{^{1}H} NMR (67.9 MHz, CDCl$_3$) δ 17.7 (*C*H$_3$), 21.0 (*C*H$_3$), 50.2 (CH$_2$*C*H$_2$), 51.9 (*C*H$_2$CH$_2$), 122.0 (CH=*C*H), 122.6 (*C*H=CH), 129.3 (*C*H$_{aryl}$), 134.6 ($^{ipso}C_{aryl}$), 135.3 ($^{ipso}C_{aryl}$), 139.4

(^{ipso}C_{aryl}) (*C*Ag) not detected; MS (TOF ES$^+$) *m/z* 618 ([M-Ag-H]$^+$, 43 %), 548 (100, [M-2Cl-Ag-H]$^+$). Anal. [found (Calc.)] for $C_{28}H_{35}Ag_2Cl_2N_5$: C 45.35 (46.16), H 4.91 (4.84), N 9.27 (9.62).

[(^{tBu}CN(Bn)C^{tBu})PdCl$_2$] (12): Dichloromethane solutions (10 mL) of [$PdCl_2(CH_3CN)_2$] (107 mg, 0.41 mmol) and **8** (10 mL, 285 mg, 0.41 mmol) were added simultaneously to dichloromethane (20 mL) and stirred at -80 °C for 10 mins in the absence of light. A precipitate formed immediately. The solution was warmed to room temperature and stirred for a further 1hr. The mixture was filtered and the volatiles removed from the filtrate under reduced pressure to give **12** as a yellow solid. Yield = 156 mg, 65 %. ^{1}H NMR (500 MHz, $CDCl_3$, 233K) 1.93 (18H, s, C*H*$_3$), 3.29 (2H, m, (N(Bn)CH$_2$C*H*$_2$), 3.77 (1H, d, $^2J_{H-H}$ = 13.6, PhC*H*$_2$), 3.95 (1H, d, $^2J_{H-H}$ = 13.6, PhC*H*$_2$), 3.96 (2H, m, N(Bn)C*H*$_2$), 4.62 (2H, m, N(Bn)CH$_2$C*H*$_2$) 5.36 (2H, m, N(Bn)C*H*$_2$) 6.94 (2H, d, $^3J_{H-H}$ = 1.9, C*H*=CH) 7.02 (2H, d, $^3J_{H-H}$ = 1.9, CH=C*H*), 7.28 – 7.42 (5H, m, C*H*$_{aryl}$); ^{13}C NMR (100.5 MHz, $CDCl_3$) 31.9 (*C*H$_3$), 47.2 (*C*H$_2$CH$_2$), 49.8 (CH$_2$*C*H$_2$), 58.2 (*C*(CH$_3$)), 59.0 (Ph*C*H$_2$), 117.8 (CH=CH), 125.2 (CH=CH), 127.2 (*C*H$_{aryl}$), 128.1 (*C*H$_{aryl}$), 128.4 (*C*H$_{aryl}$), 138.1 (^{ipso}C_{aryl}), 165.6 (*C*Pd). MS (TOF ES$^+$) *m/z* 548 ([M-Cl$^+$] 38 %) 512 (100, [M-2Cl-H]$^+$). HRMS calc. for $C_{18}H_{30}N_5Pd$: 546.1777, found 546.1770. Anal. [found (Calc.)] for $C_{25}H_{37}N_5PdCl_2$ (+ 0.5 $CHCl_3$ (analysis performed on NMR sample): C 48.18 (47.51), H 5.43 (5.86), N 10.08 (10.86).

[(^{Mes}CN(H)C^{Mes})PdCl$_2$] (13): Compound 13 was prepared as an off white powder following an analogous procedure as for 12 using $PdCl_2(MeCN)_2$ (28 mg, 0.110 mmol) and 11 (20 mL, 80 mg, 0.110 mmol). Yield = 40 mg, 59%. ^{1}H NMR (270 MHz, $CDCl_3$), δ 2.01 (6 H, s, C*H*$_3$), 2.55 (6H, s, C*H*$_3$), 2.56 (6H, s, C*H*$_3$), 2.57 (2 H, m, C*H*$_2$), 3.82 (2 H, m, C*H*$_2$), 4.33 (2 H, m, C*H*$_2$), 4.40 (2 H, m, C*H*$_2$), 6.73 (2 H, d, $^3J_{H-H}$ = 1.9 Hz, C*H*=CH), 6.83 (2 H, s, C*H*$_{aryl}$), 6.86 (2 H, s, C*H*$_{aryl}$), 7.09 (2 H, d, $^3J_{H-H}$ = 1.9 Hz, C*H*=CH), 7.58 (1 H, broad s, N*H*). ^{13}C NMR (67.9 MHz, $CDCl_3$), 18.4 (*C*H$_3$), 19.7 (*C*H$_3$), 21.0 (*C*H$_3$), 49.7 (*C*H$_2$CH$_2$), 51.3 (CH$_2$*C*H$_2$), 121.2 (*C*H=CH), 123.5 (CH=*C*H), 128.5 (*C*$_6$H$_2$(CH$_3$)$_3$), 129.0 (*C*$_6$H$_2$(CH$_3$)$_3$), 138.3 (*C*$_6$H$_2$(CH$_3$)$_3$), 166.8 (*C*Pd). MS (ESI), m/z 584 ([M-Cl]$^+$, 100%), 548 ([M-2Cl]$^+$, 85%).

[(^{tBu}CN(Bn)C^{tBu})Pd(NCMe)$_2$][BF$_2$]$_2$ (15): An acetonitrile solution (2 mL) of $AgBF_4$ (27 mg, 0.14 mmol) was added to an acetonitrile solution (5 mL) of **12** (41 mg, 0.07 mmol) immediately giving a white precipitate and the mixture stirred in the dark for 1 hr. The mixture was filtered and the volatiles removed from the filtrate under reduced pressure to give **15** as a pink solid. Yield = 43 mg, 80 %. ^{1}H NMR (500 MHz, CD_3CN, 238K) 1.82 (18H, s, C*H*$_3$), 2.96 (2H, m, C*H*$_2$CH$_2$), 3.16 (2H, m, CH$_2$C*H*$_2$), 4.02 (2H, s, PhC*H*$_2$), 4.33 (2H, m, C*H*$_2$CH$_2$), 4.83 (2H, m, C*H*$_2$CH$_2$), 7.33 – 7.45 (9H, CH=CH, Ph); ^{13}C NMR (67.9 MHz, CD_3CN, 300 K) 32.3 (*C*H$_3$), 52.2 (*C*H$_2$CH$_2$), 56.4 (*C*(CH$_3$)), 66.1 (CH$_2$*C*H$_2$), 73.0 (Ph*C*H$_2$), 123.0 (CH=CH), 124.0 (CH=CH), 129.8 (*C*H$_{aryl}$), 130.0 (*C*H$_{aryl}$), 133.5 (*C*H$_{aryl}$), 140.1 (^{ipso}C_{aryl}), 158.8 (*C*Pd). Anal. [found (Calc.)] for $C_{29}H_{43}N_7B_2F_8Pd$: C 45.35 (45.25), H 6.00 (5.63), N 12.43 (12.74).

[(^{Mes}CN(H)C^{Mes})Pd(NCMe)$_2$][BF$_2$]$_2$ (16): Compound **17** was prepared as a white solid following an analogous procedure as for **15** using $AgBF_4$ (9.5mg, 4.8 x 10^{-5} mol) and **13** (15 mg, 2.4 x 10^{-5} mol). ^{1}H NMR (270 MHz, CD_3CN), δ 2.27 (6 H, s, C*H*$_3$), 2.34 (12 H, s, C*H*$_3$), 3.21 (2 H, m, C*H*$_2$), 3.30 (2 H, m, C*H*$_2$), 4.31 (2 H, m, C*H*$_2$), 4.36 (2 H, m, C*H*$_2$), 5.27 (1 H, broad s, N*H*), 6.97 (2 H, s, C*H*$_{aryl}$), 7.08 (2 H, s, C*H*$_{aryl}$), 7.12 (2 H, d, ^3J = 1.8 Hz, C*H*=CH), 7.44 (2 H, d, ^3J = 1.8 Hz, CH=C*H*). ^{13}C NMR (67.9 MHz, CD_3CN), δ 19.4 (*C*H$_3$), 20.8 (*C*H$_3$), 49.0 (*C*H$_2$CH$_2$), 52.3 (CH$_2$*C*H$_2$), 123.6 (*C*H=CH), 124.4 (CH=*C*H), 125.5 (*C*$_6$H$_2$(CH$_3$)$_3$), 130.5 (*C*$_6$H$_2$(CH$_3$)$_3$), 130.9 (*C*$_6$H$_2$(CH$_3$)$_3$), 140.9 (*C*$_6$H$_2$(CH$_3$)$_3$), *C*Pd not detected.

[(^{tBu}CN(H)C^{tBu})Pd(NCMe)$_2$][BF$_2$]$_2$ (17): Compound **17** was prepared as a white solid following an analogous procedure as for **15** using an acetonitrile solution (3 mL) of $AgBF_4$ (36 mg, 0.19 mmol) and an acetonitrile (5 mL) suspension of **14** (47 mg, 0.095 mmol). Yield = 54 mg, 89 %. ^{1}H NMR (500 MHz, CD_3CN, 233 K) 1.98 (18H, s, C*H*$_3$), 2.23 (1H, m, C*H*$_2$CH$_2$), 2.70 (1H, m, C*H*$_2$CH$_2$), 2.95 (1H, m, CH$_2$C*H*$_2$), 3.09 (1H, m, CH$_2$C*H*$_2$), 4.02 (1H, m, CH$_2$C*H*$_2$) 4.23 (1H, m, CH$_2$C*H*$_2$), 4.35 (1H, m, CH$_2$C*H*$_2$), 4.83 (1H, m, CH$_2$C*H*$_2$), 5.72 (1H, m, N*H*), 7.32 (2H, d, $^3J_{H-H}$ = 1.9, CH=C*H*), 7.38 (2H, d, $^3J_{H-H}$ = 1.9, C*H*=CH); ^{13}C NMR (67.9 MHz, CD_3CN, 300K) 32.0 (*C*H$_3$), 51.0 (*C*H$_2$), 52.4 (*C*H$_2$), 60.4 (*C*(CH$_3$)), 121.8 (*C*H=CH), 123.8 (*C*H=CH), 160.2(*C*Pd).; MS (FAB$^+$) *m/z* 422 (100, [M-2BF$_4$ – NCCH$_3$]$^+$). Anal. [found (Calc.)] for $C_{20}H_{34}N_6B_2F_8Pd$: C 37.44 (37.62), H 5.30 (5.37), N 13.12 (13.16).

Catalytic procedures

Heck: Dimethylacetamide (DMA) (2 mL), NaOAc (38 mg, 0.46 mmol), tetra-n-butyl ammonium bromide (13 mg, 0.041 mmol), and a DMA solution of the relevant palladium complex were heated to 140 °C under argon. Subsequently, aryl halide (0.41 mmol), n-butyl acrylate (82 µL, 0.57 mmol) and diethylene glycol dibutyl ether (internal standard, 90 µL, 0.41 mmol) were added and the catalytic mixture stirred at 140 °C for the relevant time period. Upon cooling, the mixture was filtered and a 100 µL portion diluted with a DMA (1.5 mL) and analyzed by GC.

Hydroamination: Toluene (0.25 mL) was added to the relevant palladium complex (6 µmol) under an inert atmosphere into a vial fitted with a rubber septum. The amine (0.31 mmol), methacrylonitrile (105 µL,1.25 mmol) and in select reactions (see table 3) trifluoromethane sulphonic acid (5.5 µL, 60µmol) were injected via syringe. The vial was then sealed and heated to the required temperature for 24 h. Upon cooling, toluene (1.2 mL) was added and the mixture filtered. Diethylene glycol dibutyl ether (internal standard, 60 µL, 24 µmol) was then added and the mixture analyzed by GC.

Crystallographic information

Single crystal diffraction data for **2** was recorded on a Bruker Smart 6000 II diffractometer equipped with a copper source and a CCD detector system and on a Bruker Smart 6000 diffractometer equipped with a molybdenum source with a CCD detector for **4**, **12**, and **17**. Structures were solved and refined using SHELX programs.[25] All Hydrogen atoms were placed in calculated positions and a riding model was subsequently used. For **2**, the hydrogen atoms of water of cocrystallisation are not included. See http://www.rsc.org/suppdata/cc/XXX for crystallographic files in CIF format.

Colourless crystals of **2** were grown by layering acetonitrile onto a water solution of **2**. *Crystal data* for **2**.2H_2O: $C_{25}H_{39}Cl_2N_5O_2$, dimensions 0.30 x 0.08 x 0.08 mm, M_r = 516.54, triclinic P1, a = 8.3231(3), b = 9.7685(3), c = 9.9897(3) Å, α = 68.850(2), β = 78.751(2), γ = 89.4830(10)°, V = 741.81(4)Å^3, Z = 1, $\lambda(Cu_{K\alpha})$ = 1.54178 Å, ρ_{calc} = 1.156 g cm^{-3}, T = 296(2) K, F(000) = 278, θ range for data collection 4.81 – 70.51°, limiting indices $-9 \leq h \leq 7$, $-11 \leq k \leq 10$, $-12 \leq l \leq 11$ 4382/3069 collected/unique reflections (R(int) = 0.0349), absolute structure parameter 0.07(2), goodness of fit on F^2 = 1.057, $\Delta\rho_{max/min}$ = 0.642/-0.646 e Å^{-3}, final *R indices* ($I > 2\sigma(I)$) $R1$ = 0.0781, $wR2$ = 0.1751. CCDC XXX/XXXX

Colourless crystals of **4**[BPh_4]$_2$ were grown from cooling to –10 °C a mixture of **4**.[Cl]$_2$ and $NaBPh_4$ in acetonitrile. *Crystal data* for **4**[BPh_4]$_2$.MeCN: crystals, $C_{68}H_{76}B_2N_6$, dimensions 0.20 x 0.20 x 0.20 mm, M_r = 998.97, triclinic P-1, a = 11.6678(7), b = 13.3876(8), c = 18.3438(11) Å, α = 86.420(2), β = 80.4290(10), γ = 89.4830(10)°, V = 2820.0(3) Å^3, Z = 2, $\lambda(Mo_{K\alpha})$ = 0.71073 Å, ρ_{calc} = 1.176 g cm^{-3}, T = 273(2) K, F(000) = 1072, θ range for data collection 1.13 – 27.55°, limiting indices $-14 \leq h \leq 15$, $-17 \leq k \leq 15$, $-22 \leq l \leq 23$ 19815/12926 collected/unique reflections (R(int) = 0.0203), goodness of fit on F^2 = 1.047, $\Delta\rho_{max/min}$ = 0.321/-0.202 e Å^{-3}, final *R indices* ($I > 2\sigma(I)$) $R1$ = 0.0466, $wR2$ = 0.1188. CCDC XXX/XXXX

Colourless crystals of **12** were grown from evaporation of a dichloromethane solution of **12**. *Crystal data* for **12**: $C_{25}H_{37}Cl_2N_5Pd$, dimensions 0.20 x 0.15 x 0.15 mm, M_r = 584.90, triclinic P-1, a = 12.9590(11), b = 13.4961(11), c = 16.3190(14) Å, α= 105.876(2), β= 102.093(2), γ = 92.241(2)°, V = 2670.2(4) Å^3, Z = 4, $\lambda(Mo_{K\alpha})$ = 0.71073 Å, ρ_{calc} = 1.455 g cm^{-3}, T = 273(2) K, F(000) = 1208, θ range for data collection 1.33 – 28.32°, limiting indices $-16 \leq h \leq 17$, $-17 \leq k \leq 13$, $-21 \leq l \leq 21$ 19413/13121 collected/unique reflections (R(int) = 0.0433), goodness of fit on F^2 = 0.965, $\Delta\rho_{max/min}$ = 1.322/-0.969 e Å^{-3}, final *R indices* ($I > 2\sigma(I)$) $R1$ = 0.0474, $wR2$ = 0.0986. CCDC XXX/XXXX

Colourless crystals of **17** were grown from evaporation of an acetonitrile solution of **17**. *Crystal data* for **17**.MeCN: $C_{22}H_{37}B_2F_8N_7Pd$, dimensions 0.25 x 0.15 x 0.10 mm, M_r = 679.61, monoclinic P2$_1$/n, a = 13.3436(9), b = 12.2206(9), c = 18.1927(14) Å, β = 94.253(2)°, V = 2958.5(4) Å^3, Z = 4, $\lambda(Mo_{K\alpha})$ = 0.71073 Å, ρ_{calc} = 1.526 g cm^{-3}, T = 273(2) K, F(000) = 1208, θ range for data collection 1.83 – 24.99°, limiting indices $-15 \leq h \leq 15$, $-14 \leq k \leq 14$, $-21 \leq l \leq 14$ 16217/5203 collected/unique reflections (R(int) = 0.0532), goodness of fit on F^2 = 1.044, $\Delta\rho_{max/min}$ = 1.047/-0.834 e Å^{-3}, final *R indices* ($I > 2\sigma(I)$) $R1$ = 0.0445, $wR2$ = 0.0978. CCDC XXX/XXXX.

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References

1. a) K. Denk, P. Sirsch, and W. A. Herrmann, *J. Organomet. Chem.*, 2002, **649**, 219.; b) M. T. Lee and C. H. Hu, *Organometallics*, 2004, **23**, 976.; b) R. Dorta, E. D. Stevens, N. M. Scott, C. Costabile, L. Cavallo, C. D. Hoff, and S. P. Nolan, *J. Am. Chem. Soc.*, 2005, **127**, 2485.; c) R. H. Crabtree, *J. Organomet. Chem.*, 2005, **690**, 5451.
2. a) M. C. Perry, X. H. Cui, M. T. Powell, D. R. Hou, J. H. Reibenspies, and K. Burgess *J. Am. Chem. Soc.*, 2003, **125**, 113.; b) V. Cesar, S. Bellemin-Laponnaz, and L. H. Gade, *Chem. Soc. Rev.*, 2004, **33**, 619.
3. a) A. R. Chianese, X. W. Li, M. C. Janzen, J. W. Faller, and R. H. Crabtree, *Organometallics*, 2003, **22**, 1663.; b) D. C. Graham, K. J. Cavell, and B. F. Yates, *Dalton Trans.*, 2005, 1093.; c) S. Burling, S. Douglas, M. F. Mahon, D. Nama, P. S. Pregosin, and M. K. Whittlesey, *Organometallics*, 2006, **25**, 2642.; d) L. C. Silva, P. T. Gomes, L. F. Veiros, S. I. Pascu, M. T. Duarte, S. Namorado, J. R. Ascenso, and A. R. Dias, *Organometallics*, 2006, **25**, 4391.; e) J. W. Faller and P. P. Fontaine, *J. Organomet. Chem.*, 2006, **691**, 5798.
4. a) K. Ofele, W. A. Herrmann, D. Mihalios, M. Elison, E. Herdtweck, T. Priermeier, and P. Kiprof, *J. Organomet. Chem.*, 1995, **498**, 1.; b) 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.; c) R. E. Douthwaite, M. L. H. Green, P. J. Silcock, and P. T. Gomes, *J. Chem. Soc. Dalton Trans.*, 2002, 1386.; d) J. R. Miecznikowski, S. Grundemann, M. Albrecht, C. Megret, E. Clot, J. W. Faller, O. Eisenstein, and R. H. Crabtree, *Dalton Trans.*, 2003, 831.; e) M. Froseth, A. Dhindsa, H. Roise, and M. Tilset, Dalton Trans., 2003, 4516.; f) P. L. Arnold, S. A. Mungur, A. J. Blake, and C. Wilson, *Angew. Chem. Int. Ed.*, 2003, **42**, 5981.
5. For a recent review of pincer type NHC ligands see D. Pugh and A. A. Danopoulos, *Coord. Chem. Rev.*, 2007, **251**, 610.
6. a) D. S. McGuinness and K. J. Cavell, *Organometallics*, 2000, **19**, 741.; b) E. Peris, J. A. Loch, J. Mata, and R. H. Crabtree, *Chem. Commun.*, 2001, 201.; c) F. E. Hahn, M. C. Jahnke, V. Gomez-Benitez, D. Morales-Morales, and T. Pape, *Organometallics*, 2005, **24**, 6458.
7. a) D. S. McGuinness, V. C. Gibson, D. F. Wass, and J. W. Steed, *J. Am. Chem. Soc.*, 2003, **125**, 12716; b) D. S. McGuinness, V. C. Gibson, and J. W. Steed, *Organometallics*, 2004, **23**, 6288.
8. a) A. A. Danopoulos, A. A. D. Tulloch, S. Winston, G. Eastham, and M. B. Hursthouse, *Dalton Trans.*, 2003, 1009.; b) E. Mas-Marza, M. Sanau, and E. Peris, *Inorg. Chem.*, 2005, **44**, 9961.
9. S. Grundemann, M. Albrecht, J. A. Loch, J. W. Faller, and R. H. Crabtree, *Organometallics*, 2001, **20**, 5485.
10. R. E. Douthwaite, M. L. H. Green, P. J. Silcock, and P. T. Gomes, *Organometallics*, 2001, **20**, 2611.
11. R. E. Douthwaite, J. Houghton, and B. M. Kariuki, *Chem. Commun.*, 2004, 698.
12. I. S. Edworthy, M. Rodden, S. A. Mungur, K. M. Davis, A. J. Blake, C. Wilson, M. Schroder, and P. L. Arnold, *J. Organomet. Chem.*, 2005, **690**, 5710.
13. H. M. J. Wang and I. J. B. Lin, *Organometallics*, 1998, **17**, 972.
14. a) D. S. Clyne, J. Jin, E. Genest, J. C. Gallucci, and T. V. RajanBabu, *Org. Lett.*, 2000, **2**, 1125.; b) M. C. Perry, X. H. Cui, and K. Burgess, *Tetrahedron: Asymmetry.*, 2002, **13**, 1969.; c) C. Marshall, M. F. Ward, and W. T. A. Harrison, *Terahedron Lett.* 2004, **45**, 5703.; d) K. S. Coleman, S. Turberville, S. I. Pascu, and M. L. H. Green, *J. Organomet. Chem.*, 2005, **690**, 653.
15. a) W. A. Herrmann, M. Elison, J. Fischer, C. Kocher, and G. R. J. Artus, *Angew. Chem. Int. Ed. Engl.*, 1995, **34**, 2371.; b) J. Schwarz, V. P. W. Bohm, M. G. Gardiner, M. Grosche, W. A. Herrmann, W. Hieringer, and G. Raudaschl-Sieber, *Chem. Eur. J.*, 2000, **6**, 1773.; c) A. M. Magill, D. S. McGuinness, K. J. Cavell, G. J. P. Britovsek, V. C. Gibson, A. J. P. White, D. J. Williams, A. H. White, and B. W. Skelton, *J. Organomet. Chem.*, 2001, **617**, 546.; d) D. J. Nielsen, K. J. Cavell, B. W. Skelton, and A. H. White, *Inorg. Chim. Acta*, 2002, **327**, 116.; e) J. A. Loch, M. Albrecht, E. Peris, J. Mata, J. W. Faller,

and R. H. Crabtree, *Organometallics*, 2002, **21**, 700.; f) A. C. Hillier, G. A. Grasa, M. S. Viciu, H. M. Lee, C. L. Yang, and S. P. Nolan, *J. Organomet. Chem.*, 2002, **653**, 69.; g) E. Diez-Barra, J. Guerra, R. I. Rodriguez-Curiel, S. Merino, and J. Tejeda, *J. Organomet. Chem.*, 2002, **660**, 50.; h) E. Peris and R. H. Crabtree, *Coord. Chem. Rev.*, 2004, **248**, 2239.

16. a) A. H. M. de Vries, J. Mulders, J. H. M. Mommers, H. J. W. Henderickx, and J. G. de Vries, *Org. Lett.*, 2003, **5**, 3285.; b) M. T. Reetz and J. G. de Vries, *Chem. Commun.*, 2004, 1559.
17. S. Burling, L. D. Field, H. L. Li, B. A. Messerle, and P. Turner, *Eur. J. Inorg. Chem.*, 2003, 3179.
18. a) S. Gischig and A. Togni, *Organometallics*, 2004, **23**, 2479.; b) S. Gischig and A. Togni, *Eur. J. Inorg. Chem.*, 2005, 4745.; c) L. D. Field, B. A. Messerle, K. Q. Vuong, and P. Turner, *Organometallics*, 2005, **24**, 4241.
19. a) A. L. Seligson and W. C. Trogler, *Organometallics*, 1993, **12**, 744.; b) M. Kawatsura and J. F. Hartwig, *Organometallics*, 2001, **20**, 1960.; c) L. Fadini and A. Togni, *Chem. Commun.*, 2003, 30.; d) J. F. Hartwig, *Pure Appl. Chem.*, 2004, **76**, 507.
20. T. E. Muller and M. Beller, *Chem. Rev.*, 1998, **98**, 675.
21. a) P. Diversi, L. Ermini, G. Ingrosso, A. Lucherini, C. Pinzino, and L. Sagramora, *J. Organomet. Chem.*, 1995, **494**, C1.; b) M. Beller, C. Breindl, M. Eichberger, C. G. Hartung, J. Seayad, O. R. Thiel, A. Tillack, and H. Trauthwein, *Synlett*, 2002, 1579.
22. H. M. Senn, P. E. Blochl, and A. Togni, *J. Amer. Chem. Soc.*, 2000, **122**, 4098.
23. W. L. F. Armarego and D. D. Perrin, *'Purification of Laboratory Chemicals'*, Butterworth-Heinemann, 1997.
24. G. K. Anderson and M. Lin, *Inorg. Synth.*, 1990, **28**, 60.
25. G. A. Sheldrick, *Program for crystal structure refinement, University of Göttingen*, 1997.

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Fig./Scheme XX Caption.

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Table XX Caption

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