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Synthesis of chiral imino- and amino-imidazolium salts and of chelating amino-*N*-heterocyclic carbene palladium(II) complexes

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Abstract

A new preparation of chiral imino-imidazolium salts has been developed by condensation of chiral primary amines with 1-(2-oxo-2-phenyl-ethyl)-imidazolium salts in chloroform. This reaction gave the (*E*)-imino-imidazolium salts with stereoselectivities superior to 95:5. The structure of the imines were determined by NMR analyses. Reduction of the chiral (*E*)-imino-imidazolium salts with $NaBH_4$ in MeOH led to amino-imidazolium salts as a mixture of diastereomers with selectivities ranging from 84:16 to 90:10. The major diastereoisomer could be purified in some cases by crystallization and the absolute configurations were determined by X-ray diffraction. Chelating amino-*N*-heterocyclic carbene dichloro palladium(II) complexes were obtained in two steps via formation of the corresponding silver(I) complexes and reaction of these latters with bis(acetonitrile)dichloropalladium. Crystal structure details of a *cis*-dichloro amino-imidazol-2-ylidene palladium complex are presented and confirmed the formation of a six-membered Pd-metallocycle.

Keywords: Chiral imino- and amino-imidazolium salts; Chelating amino-*N*-heterocyclic carbenes; Palladium(II)-metallocycles

1. Introduction

N-heterocyclic carbenes (NHC) have emerged as an important family of ligands with strong σ-donor electronic properties and have now been used in a wide range of catalytic reactions [1–4].

Lappert and coworkers were the first to report in 1983, the synthesis of chiral Rh(I) and Co(I) imidazolinylidene complexes [5]. In the last 10 years, many efforts have been made to synthesize novel chiral NHC ligands and their corresponding metal complexes. Some of these complexes have been tested in asymmetric catalysis and excellent levels of enantioselectivity could be reached (up to >99%) [6–8]. Among these chiral ligands, some heteroditopic NHC–N ligands were reported. Several research groups have described the synthesis and use of NHC–oxazoline ligands [9–16]. Such ligands gave good results particularly in the iridium catalyzed hydrogenation of alkenes [10,11,14] and the rhodium catalyzed hydrosilylation of ketones [13]. The best enantioselectivities in palladium catalyzed reactions were also obtained using heteroditopic NHC–imino palladium(II) complexes, reported in 2003 by Douthwaite [17]. These complexes led to ee up to 92% in the asymmetric allylic alkylation reaction.

Several other achiral or chiral racemic palladium(II) complexes with chelating NHC–N ligands have been reported, including NHC–pyridyl [18–23], NHC–amino [23,24], NHC–amido [24], NHC–imino [25–28] and NHC–enamino complexes [29].

We wish to report here a straightforward synthesis of chiral imino-imidazolium salts from 1-(2-oxo-ethyl)-imidazolium salts. The diastereoselective reduction of the chiral imines afforded amino-imidazoliums salts. The synthesis of chelating NHC–amino Pd(II) complexes from these azoliums as well as the structure of one of these complexes are presented.

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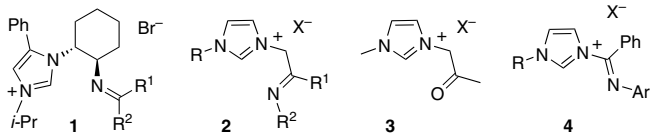


Fig. 1. Imino-imidazolium salts.

2. Results and discussion

2.1. Synthesis of chiral imino-imidazolium salts

Several imino-imidazolium salts have been reported in the literature (Fig. 1). Chiral salts **1** were obtained by Douthwaite by reaction of the corresponding primary amine with an excess of aldehyde ($R^1 = H$) or with acetone ($R^1 = R^2 = Me$) in the presence of $MgSO_4$ or molecular sieves [17]. For the synthesis of imino-imidazolium salts **2**, the condensation of α-chloroimines with monosubtituted imidazoles was found to be an efficient procedure [25,29]. Alternatively, imidazoliums of type **2** were obtained by condensation of 1-(2-oxo-ethyl)-imidazoles with amines followed by alkylation of the imidazole with methyl trifluoromethanesulfonate to form the azolium [30]. The direct condensation of 1-(2-oxo-ethyl)-imidazolium **3** with amines was reported to give undesired decomposition reactions [25]. Imidazolium salts **4** were prepared by reaction of iminoyl chlorides with imidazoles [26,27,31,32].

Looking for a straightforward method to synthesize various chiral imino-imidazolium salts, we first tested the condensation of 1-(2-oxo-ethyl)-imidazolium salt **5** with chiral amines in benzene or toluene. This reaction gave poor or no conversion, one of the main problem being the low solubility of **5** in these apolar solvents, even at high temperature. These solvents are generally necessary to remove the water formed by azeotropic distillation and to displace the equilibrium. Looking for a solvent capable of forming an azeotrope with water and in which the salts **5**–**8** are soluble, we found that chloroform could be appropriate [33]. The reaction of salts **5**–**8** with 3 equivalents of a chiral amine in $CHCl_3$ for 60 h at 90 °C effectively afforded cleanly the corresponding imino-imidazolium salts **9**–**15** in 70–92% yields after precipitation (Scheme 1 and Table 1). The excess of amine is removed by washing the salt with Et_2O or THF. The main impurity formed in the reaction is the chlorhydrate of the starting amine and is probably due to the generation of hydrochloric acid by decomposition of $CHCl_3$ under prolonged heating. This chlorhydrate could not be separated from the imidazolium salts after precipitation. Thus, the reaction solution must be carefully neutralized by stirring with solid $NaHCO_3$ for 1 h before precipitation and washing of the salts.

Table 1
Formation of imino-imidazolium salts

Imine	R	Ar	R^1	X	Yield (%)
9	Mes	Ph	Me	Cl	87
10	Mes	*p*-Cl-C_6H_4	Me	Cl	70
11	2,6-(*i*-Pr)$_2C_6H_3$	Ph	Me	Cl	92
12	2,6-(*i*-Pr)$_2C_6H_3$	*p*-Cl-C_6H_4	Me	Cl	70
13	2,6-(*i*-Pr)$_2C_6H_3$	Ph	Et	Cl	78
14	*t*-Bu	Ph	Me	Cl	88
15	*t*-Bu	Ph	Me	Br	76

The ^1H NMR of these imino-salts showed the presence of one isomer highly predominant (>95:5). Only traces of the minor isomer could be detected in some spectra. The stereochemistry of the major isomer was determined by nOe experiments on **10**, after determination of ^1H and ^{13}C assignments using COSY, HMBC and HMQC experiments and was found to be (*E*) according to the CIP rules (Fig. 2). The phenyl group of the imine and the alkyl group on the nitrogen atom are in a *cis* position. Such a geometry may be highly favoured by a strong intramolecular hydrogen bond between the nitrogen of the imine and the acidic hydrogen of the azolium salt. The same type of favoured geometry was reported by Palmieri and coworkers for the imine **16** [34].

Surprisingly, prolonging standing of the salts **10** and **12** ($R^1 = p$-ClC_6H_4) in $CDCl_3$ (NMR tube, 16 h) led to 80% (R = Mes) and 66% (R = 2,6-^{i}PrC_6H_3) deuteration of the imine α-methylene position and of the N–C*H*=N acidic position of the imidazolium ring (Scheme 2). These deuterations show that an imine–enamine equilibrium occurs but also that a free carbene may be generated during the process. Stirring the imino-imidazolium salt **10** with 5 equivalent of K_2CO_3 in $CDCl_3$ led to incorporation of 97–98%

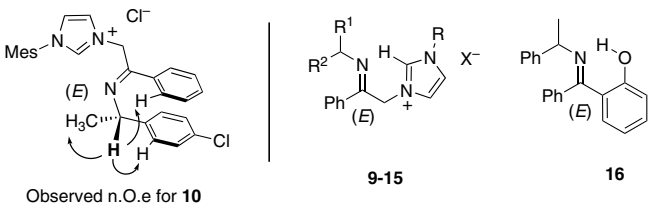
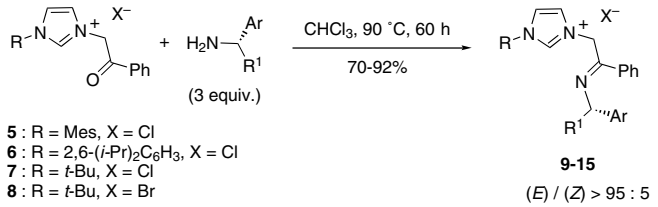
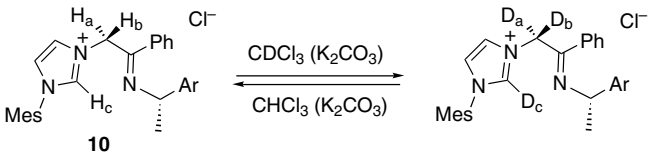


Fig. 2. Favoured structure of imino-imidazolium salts.



Scheme 1.



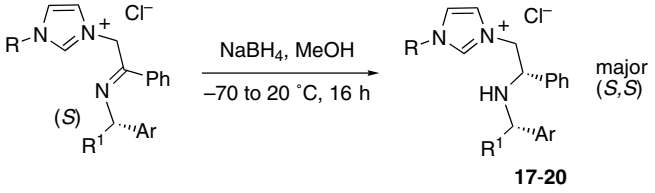
Scheme 2.

deuterium in the three positions after 7 h. Each deuterium (D_a, D_b, D_c) is incorporated within nearly the same rate during the reaction. Thus, deuteration of imine α-position is two times faster than deuteration of the azolium ring. The reaction is reversible: the protonation of the D_3-salt by $CHCl_3$ in the presence of K_2CO_3 was also effective but slower than the initial deuteration (50–60% hydrogen incorporation after 7 h).

2.2. Synthesis of chiral amino-imidazolium salts

The reduction of the imino salts using $NaBH_4$ in MeOH gave the corresponding amino-imidazolium salts **17**–**20** in 65–99% yield and with d.r. ranging from 84:16 to 90:10 (Scheme 3 and Table 2). The addition of $NaBH_4$ was performed at −70 °C and the mixture was allowed to warm to ambient temperature. No significant change in the diastereoselectivity was observed when the addition is performed at 0 °C but the procedure at −70 °C led to cleaner crude products and enhanced yields. Surprisingly, the same reaction performed in EtOH led only to degradation products. The use of sodium borohydride in the reduction of chiral imines resulting from the condensation of acetophenone with α-methylbenzylamine or similar chiral amines was already reported [35]. However, the most frequently used method is the hydrogenation catalyzed by Pd/C [36–38]. Our attempts to reduce the imino-imidazolium salt by this procedure led to amino-imidazolium salts with low d.r. in the presence of several by-products. No improvement of the diastereoselectivity was obtained by using zinc borohydride that was reported to give better results than the $NaBH_4$/MeOH system in the reduction of similar enantiopure imines [34].

The separation of the major diastereomer could be performed by several crystallisations in a mixture of dichloromethane, acetone and ether. By this procedure, the amino-imidazolium salts **17** and **19** were obtained respectively in 36% and 46% yield without detectable trace of the minor isomer. Crystals of **18** suitable for X-ray analysis were grown by the same method. The molecular structure of this salt allowed us to assign the (*S*,*S*) configuration to the major diastereomer. The stereochemical outcome of this reduction is in accordance with the model proposed for the reduction of chiral imines resulting from the condensation of acetophenone with α-methylbenzylamine [35] (Scheme 4).



Scheme 3.

Table 2
$NaBH_4$ reduction of imino-imidazolium salts

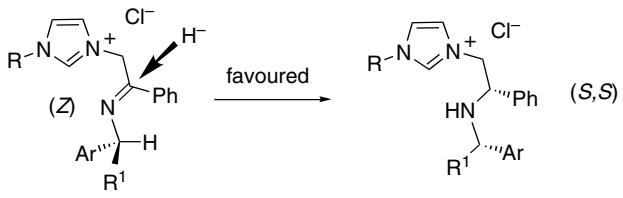
Amine	R	Ar	R^1	Yield (%)	dr[b]
17	Mes	Ph	Me	91 (36[a])	90:10 (>98:2[c])
18	2,6-(*i*-Pr)$_2$C$_6$H$_3$	Ph	Me	87	86:14
19	2,6-(*i*-Pr)$_2$C$_6$H$_3$	Ph	Et	99 (46[a])	85:15 (>98:2[c])
20	*t*-Bu	Ph	Me	65	85:15

[a] Yield of pure major diastereomer isolated by crystallisation.
[b] Ratio determined by ^{1}H NMR (400 MHz).
[c] Diastereomeric excess after recrystallisation.

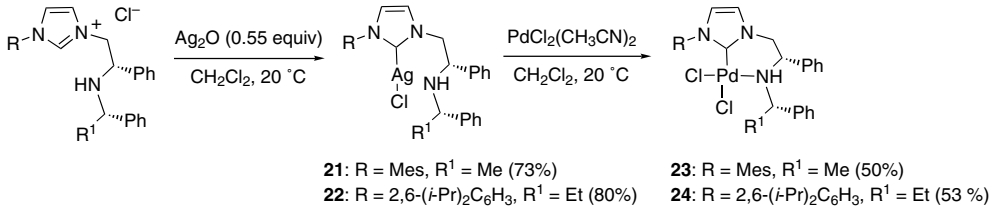
2.3. Synthesis of amino-NHC palladium(II) complexes

Palladium(II) complexes with achiral tridentate amino-NHC-amino ligands were reported by Cavell and coworkers in 2001 [23]. Douthwaite also described in 2004 the synthesis of a Pd(II) complex with an achiral tridentate chelating NHC-amino-NHC ligand [24]. In these two cases, the complexes were prepared from the azolium salt by prior formation of the silver(I) complex, then transfer of the carbene ligand to the precursor palladium complex. Ag(I) complexes bearing bidentate amino-NHC ligands were also reported by Arnold [39]. These complexes were obtained by treatment of the azolium salt with Ag_2O. Tridentate amino-NHC-amino ligands could also be generated by deprotonation of the imidazolium salt with KHMDS [40]. The use of Ag_2O to generate silver NHC complexes, initially reported by Lin and co-workers [41], and the transfer of the NHC ligands from silver to a transition metal is one of the widely used method to form NHC complexes [1–4,6–8,42,43].

The amino-NHC silver complexes **21** and **22** were obtained respectively in 73% and 80% yield by treatment of the corresponding azolium salts **17** and **19** with 0.55 equivalent of Ag_2O in CH_2Cl_2 at 20 °C for 16 h (Scheme 5). The reaction was performed with exclusion of light. The carbene carbon was not detectable in the ^{13}C NMR spectrum of complex **21**, but appeared as a doublet of doublet at 181 ppm in complex **22** with two coupling constants of 272 Hz (J^1 ^{109}Ag–^{13}C) and 236 Hz (J^1 ^{107}Ag–^{13}C). Dichloro palladium(II) complexes **23** and **24** were obtained by stirring a solution of the silver complexes in CH_2Cl_2 with 1 equivalent of bis(acetonitrile)dichloropalladium for 1 h. The complexes **23** and **24** were respectively isolated in 50% and 53% yield after filtration of the silver salts, concentration, dissolution of the crude in $CHCl_3$ or CH_2Cl_2 and precipitation with Et_2O.



Scheme 4.



Scheme 5.

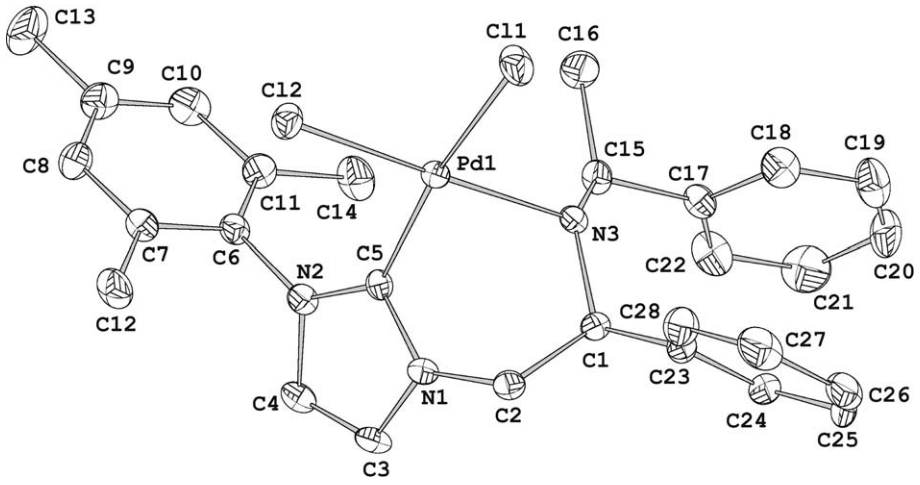


Fig. 3. Molecular structure of palladium complex **23**. Hydrogen atoms are omitted for clarity.

Yellow single crystals suitable for X-ray analysis were obtained by cooling at 4 °C a concentrated solution of the crude complex **23** in $CHCl_3$. The complex crystallises together with three molecules of $CHCl_3$. The structure of **23** is presented in Fig. 3. The crystallographic data are shown in Table 3. Selected bond lengths and angles are given in Table 4.

This structure confirmed the formation of a *cis*-dichloro palladium(II) complex with a chelating amino-NHC ligand, the six-membered Pd-metallocycle having a boat-like conformation. It also showed a distorted square–planar coordination around the palladium center. The palladium–carbene bond length is of about 1.975 Å. The Pd–Cl bond length *trans* to the NHC ligand is longer than the Pd–Cl bond *trans* to the amine due to the strongly σ-donating effect of the carbene. The structure of this complex is more or less similar to the one of a six-membered chelating imino–NHC palladium(II) complex reported by Douthwaite and co-workers in 2003 [17].

2.4. Catalysis – Allylic alkylation with a chelating amino-NHC ligand

The potential application of these chelating chiral ligands was tested on the asymmetric allylic alkylation of (*E*)-1,3-diphenylprop-3-en-yl acetate with dimethyl malonate (Scheme 6). A test reaction was performed at 20 °C using 7 mol. % of silver complex **21** and 3 mol. % of $[Pd(allyl)Cl]_2$. After 16 h at 20 °C, the product was isolated in 41% yield and 60% ee. The conditions were not optimised.

2.5. Synthesis of imino-NHC complexes

Since we have developed a method to synthesize various chiral imino-imidazolium salts, it was also of interest to acceed to the corresponding imino-NHC complexes. Several metal complexes (Pd, Pt, Rh, Ni) with non enolisable imino-NHC ligands have been reported [17,26,28,32,44]. Such complexes could be synthesized either from the corresponding silver complex or from the free carbene obtained by treatment of the imidazolium salt with an appropriate base [28,44]. Most of these complexes were obtained from iminoylimidazolium salts **4** (Fig. 1) [26,28,32] or from aromatic aldimines [44]. By contrast, complexes with enolisable imino-NHC ligands, derived from azolium salts of type **2** (Fig. 1), could not be synthesized through the free carbene. Several of these complexes have been obtained by prior formation of the silver complex [23,26].

Treatment of the imino-imidazolium salt **9** with Ag_2O in CH_2Cl_2 afforded the silver complex **25** in 80% yield. The IR spectrum of **25** shows a $\nu_{C=N}$ absorption at 1647 cm^{-1} which is essentially unchanged compared to that seen for the corresponding imidazolium salt **9** (1657 cm^{-1}). This suggests, as already observed [23], that the imino-NHC is bonded in a monodentate fashion to silver through the carbene carbon. Unfortunately, reaction of **25** with $PdCl_2(CH_3CN)_2$ in CH_2Cl_2 at 20 °C led to untractable reaction mixtures and no improvement was observed at lower temperatures.

Direct reactions of imidazolium salts with basic transition metal salts were also frequently used to generate

Table 3
Crystallographic data for compound **23**

Compound	**23**
Formula	$C_{31}H_{34}Cl_{11}N_3Pd$
Fw	945.01
Crystal system	Orthorhombic
a (Å)	10.6921 (15)
b (Å)	16.4551 (18)
c (Å)	23.849 (3)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	1495.9 (8)
Z	4
Space group	$P2_12_12_1$
Crystal shape	Parallelepiped
Crystal colour	Yellow
Linear absorption coefficient μ (cm^{-1})	11.68
Density ρ (g cm^3)	1.50
Diffractometer	KAPPACCD-Enraf Nonius
Radiation	Mo Kα ($\lambda = 0.71073$ Å)
Temperature (K)	250
θ Limits (°)	2–30
Octants collected	−14, 15; −23, 22; −33, 22
Number of data collected	27,539
Number of unique data collected	11,724
Number of unique data used for refinement	$7327(F_o)^2 > 3\sigma(F_o)^2$
Merging R	0.032
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.0684
Rw[a] $= [\sum w(\|\|F_o\| - \|F_c\|\|)^2/\sum wF_o^2]^{1/2}$	0.0706
Absorption correction	SADABS
Secondary extinction coefficient	None
Goodness of fit	1.075
Nb of variables	357
$\Delta\rho$min (e/Å^3)	−2.24
$\Delta\rho$max (e/Å^3)	2.61

[a] Weighting scheme of the form $w = w'[1 - ((|| F_o| - |F_c||)/6\sigma(F_o))^2]^2$ with $w' = 1/\Sigma_r A_r T_r(X)$ with coefficients 1.10, −1.53, 0.0762, −0.770 and −0.481 for a Chebyshev serie for which $X = Fc/Fc(max)$.

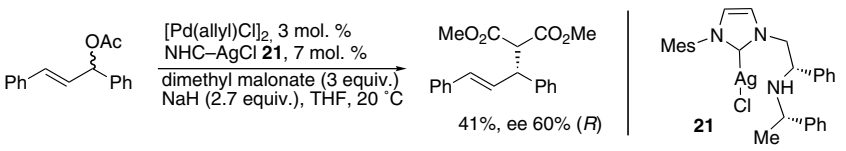
Table 4
Selected bond lengths (Å) and angles (°) for **23**

Compound	**23**
Bond lengths	
Pd(1)–Cl(1)	2.3690(18)
Pd(1)–Cl(2)	2.3008(17)
Pd(1)–C(5)	1.975(5)
Pd(1)–N(3)	2.117(5)
C(5)–N(1)	1.349(7)
C(5)–N(2)	1.365(8)
C(3)–N(1)	1.369(8)
C(4)–N(2)	1.407(8)
C(4)–C(3)	1.332(11)
Bond angles	
C(5)–Pd(1)–N(3)	88.7(2)
Cl(1)–Pd(1)–Cl(2)	91.88(7)
C(5)–Pd(1)–Cl(2)	92.75(17)
N(3)–Pd(1)–Cl(1)	86.82(15)
N(3)–Pd(1)–Cl(2)	178.35(15)
C(5)–Pd(1)–Cl(1)	169.23(19)
Pd(1)–N(3)–C(1)	117.5(4)
Pd(1)–C(5)–N(1)	118.2(4)
Pd(1)–C(5)–N(2)	136.5(4)
Pd(1)–N(3)–C(15)	110.7(4)
C(1)–N(3)–C(15)	111.0(5)

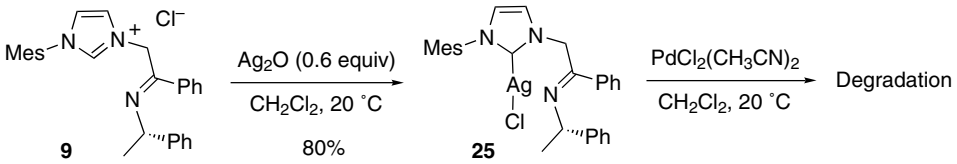
NHC complexes [1–4,6–8]. Reaction of imino-imidazolium salt **13** with $Pd(OAc)_2$ in refluxing THF led after work-up to a brown solid. The ^{1}H NMR spectrum of this solid in $CDCl_3$ was unexploitable. The same reaction performed at 20 °C in the presence of bases also led to the same result. We observed then that the treatment of salts **9**–**14** with 1 equivalent of $Pd(OAc)_2$ and 4 equivalent of LiCl in THF at 0 °C led in 87–100% yield to new complexes from which structure could not be exactly determined. The ^{1}H NMR spectra of these complexes are well defined and show that the diastereotopic methylene protons are shifted to low-field compared to those of the corresponding salts. For example, signals corresponding to the methylene protons of **14** (two doublets at 5.77 and 5.94 ppm) are shifted to 7.79 and 7.88 ppm in the complex. Moreover, the IR spectrum shows a $\nu_{C=N}$ absorption at 1628 cm^{-1} instead of 1663 cm^{-1} for the imidazolium salt **14**. This suggests that an imino-Pd complex is formed. However, for most of these complexes, the ^{1}H NMR spectra still showed three singlet resonance that integrate each for one hydrogen and may fit with the three protons of the imidazolium ring. Treatment of these complexes with NEt_3 in THF led to the starting imidazolium salts. These observations suggested that these complexes are probably imino-imidazolium $PdCl_2$ complexes and not imino-NHC complexes. The enamine form, observed by Coleman and co-workers after reaction of an imino-NHC silver complex with $PdCl(CH_3CN)_2$ [26], was not detected. ^{13}C NMR spectra could not be obtained with acceptable resolution since the complexes are poorly stable in solution. Mass spectroscopy analyses confirmed the formation of palladium complexes but did not allowed us to make a distinction between an azolium salt and a free carbene. Finally, reaction of these palladium complexes with *t*-BuOK in THF also led to degradation products and not to the expected imino-NHC complexes or enamino-NHC complexes. All these observations and the results of the deuteration experiments showed in Scheme 2, underline that in the case of enolisable imino-imidazoliums salts **9**–**15**, the methylene protons are more acidic than the N–C*H*=N proton of the imidazolium ring. A similar observation was reported by Bilstein after unsuccessful attempts to generate NHC from 2-imino-2-phenyl ethyl imidazolium salts of type **2** (Fig. 1, R^1 = Ph) [30] (see Scheme 7).

3. Conclusion

We have developed an efficient procedure for the synthesis of a new class of chiral imino-imidazolium salts. The diastereoselective reduction of these compounds led to amino-imidazolium salts. Pure diastereomers could be obtained by recrystallisation. New chiral amino–NHC silver(I) and palladium(II) complexes were synthesized from these azoliums. The preparation of a range of chiral ligands can be envisaged by this methodology. Amino–NHC ligands can be used in asymmetric allylic alkylation reaction. Currently, moderate results were obtained in this



Scheme 6.



Scheme 7.

reaction with the ligand tested. The optimisation of this reaction and the use of these chelating chiral amino–NHC ligands in other reactions in asymmetric catalysis are under investigation.

4. Experimental

All experiments were performed under argon using standard Schlenk techniques unless stated otherwise. Solvents were dried over the appropriate drying agent and distilled under dinitrogen. Sodium benzophenone ketyl (THF, Et_2O), CaH_2 (CH_2Cl_2). EtOH, MeOH and $CHCl_3$ of analytical grade type were used without special drying or distillation. All reagents were purchased from Acros or Aldrich and used as received unless otherwise stated. 1-Mesitylimidazole and 1-(2,6-*i*-$Pr_2C_6H_3$)-imidazole were prepared according to Zhang [45]. In the case of 1-mesitylimidazole, the purification by chromatography described was replaced by several recrystallisations in cyclohexane to give the pure product in 35% yield. 1-(2,6-*i*-$Pr_2C_6H_3$)-Imidazole can also be recrystallised in *n*-pentane. 1-*tert*-Butyl-imidazole was prepared according to Gridnev [46]. Microanalyses were performed by the microanalytical service ICSN (CNRS). NMR spectra were recorded on a Bruker ARX 400 or AC 200 Q instrument, in $CDCl_3$, CD_2Cl_2 or CD_3OD as the solvent. Optical rotations were measured on a Perkin–Elmer 343.

4.1. Preparation of 1-(2-oxo-2-phenyl)ethyl imidazolium salts

4.1.1. 3-Mesityl-1-(2-oxo-2-phenyl)ethyl imidazolium chloride (5)

A solution of 1-mesitylimidazole (3 g, 16.1 mmol) and 2-chloroacetophenone (2.98 g, 19.3 mmol) in dry THF (20 mL) was stirred for 16 h at 20 °C then heated at reflux for 3 h. After cooling, the precipitate formed was filtered, washed with Et_2O and dried to give 3.39 g (62%) of an off white solid. M.p. 207 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.15 (s, 6H), 2.38 (s, 3H), 6.82 (s, 2H, CH_2C=O), 7.05 (s, 2H), 7.21 (t, 1H, *J* 1.5 Hz), 7.57 (t, 2H, $J = 8$ Hz), 7.67 (t, 1H, $J = 8$ Hz), 7.74 (t, 1H, $J = 1.5$ Hz), 8.19 (d, 2H, $J = 8$ Hz), 10.40 (s, 1H, N–C*H*=N). ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.5, 21.1, 56.1 (*C*H_2), 122.1, 125.1, 128.6, 129.0, 129.7, 130.7, 133.7, 134.3, 134.4, 139.1 (N–*C*H=N), 141.2, 191.2 (*C*=O). Anal. Calc. for $C_{20}H_{21}ClN_2O$ ($M_W = 340.85$) C, 70.48; H, 6.21; N, 8.22. Found: C, 70.29; H, 6.26; N, 8.21%. IR (ATR diamond) $\nu_{C=O}$ 1703 cm^{-1}.

4.1.2. 3-(2,6-Diisopropylphenyl)-1-(2-oxo-2-phenyl)ethyl imidazolium chloride (6)

A solution of 1-(2,6-diisopropylphenyl)imidazole (4.43 g, 19.4 mmol) and 2-chloroacetophenone (8.96 g, 58.2 mmol) in dry THF (20 mL) was stirred for 6 h at reflux. After cooling, Et_2O was added and the precipitate formed was filtered, washed with Et_2O and dried to give 6.4 g (94%) of a white solid. M.p. 98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.12 (d, 6H, $J = 6.6$ Hz), 1.19 (d, 6H, $J = 6.6$ Hz), 2.34 (m, 2H, $J = 6.6$ Hz), 6.77 (s, 2H, CH_2C=O), 7.14 (s, 1H), 7.26 (d, 2H, $J = 8$ Hz), 7.45–7.51 (m, 3H), 7.58 (t, 1H, $J = 7.5$ Hz), 7.85 (d, 1H, $J = 8.3$ Hz), 8.11 (d, 2H, $J = 7.5$ Hz), 10.20 (s, 1H, N–C*H*=N). ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.3, 28.7, 56.1 (*C*H_2), 123.2, 124.7, 128.8, 129.2, 130.1, 132.0, 133.5, 134.8, 139.8 (N–*C*H=N), 145.53, 191.0 (*C*=O). Exact MS (ESI+ in MeOH sens = 1.00e^8) m/e = 348.26 for $C_{23}H_{27}N_2O$ (M^+–Cl). IR (ATR diamond) $\nu_{C=O}$ 1696 cm^{-1}.

4.1.3. 3-tert-Butyl-1-(2-oxo-2-phenyl)ethyl imidazolium chloride (7)

A solution of 1-*tert*-butylimidazole (2 g, 16.1 mmol) and 2-chloroacetophenone (2.97 g, 19.2 mmol) in dry THF (18 mL) was stirred for 16 h at 20 °C then heated at reflux for 2 h. After cooling, the precipitate formed was filtered, washed with Et_2O and dried to give 4.46 g (99%) of a white solid. M.p. 250 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.76 (s, 9H), 6.49 (s, 2H, CH_2C=O), 7.35 (s, 1H), 7.43 (s, 1H), 7.57 (dd, 2H, $J = 8.1$ and 7.3 Hz), 7.69 (t, 1H, $J = 7.3$ Hz), 8.15 (d, 2H, $J = 8.1$ Hz), 11,03 (s, 1H, N–C*H*=N). ^{13}C NMR (100 MHz, CD_3OD, the salt is little soluble in $CDCl_3$) δ

30.7, 57.4 (CH_2), 62.3, 121.8, 126.5, 130.2, 131.0, 136.0, 136.5, 138.0 (N–*C*H=N), 193.1 (*C*=O). Anal. Calc. for $C_{15}H_{19}ClN_2O$ ($M_W = 278.78$) C, 64.63; H, 6.87; N, 10.05. Found: C, 64.31; H, 7.17; N, 9.83%. IR (ATR diamond) $\nu_{C=O}$ 1694 cm^{-1}.

4.1.4. 3-tert-Butyl-1-(2-oxo-2-phenyl)ethyl imidazolium bromide (*8*)

A solution of 1-*tert*-butylimidazole (1.68 g, 13.5 mmol) and 2-bromoacetophenone (2.67 g, 13.5 mmol) in dry THF (15 mL) was stirred for 16 h at 20 °C. The precipitate formed was filtered, washed with Et_2O and dried to give 4.06 g (93%) of a white solid. M.p. 225 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.80 (s, 9H), 6.22 (s, 2H, C*H*$_2$C=O), 7.43 (s, 2H), 7.60 (t, 2H, $J = 8$ Hz), 7.72 (t, 1H, $J = 8$ Hz), 8.13 (d, 2H, $J = 8$ Hz), 9,61 (s, 1H, N–C*H*=N). ^{13}C NMR (100 MHz, CD_3OD, the salt is little soluble in $CDCl_3$) δ 30.7, 57.5 (CH_2), 62.3, 121.8, 126.5, 130.2, 131.0, 136.0, 136.5, 137.9 (N–*C*H=N), 193.0 (*C*=O). Anal. Calc. for $C_{15}H_{19}BrN_2O$ ($M_W = 323.23$) C, 55.74; H, 5.92; N, 8.67. Found: C, 55.56; H, 6.01; N, 8.53%. IR (ATR diamond) $\nu_{C=O}$ 1697 cm^{-1}.

4.2. General procedure for the preparation of imino-imidazolium salts

In a screw-cap tube flushed with argon were added the 1-(2-oxo-2-phenyl)ethyl imidazolium salt **5**–**8** (1 mmol), the chiral amine (3 mmol) and 2 mL of $CHCl_3$. A paper trap filled with molecular sieves 4 Å was placed at the top of the tube before closing. The mixture was stirred under argon at 90 °C (oil bath) for 60 h. After cooling, CH_2Cl_2 (2 mL) and $NaHCO_3$ (300 mg, 3.5 mmol) were added and the mixture was stirred vigorously for 1 h, filtered under dinitrogen and concentrated. Imino-imidazolium salts **9**–**13** were precipitated from the crude by several washing of the residue with dry Et_2O. Imino-imidazolium salts **14**–**15** were precipitated in THF and washed with the same solvent. The reaction could be performed on a 3 mmol scale. In this case the precipitation of the imino-imidazolium salts **9**–**13** was more difficult and after addition of dry Et_2O the reaction vessel was placed in an ultrasonic bath for 5 min. Et_2O was removed. The procedure was repeated several times until the solid precipitate.

4.2.1. 3-Mesityl-1-[2-{(S)-1-(phenyl)ethylimino}-2-phenyl ethyl] imidazolium chloride (*9*)

Yield 87%, pale orange powder. M.p. 83 °C. $[\alpha]_D^{20} = -5$ (*c* 1.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (d, 3H, $J = 6.6$ Hz), 2.00 (s, 3H), 2.10 (s, 3H), 2.35 (s, 3H), 4.60 (q, 1H, $J = 6.6$ Hz), 5.66 (d, 1H, $J = 17.4$ Hz, C*H*H–C=N), 6.32 (d, 1H, $J = 17.4$ Hz, CH*H*–C=N), 6.99 (s, 2H), 7.12–7.15 (m, 3H), 7.20–7.29 (m, 3H), 7.42–7.55 (m, 5H), (t, 1H, $J = 1.5$ Hz), 7.67 (t, 1H, $J = 1.5$ Hz), 10.47 (s, 1H, N–C*H*=N). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 17.3, 17.4, 20.9, 24.8, 55.9 (CH_2), 60.2 (CH_3CHN), 122.1 (*C*H=CH), 124.8 (CH=*C*H), 126.2, 126.7, 127.4, 128.4, 128.8, 129.5, 129.6, 131.1, 134.2, 134.6, 139.6 (N–*C*=N), 141.0, 141.6, 145.3, 162.2 (CH_2C=N). Exact MS (ESI+ in MeOH sens = 4.10e^6): m/e = 408.23 for $C_{28}H_{30}N_3$ (M^+–Cl). IR (ATR diamond) $\nu_{C=N}$ 1657 cm^{-1}.

4.2.2. 3-Mesityl-1-[2-{(S)-1-(p-chlorophenyl)ethylimino}-2- phenyl ethyl] imidazolium chloride (*10*)

Yield 70%, off white solid. M.p. 121 °C. $[\alpha]_D^{20} = -24$ (*c* 1.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (d, 3H, $J = 6.3$ Hz), 1.98 (s, 3H), 2.07 (s, 3H), 2.35 (s, 3H), 4.56 (q, 1H, $J = 6.3$ Hz), 5.72 (d, 1H, $J = 17.3$ Hz, CH*H*–C=N), 6.27 (d, 1H, $J = 17.3$ Hz, C*H*H–C=N), 6.99 (s, 2H), 7.07 (d, 2H, $J = 8.5$ Hz, *meta* position of the chloride in C_6H_4Cl), 7.12 (s, 1H, C*H*=CH), 7.23 (d, 2H, $J = 8.5$ Hz, *ortho* position of the chloride in C_6H_4Cl), 7.40–7.53 (m, 5H), 7.70 (s, 1H, CH=C*H*), 10.49 (s, 1H, N–C*H*=N). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 17.6, 17.7, 25.0, 56.3 (CH_2), 59.9 (CH_3–*C*H–N), 122.4 (Mes-N-*C*H=CH), 125.0 (CH=*C*H–N–CH_2), 127.7, 128.1, 128.8, 129.2, 130.0, 131.4, 132.5, 134.5, 134.9, 140.2 (N–*C*=N), 141.5, 144.2, 163.2 (CH_2C=N). Exact MS (ESI+ in MeOH sens = 3.72e^7): m/e = 442.2 for $C_{28}H_{29}N_3Cl$ (M^+–Cl). IR (ATR diamond) $\nu_{C=N}$ 1662 cm^{-1}.

4.2.3. 3-(2,6-Diisopropylphenyl)-1-[2-{(S)-1-(phenyl)-ethylimino}-2-phenyl ethyl] imidazolium chloride (*11*)

Yield 92%, yellow solid. M.p. 125 °C. $[\alpha]_D^{20} = +4$ (*c* 1.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.14 (d, 3H, $J = 6.8$ Hz), 1.18 (d, 3H, $J = 6.8$ Hz), 1.22 (d, 3H, $J = 6.8$ Hz), 1.24 (d, 3H, $J = 6.8$ Hz), 1.29 (d, 3H, $J = 6.3$ Hz), 2.33 (m, 1H, $J = 6.8$ Hz), 2.49 (m, 1H, $J = 6.8$ Hz), 4.66 (q, 1H, $J = 6.3$ Hz), 5.58 (d, 1H, $J = 17.4$ Hz, CH*H*–C=N), 6.56 (d, 1H, $J = 17.4$ Hz, C*H*H–C=N), 7.12–7.40 (m, 8H), 7.45–5.57 (m, 6H), 7.65 (s, 1H), 10.60 (s, 1H, N–C*H*=N). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 23.9, 24.1, 24.2, 24.8, 28.4, 28.5, 55.9 (CH_2), 60.0, 123.0, 124.5, 124.9, 126.1, 126.6, 127.5, 128.4, 128.7, 129.4, 130.6, 131.6, 134.4, 140.0 (N–*C*=N), 145.4, 145.6, 162.5 (CH_2C=N). Exact MS (ESI+ in MeOH sens = 2.09e^6): m/e = 450.25 for $C_{31}H_{36}N_3$ (M^+–Cl). IR (ATR diamond) $\nu_{C=N}$ 1662 cm^{-1}.

4.2.4. 3-(2,6-Diisopropylphenyl)-1-[2-{(S)-1-(p-chlorophenyl)ethylimino}-2-phenyl ethyl] imidazolium chloride (*12*)

Yield 70%, pale orange solid. M.p. 131 °C. $[\alpha]_D^{20} = -20$ (*c* 1.3, $CHCl_3$). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 1.03 (d, 3H, $J = 6.5$ Hz), 1.05 (d, 3H, $J = 6.5$ Hz), 1.07 (d, 3H, $J = 6.5$ Hz), 1.09 (d, 3H, $J = 6.5$ Hz), 1.17 (d, 3H, $J = 6.5$ Hz), 2.24 (m, 1H, $J = 6.5$ Hz), 2.35 (m, 1H, $J = 6.5$ Hz), 4.50 (q, 1H, $J = 6.5$ Hz), 5.65 (d, 1H, $J = 17.4$ Hz, C*H*H–C=N), 6.21 (d, 1H, $J = 17.4$ Hz, CH*H*–C=N), 7.05 (d, 2H, $J = 8.5$ Hz), 7.13 (s, 1H), 7.17 (d, 2H, $J = 8.5$ Hz), 7.25 (dd, 2H, $J = 8$ and 2 Hz), 7.32–7.36 (m, 3H), 7.43–7.51 (m, 3H), 7.81 (s, 1H), 10.60 (s, 1H, N–C*H*=N). 13C NMR (100 MHz, CD_2Cl_2) δ 24.3, 24.4, 24.5, 25.1, 28.8, 28.9, 56.4 (CH_2), 59.8, 123.4, 124.8, 125.0, 127.8, 128.0,

128.8, 129.2, 130.0, 130.8, 132.1, 132.5, 134.4, 140.6 (N–*C*=N), 144.3, 145.9, 163.4 (CH_2C=N). Exact MS (ESI+ in MeOH sens = 4.14e^7): m/e = 484.3 for $C_{31}H_{35}N_3Cl$ (M^+–Cl). IR (ATR diamond) $\nu_{C=N}$ 1663 cm^{-1}.

4.2.5. 3-(2,6-Diisopropylphenyl)-1-[2-{(S)-1- (phenyl)-propylimino}-2-phenyl ethyl] imidazolium chloride (**13**)

Yield 78%, white solid. M.p. 241 °C. $[\alpha]_D^{20} = -17$ (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.68 (t, 3H, *J* = 7.3 Hz), 1.15 (d, 3H, *J* = 6.8 Hz), 1.22 (d, 3H, *J* = 6.8 Hz), 1.25 (d, 3H, *J* = 6.8 Hz), 1.28 (d, 3H, *J* = 6.8 Hz), 1.60 (dq, 1H, *J* = 7.3 and 6.6 Hz, CH_3CHH), 1.64 (dq, 1H, *J* = 7.3 and 6.6 Hz, CH_3CHH), 2.33 (m, 1H, *J* = 6.8 Hz), 2.53 (m, 1H, *J* = 6.8 Hz), 4.36 (t, 1H, *J* = 6.6 Hz), 5.45 (d, 1H, *J* = 17.4 Hz, CH*H*–C=N), 6.76 (dd, 1H, *J* = 17.4 and 2 Hz, C*H*H–C=N), 7.14–7.19 (m, 3H), 7.22–7.36 (m, 5H), 7.43–7.62 (m, 7H), 10.75 (s, 1H, N–C*H*=N). ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.9 (CH_2CH_3), 24.0, 24.3, 24.4, *24.7,* 28.3, 28.6, 32.5 (CH_2CH_3), 56.2 (CH_2C=N), 66.9, 123.0, 124.3, 124.5, 124.6, 126.4, 126.6, 126.9, 127.3, 127.6, 128.5, 128.8, 129.6, 130.3, 131.7, 133.8, 139.9 (N–*C*=N), 144.3, 145.4, 145.5, 162.6 (CH_2C=N). Exact MS (ESI+ in MeOH sens = 5.28e^7): m/e = 464.3 for $C_{32}H_{38}N_3$ (M^+–Cl). IR (ATR diamond) $\nu_{C=N}$ 1664 cm^{-1}.

4.2.6. 3-tert-Butyl-1-[2-{(S)-1-(phenyl)ethylimino}-2-phenyl ethyl] imidazolium chloride (**14**)

Yield 88%, white solid. M.p. 64 °C. $[\alpha]_D^{20} = -36$ (*c* 1, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (d, 3H, *J* = 6.3 Hz), 1.72 (s, 9H), 4.57 (q, 1H, *J* = 6.3 Hz), 5.46 (d, 1H,*J* = 17.4 Hz, C*H*H–C=N), 5.94 (d, 1H, *J* = 17.4 Hz, CH*H*–C=N), 7.10–7.13 (m, 2H), 7.22–7.30 (m, 3H), 7.33–7.36 (m, 2H), 7.40–7.50 (m, 5H), 10.96 (s, 1H, N–C*H*=N). ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.2, 30.0, 55.7 (CH_2), 59.9 ($C(CH_3)$), 60.4 (N–*C*H–CH_3), 118.2, 123.8, 126.1, 126.8, 127.2, 128.4, 128.9, 129.5, 133.8, 137.5 (N–*C*=N), 145.2, 161.6 (CH_2C=N). Anal. Calc. for $C_{23}H_{28}ClN_3 \cdot H_2O$ (M_W = 399.96) C, 69.07; H, 7.56; N, 10.51. Found: C, 69.15; H, 7.27; N, 10.41%. IR (ATR diamond) $\nu_{C=N}$ 1663 cm^{-1}.

4.2.7. 3-tert-Butyl-1-[2-{(S)-1-(phenyl)ethylimino}-2-phenyl ethyl] imidazolium bromide (**15**)

Yield 76%, white solid. M.p. 80 °C. $[\alpha]_D^{20} = -39$ (*c* 1.3, CH_2Cl_2). ^{1}H NMR (400 MHz, DCl_3) δ 1.27 (d, 3H, *J* = 6.6 Hz), 1.73 (s, 9H), 4.57 (q, 1H, *J* = 6.6 Hz), 5.45 (d, 1H, *J* = 17.4 Hz, CH*H*–C=N), 5.92 (dd, 1H, *J* = 17.4 and 4.5 Hz, C*H*H–C=N), 7.10–7.12 (m, 2H), 7.15–7.50 (m, 10H), 10.69 (br s, 1H, N–C*H*=N). ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.2, 30.1, 55.8 (CH_2), 60.1 ($C(CH_3)$), 60.4 (N–*C*H–CH_3), 118.1, 123.9, 126.1, 126.8, 127.2, 128.4, 128.9, 129.6, 133.7, 137.2 (N–*C*=N), 145.1, 161.4 (CH_2C=N). Anal. Calc. for $C_{23}H_{28}BrN_3$ (M_W = 426.39) C, 64.79; H, 6.62; N, 9.85. Found: C, 64.67; H, 6.79; N, 9.67%. IR (ATR diamond) $\nu_{C=N}$ 1663 cm^{-1}.

4.3. General procedure for the $NaBH_4$ reduction of imino-imidazolium salts

The imino-imidazolium salt (0.22 mmol) was dissolved in MeOH (5 mL) under argon. The solution was cooled to –70 °C and $NaBH_4$ (33 mg, 0.88 mmol) was added by portions. The mixture was stirred overnight, during which period it was allowed to gradually warm to 20 °C. A saturated aqueous NH_4Cl solution (5 mL) was added and the mixture was stirred vigorously for 10 min. Solid K_2CO_3 was added and the mixture was stirred for 10 min. The methanol was evaporated and the resulting mixture was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and concentrated. The product was washed with Et_2O and dried under vacuum.

4.3.1. 3-Mesityl-1-[(2S)-2-{(S)-1-(phenyl)ethylamino}-2-phenyl ethyl] imidazolium chloride (**17**)

Yield 91%, pale orange solid. 90:10 Mixture of diastereomers. The major diastereomer was separated by crystallisation. The crude was dissolved in a minimum of CH_2Cl_2 and diluted with acetone. Et_2O was then added until the mixture becomes cloudy and the mixture was cooled at 4 °C for 16 h. This procedure afforded 52% of small colorless needles with a *dr* of 94:6. A second crystallisation in the same conditions led to 36% of the major diastereomer with a *dr* >98:2 (the minor isomer was not detectable in the NMR spectrum). White powder, M.p. 113 °C. $[\alpha]_D^{20} = +101$ (*c* 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 (d, 3H, *J* = 6.5 Hz), 1.95 (s, 3H), 2.03 (s, 3H), 2.36 (s, 3H), 2.79 (br s, 1H, N*H*), 3.80 (q, 1H, *J* = 6.5 Hz), 4.33 (dd, 1H, *J* = 6 and 5 Hz, CH_2–C*H*–NH), 4.98 (dd, 1H, *J* = 13.6 and 6 Hz, CH*H*–CH–NH), 5.15 (dd, 1H, *J* = 13.6 and 5 Hz, C*H*H–CH–NH), 6.92 (t, 1H, *J* = 1.5 Hz, C*H*=CH), 6.99 (br s, 2H), 7.11 (t, 1H, *J* = 1.5 Hz, CH=C*H*) 7.19–7.33 (m, 10H), 10.42 (t, 1H, *J* = 1.5 Hz, N–C*H*=N). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 17.3, 17.5, 21.0, 22.7 (CH_3–CH), 54.5 (CH_3–*C*H–NH), 54.7 (CH_2), 59.7 (CH_2–*C*H–NH), 121.6 (*C*H=CH), 123.3 (CH=*C*H), 126.5, 126.7, 127.4, 127.8, 128.1, 128.3, 128.9, 129.7, 130.7, 134.3, 139.3 (N–*C*H=N), 141.1, 145.5. Exact MS (ESI+ in CH_3CN sens = 4.17e^6): m/e = 410.2 for $C_{28}H_{32}N_3$ (M^+–Cl).

4.3.2. 3-(2,6-Diisopropylphenyl)-1-[(2S)-2-{(S)-1-(phenyl)ethylamino}-2-phenyl ethyl] imidazolium chloride (**18**)

Yield 87%, yellow solid. 86:14 Mixture of diastereomers. *Major diastereomer*: ^{1}H NMR, (400 MHz, $CDCl_3$) δ 1.07–1.12 (m, 9H), 1.21 (d, 3H, *J* = 6.6 Hz), 1.36 (d, 3H, *J* = 6.1 Hz), 2.16–2.31 (m, 2H), 3.79 (q, 1H, *J* = 6.6 Hz), 4.29 (dd, 1H, *J* = 6.3 and 4.5 Hz), 4.90 (dd, 1H, *J* = 13.6 and 6.3 Hz), 5.17 (dd, 1H, *J* = 13.6 and 4.5 Hz), 6.86 (s, 1H), 6.96–7.51 (m, 14H), 10.33 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.9, 24.0, 24.1, 24.2, 24.4 (CH_3), 28.5 ($CH(CH_3)_2$), 54.7 (N–*C*H–CH_3), 54.9 (CH_2), 59.6 (CH_2–*C*H–Ph), 122.8, 123.7, 124.4, 124.5, 126.4, 126.7, 127.4, 128.0, 128.3, 128.7, 130.3, 131.6, 139.3 (N–*C*H=N),

139.8, 145.3, 145.5. Exact MS (ESI+ in CH_3CN sens = 2.09e[6]): m/e = 452.3 for $C_{31}H_{38}N_3$ (M^+–Cl). The crude salt was recrystallised twice in CH_2Cl_2/acetone/Et_2O to give colorless needles suitable for X-ray diffraction analysis. The NMR spectrum of the crystals obtained showed the presence of the major diastereomer only.

4.3.3. 3-(2,6-Diisopropylphenyl)-1-[(2S)-2-{(S)-1-(phenyl)propylamino}-2-phenyl ethyl] imidazolium chloride (**19**)

Yield 99%, yellow solid. Mixture of diastereomers 85:15. The same procedure was followed for the separation of the major diastereomer by crystallisation. The first crystallisation afforded 62% of small colorless needles with a *dr* of 97:3. A second crystallisation in the same conditions led to 46% of the major diastereomer with a *dr* >98:2 (the minor isomer was not detectable in the NMR spectrum). White powder. M.p. 245 °C. $[\alpha]_D^{20} = +31.6$ (*c* 2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.74 (t, 3H, $J = 7.5$ Hz), 1.06–1.10 (m, 9H), 1.20 (d, 3H, $J = 6.8$ Hz), 1.65 (m, 1H, C*H*H–CH_3), 1.84 (m, 1H, CH*H*–CH_3), 2.16 (m, 1H, $J = 7$ Hz, C*H*(CH_3)$_2$), 2.23 (m, 1H, $J = 7$ Hz, C*H*(CH_3)$_2$), 2.72 (br s, 1H, N*H*), 3.56 (dd, 1H, $J = 8.3$ and 4.8 Hz, Et-C*H*–N), 4.32 (dd, 1H, $J = 6$ and 4.5 Hz, N–CH_2–C*H*–NH), 5.00 (dd, 1H, $J = 6$ and 13.9 Hz, N–CH*H*–CH–NH), 5.16 (dd, 1H, $J = 4.5$ and 13.9 Hz, N–C*H*H–CH–NH), 6.95 (t, 1H, $J = 1.5$ Hz, C*H*=CH), 7.13–7.32 (m, 10H), 7.38 (t, 1H, $J = 1.5$ Hz), 7.50 (t, 1H, $J = 7.8$ Hz), 10.37 (s, 1H, N–C*H*=N). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 10.4 (*C*H_3–CH_2), 24.0, 24.1, 24.3, 24.5, (CH(*C*H_3)$_2$), 28.5 (*C*H(CH_3)$_2$), 29.5 (*C*H_2–CH_3), 54.4 (*C*H_2–N), 59.7 (N–CH_2–*C*H–N), 61.3 (Et-*C*H–N), 122.6 (*C*H=CH), 123.3 (CH=*C*H), 124.5, 124.6, 126.7, 127.2, 127.3, 128.0, 128.3, 128.7, 130.3, 131.7, 139.3, 139.6 (N–*C*H=N), 143.5, 145.3. Anal. Calc. for $C_{32}H_{40}ClN_3$ ($M_W = 502.13$) C, 76.54; H, 8.03; N, 8.37. Found: C, 76.53; H, 8.12; N, 8.35%.

4.3.4. 3-tert-butyl-1-[(2S)-2-{(S)-1-(phenyl)ethylamino}-2-phenyl ethyl] imidazolium chloride (**20**)

Yield 65%, white solid. 85:15 Mixture of diastereomers. *Major diastereomer*: ^{1}H NMR, (400 MHz, $CDCl_3$) δ 1.28 (d, 3H, $J = 6.6$ Hz), 1.66 (s, 9H), 3.77 (q, 1H, $J = 6.6$ Hz), 4.17 (dd, 1H, $J = 7$ and 5.3 Hz), 4.69 (dd, 1H, $J = 13.8$ and 5.3 Hz), 4.75 (dd, 1H, $J = 13.8$ and 7 Hz), 6.96 (br s, 1H), 7.12 (t, 1H, $J = 1.8$ Hz), 7.15–7.39 (m, 10H), 10.82 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$). δ 23.0, 30.0, 54.3 (*C*H2), 54.6, 59.8, 118.3, 122.9, 126.4, 126.8, 127.2, 128.0, 128.3, 128.8, 137.1 (N–*C*H=N), 139.5, 145.6. Exact MS (ESI+ in CH_3CN sens = 6.37e[6]): m/e = 348.3 for $C_{23}H_{30}N_3$ (M^+–Cl).

4.4. Preparation of amino-imidazol-2-ylidene silver (I) complexes

To a solution of imidazolium salt (1 mmol) in dry CH_2Cl_2 (15 mL) was added Ag_2O (0.55 mmol). The mixture was stirred at 20 °C for 16 h with exclusion of light, filtered through celite, concentrated under reduced pressure and dried under vaccum.

4.4.1. 3-Mesityl-1-[(2S)-2-{(S)-1-(phenyl)ethylamino}-2-phenyl ethyl] imidazol-2-ylidene AgCl (**21**)

Yield 73% from **17**, white solid. M.p. 82 °C. $[\alpha]_D^{20} = -33$ (*c* 0.3, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (d, 3H, $J = 6.6$ Hz), 1.71 (s, 3H), 1.81 (s, 3H), 2.22 (s, 3H), 3.76 (q, 1H, $J = 6.6$ Hz, CH_3–C*H*–N), 4.00 (dd, 1H, $J = 6$ and 7 Hz, CH_2–C*H*–NH), 4.31 (dd, 1H, $J = 13.4$ and 7 Hz, CH*H*–CH–NH), 4.38 (dd, 1H, $J = 13.4$ and 6 Hz C*H*HCH–NH), 6.71 (d,1H, $J = 1.5$ Hz, C*H*=CH), 6.82 (s, 1H, C*H* Mes), 6.83 (s, 1H, C*H* Mes), 6.89 (s br, 1H, CH=C*H*), 7.10 (m, 2H), 7.15–7.26 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.6, 17.7, 21.0, 23.0, 55.2 (NH–*C*H–CH_3), 57.3 (*C*H_2), 61.2 (CH_2*C*H–NH), 121.8 (*C*H=CH), 122.1 (CH=*C*H), 126.5, 127.1, 127.3, 128.2, 128.7, 129.2, 129.3, 134.5, 134.6, 135.2, 139.4, 139.7, 145.0, the carbene carbon was not detected. Anal. Calc. for $C_{28}H_{31}AgClN_3$ ($M_W = 552.89$) C, 60.83; H, 5.65; N, 7.60. Found: C, 60.79; H, 5.46; N, 7.55%.

4.4.2. 3-(2,6-Diisopropylphenyl)-1-[(2S)-2-{(S)-1-(phenyl)propylamino}-2-phenyl ethyl] imidazol-2-ylidene AgCl (**22**)

Yield 80% from **19**, white solid. M.p. 75 °C. $[\alpha]_D^{20} = -18.4$ (*c* 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (t, 3H, $J = 7.3$ Hz), 1.02 (d, 3H, $J = 6.8$ Hz), 1.06 (d, 3H, $J = 6.8$ Hz), 1.10 (d, 3H, $J = 6.8$ Hz), 1.14 (d, 3H, $J = 6.8$ Hz), 1.65 (m, 1H, C*H*H–CH_3), 1.76 (dd, 1H, $J = 6.8$ and 6 Hz, N*H*), 1.83 (m, 1H, CH*H*–CH_3), 2.10 (m, 1H, $J = 6.8$ Hz, C*H*(CH_3)$_2$), 2.19 (m, 1H, $J = 6.8$ Hz, C*H*-(CH_3)$_2$), 3.65 (m, 1H, Et-C*H*–N), 4.03 (m, 1H, N–CH_2-C*H*–N), 4.43 (dd, 1H, $J = 6.8$ and 13.8 Hz, N–CH*H*–CH–NH), 4.47 (dd, 1H, $J = 6.3$ and 13.8 Hz, N–C*H*H–CH–NH), 6.80 (s, 1H, C*H*=CH), 6.94 (s, 1H, CH=C*H*), 7.14-7.34 (m, 10H), 7.41 (t, 1H, $J = 7.8$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.6 (*C*H_3–CH_2), 23.30, 23.37, 23.41, 23.47, 27.01, 27.04, 28.9 (*C*H_2–CH_3), 55.8 (*C*H_2–N), 60.1 (N–CH_2–*C*H–N), 61.1 (Et-*C*H–N), 120.5 (d, J^3(Ag–^{13}C) 7 Hz), 122.4 (d, J^3(Ag–^{13}C) 8 Hz), 123.1, 126.1, 126.2, 127.1, 127.6, 128.0, 129.4, 133.5, 138.8, 142.2, 144.5, 181.0 (dd, J^1(^{109}Ag–^{13}C) 272 Hz and J^1(^{107}Ag–^{13}C) 236 Hz, $C_{carbene}$). Anal. Calc. for $(C_{32}H_{39}ClN_3Ag)_6(AgCl)_5$ ($M_W = 4370.56$) C, 52.76; H, 5.40; N, 5.77. Found: C, 52.77; H, 5.69; N, 5.17%.

4.4.3. 3-Mesityl-1-[(2S)-2-{(S)-1-(phenyl)ethylamino}-2-phenyl ethyl] imidazol-2-ylidene $PdCl_2$ (**23**)

A solution of Ag(I) complex **21** (88 mg, 0.16 mmol) and $PdCl_2(CH_3CN)_2$ (41.7 mg, 0.16 mmol) in CH_2Cl_2 (1.5 mL) was stirred at 20 °C for 1 h with exclusion of light, filtered through celite and concentrated under reduced pressure to give 97 mg (100%) of a brown yellow solid. The crude was dissolved in $CHCl_3$ (1 mL) and the complex was precipitated by addition of Et_2O. Yield 50% (47 mg) of a pale yellow solid. M.p. 270 °C. Single crystals suitable for X-ray

analysis were obtained by cooling a concentrated solution of the crude complex in $CHCl_3$ at 4 °C. The complex obtained contains one molecule of $CHCl_3$ and is then little soluble in this solvent. $[\alpha]_D^{20} = -19$ (*c* 0.5, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 2.13 (s, 3H), 2.18 (d, 3H, $J = 6.6$ Hz), 2.31 (s, 3H), 2.34 (s, 3H), 3.31 (dq, 1H, $J = 11.6$ and 6.6 Hz, CH_3–C*H*–NH), 3.58 (ddd, 1H, $J = 11.9$, 4.3 and 4 Hz, CH_2–C*H*–NH), 4.16 (dd, 1H, $J = 14.3$ and 4.3 Hz, C*H*H–CH–N), 5.17 (dd, 1H, $J = 14.3$ and 11.9 Hz, CH*H*–CH–N), 5.74 (dd, 1H, $J = 11.6$ and 4 Hz, N*H*), 6.89 (d, 1H, $J = 2$ Hz), 6.94–6.96 (m, 3H), 7.03–7.12 (m, 5H), 7.17–7.25 (m, 4H), 7.43 (d, 1H, $J = 2$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.6, 18.8, 21.1, 27.1 (*C*H_3–CH–N), 58.2 (*C*H_2), 62.9 (CH_2–*C*H–N), 68.6 (CH_3—*C*H), 121.3 (C*H*=CH), 124.3 (CH=C*H*), 126.7, 127.2, 128.5, 128.7, 128.8, 129.2, 129.3, 133.1, 134.5, 137.0, 137.1, 139.4, 139.7, 153.3 ($C_{carbene}$). Anal. Calc. for $(C_{28}H_{31}Cl_2N_3Pd)_7(CHCl_3)_4$ ($M_W = 4585.75$) C, 52.38; H, 4.86; N, 6.41. Found: C, 52.28; H, 4.66; N, 6.24%. $CHCl_3$ was difficult to remove totally from the solid complex (M_W of the complex = 686.89).

*4.4.4. 3-(2,6-Diisopropylphenyl)-1-[(2S)-2-{(S)-1-(phenyl) propylamino}-2-phenyl ethyl] imidazol-2-ylidene $PdCl_2$ (**24**)*

A solution of Ag(I) complex **22** (50 mg, 0.082 mmol) and $PdCl_2(CH_3CN)_2$ (21.5 mg, 0.082 mmol) in CH_2Cl_2 (1 mL) was stirred at 20 °C for 1 h with exclusion of light, filtered through celite and concentrated under reduced pressure to give 45 mg (85%) of an orange solid. The crude was dissolved in CH_2Cl_2 (1 mL) and the complex was precipitated by addition of Et_2O. Yield 53% (28 mg) of a pale orange solid. M.p. 209 °C. $[\alpha]_D^{20} = +187$ (*c* 1.8, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 0.59 (t, 3H, $J = 7.3$ Hz), 1.11 (d, 3H, $J = 6.8$ Hz), 1.12 (d, 3H, $J = 6.8$ Hz), 1.36 (d, 3H, $J = 6.6$ Hz), 1.61 (d, 3H, $J = 6.8$ Hz), 2.29 (m, 2H, C*H*$_2$–CH_3), 3.08 (dt, 1H, $J = 11$ and 4.6 Hz, Et-C*H*–NH), 3.30 (m, 1H), 3.45 (m, 1H), 3.60 (dt, 1H, $J = 11.7$ and 4.5 Hz, N–CH_2–C*H*–NH), 4.08 (dd, 1H, $J = 14.2$ and 4.5 Hz, C*H*H–CH–N), 5.22 (dd, 1H, $J = 14.2$ and 11.7 Hz, CH*H*–CH–N), 5.74 (dd, 1H, $J = 11$ and 4.5 Hz, N*H*), 6.90–6.92 (m, 2H), 6.95 (d, 1H, $J = 1.8$ Hz), 7.00–7.37. (m, 11H), 7.48 (t, 1H, $J = 7.6$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.8 (*C*H_3–CH_2), 22.3, 23.0, 25.7, 26.2 (*C*H_3, *i*-Pr), 28.8, 29.0 (*C*H, *i*-Pr), 32.O (CH_3—*C*H_2), 58.1 (N–*C*H_2), 62.6 (N–CH_2–*C*H–Ph), 74.5 (Et-*C*H–Ph), 121.7, 123.0, 124.1, 126.1, 126.6, 127.9, 128.3, 128.4, 128.6, 129.0, 129.9, 134.8, 137.8, 137.9, 143.4, 147.1, 151.4. Anal. Calc. for $(C_{32}H_{39}Cl_2N_3Pd)_7(CHCl_3)_4$ ($M_W = 5195.58$) C, 52.95; H, 5.39; N, 5.64. Found: C, 52.97; H, 5.33; N, 5.54%. $CHCl_3$ was difficult to remove totally from the solid complex (M_W of the complex = 643.00).

*4.5. 3-Mesityl-1-[2-{(S)-1-(phenyl)ethylimino}-2-phenyl ethyl] imidazol-2-ylidene AgCl (**25**)*

The procedure was the same as for **21** and **22**. Yield 83% from **9**, off white solid. M.p. 89 °C. $[\alpha]_D^{20} = -54$ (*c* 0.3, $CHCl_3$). ^1H NMR (400 MHz, CD_2Cl_2) δ 1.33 (d, 3H, $J = 6.5$ Hz), 1.83 (s, 3H), 1.92 (s, 3H), 2.31 (s, 3H), 4.52 (q, 1H, $J = 6.5$ Hz), 5.20 (d, 1H, $J = 16.4$ Hz, CH*H*–C=N), 5.23 (d, 1H, $J = 16.4$ Hz, C*H*H–C=N), 6.93 (d, 1H, $J = 1.8$ Hz), 6.95 (s, 2H), 7.10–7.50 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.5, 17.6, 21.0, 25.0, 59.5 (*C*H_2), 61.1 (N–*C*H–CH_3), 121.8, 122.7, 126.4, 126,7, 126.9, 128.5, 129.1, 129.3, 129.4, 134.3, 134.6, 134.7, 135.2, 139.5, 145.0, 163.8, the carbene carbon was not detected. Anal. Calc. for $C_{28}H_{30}AgClN_3$ ($M_W = 551.88$) C, 60.94; H, 5.48; N, 7.61. Found: C, 60.66; H, 5.91; N, 7.35%. IR (ATR diamond) $\nu_{C=N}$ 1647 cm^{-1}.

4.6. Allylic alkylation

A mixture of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (4.3 mg, 0.012 mmol) and silver complex **21** (15.3 mg, 0.028 mmol) in THF (2 mL) was stirred for 1 h at 20 °C under argon. The mixture was filtered and added to a solution of (*E*)-1,3-diphenylprop-3-en-yl acetate (100 mg, 0.396 mmol) in THF (1 mL). After 10 min, a solution of dimethyl malonate (138 μL, 1.188 mmol) and NaH (1.07 mmol) in THF (1 mL) was added dropwise. After 16 h at 20 °C, brine (3 mL) was added and the mixture was extracted with Et_2O. The organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography (SiO_2, pentane/Et_2O;9/1) to afford 53 mg (41% yield). Enantiomeric excess (60 % (*R*)) was determined by ^1H NMR with a chiral shift reagent Eu(hfc)$_3$.

5. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 288055 for compound **19** and No. 288056 for complex **23**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] D. Bourrissou, O. Guerret, F.P. Gabbaï, G. Bertrand, Chem. Rev. 100 (2000) 39.
[2] W.A. Herrmann, C. Köcher, Angew. Chem., Int. Ed. Engl. 36 (1997) 2162.
[3] W.A. Herrmann, Angew. Chem., Int. Ed. Engl. 41 (2002) 1290.
[4] L. Jafarpour, S.P. Nolan, Adv. Organomet. Chem. 46 (2001) 181.
[5] A.W. Coleman, P.B. Hitchcock, M.F. Lappert, R.K. Maskell, J.H. Müller, J. Organomet. Chem. 250 (1983) C9–C14.

[6] M.C. Perry, K. Burgess, Tetrahedron: Asymmetry 14 (2003) 951.
[7] V. César, S. Bellemin-Laponnaz, L.H. Gade, Chem. Soc. Rev. 33 (2004) 619.
[8] S. Roland, P. Mangeney, in: M. Lemaire, P. Mangeney (Eds.), Top. Organomet. Chem., vol. 15, Springer Verlag, Berlin, Heidelberg, 2005, p. 191.
[9] W.A. Herrmann, L.J. Goossen, M. Spiegler, Organometallics 17 (1998) 2162.
[10] M.T. Powell, D.-R. Hou, M.C. Perry, X. Cui, K. Burgess, J. Am. Chem. Soc. 123 (2001) 8878.
[11] M.C. Perry, X. Cui, M.T. Powell, D.-R. Hou, J.H. Reibenspies, K. Burgess, J. Am. Chem. Soc. 125 (2003) 113.
[12] V. César, S. Bellemin-Laponnaz, L.H. Gade, Organometallics 21 (2002) 5204.
[13] L.H. Gade, V. César, S. Bellemin-Laponnaz, Angew. Chem., Int. Ed. Engl. 43 (2004) 1014.
[14] T. Focken, G. Raabe, C. Bolm, Tetrahedron: Asymmetry 15 (2004) 1693.
[15] N. Schneider, V. César, S. Bellemin-Laponnaz, L.H. Gade, J. Organomet. Chem. 690 (2005) 5556.
[16] Y. Yuan, G. Raabe, C. Bolm, J. Organomet. Chem. 690 (2005) 5747.
[17] L.G. Bonnet, R.E. Douthwaite, Organometallics 22 (2003) 4187.
[18] D.S. McGuinness, K.J. Cavell, Organometallics 19 (2000) 741.
[19] A.A.D. Tulloch, A.A. Danopoulos, R.P. Tooze, S.M. Cafferkey, S. Kleihenz, M.B. Hursthouse, Chem. Commun. (2000) 1247.
[20] A.A.D. Tulloch, A.A. Danopoulos, G.J. Tizzard, S.J. Colles, M.B. Hursthouse, R.S. Hay-Motherwell, W.B. Motherwell, Chem. Commun. (2001) 1270.
[21] P.L. Chiu, C.-L. Lai, C.-F. Chang, C.-H. Hu, H.M. Lee, Organometallics 24 (2005) 6169.
[22] F.E. Hahn, M.C. Jahnke, V. Gomez-Benitez, D. Morales-Morales, T. Pape, Organometallics 24 (2005) 6458.
[23] 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, B.W. Skelton, J. Organomet. Chem. 617–618 (2001) 546.
[24] R.E. Douthwaite, J. Houghton, B. Kariuki, Chem. Commun. (2004) 698.
[25] M. Frøseth, A. Dhindsa, H. Røise, M. Tilset, J. Chem. Soc., Dalton Trans. (2003) 4516.
[26] M. Frøseth, K.A. Netland, C. Rømming, M. Tilset, J. Organomet. Chem. 690 (2005) 6125.
[27] M. Frøseth, K.A. Netland, K.W. Törnroos, A. Dhindsa, M. Tilset, J. Chem. Soc., Dalton Trans. (2005) 1164.
[28] S. Dastgir, K.S. Coleman, A.R. Cowley, M.L.H. Green, Organometallics 25 (2006) 300.
[29] K.S. Coleman, H.T. Chamberlayne, S. Tuberville, M.L.H. Green, A.R. Cowley, J. Chem. Soc., Dalton Trans. (2003) 2917.
[30] G. Steiner, H. Kopacka, K.-H. Ongania, K. Wurst, P. Preishuber-Pflügl, B. Bildstein, Eur. J. Inorg. Chem. (2005) 1325.
[31] G. Steiner, A. Krajete, H. Kopacka, K.-H. Ongania, K. Wurst, P. Preishuber-Pflügl, B. Bildstein, Eur. J. Inorg. Chem. (2004) 2827.
[32] K.S. Coleman, S. Dastgir, G. Barnett, M.J.P. Alvite, A.R. Cowley, M.L.H. Green, J. Organomet. Chem. 690 (2005) 5591.
[33] Azeotrope $CHCl_3/H_2O$: 97/3 (%).
[34] C. Cimarelli, G. Palmieri, Tetrahedron: Asymmetry 11 (2000) 2555.
[35] J.C.G. Van Niel, U.K. Pandit, Tetrahedron 41 (1985) 6011.
[36] C.G. Overberger, N.P. Marullo, R.G. Hiskey, J. Am. Chem. Soc. 83 (1961) 1374.
[37] G. Uccello-Barretta, R. Bernardini, F. Balzano, P. Salvadori, J. Org. Chem. 66 (2001) 123.
[38] A. Alexakis, S. Gille, F. Prian, S. Rosset, K. Ditrich, Tetrahedron Lett. 45 (2004) 1449.
[39] I.S. Edworthy, M. Rodden, S.A. Mungur, K.M. Davis, A.J. Blake, C. Wilson, M. Schröder, P.L. Arnold, J. Organomet. Chem. 690 (2005) 5710.
[40] L.P. Spencer, M.D. Fryzuk, J. Organomet. Chem. 690 (2005) 5788.
[41] H.M. Wang, I.J.B. Lin, Organometallics 17 (1998) 972.
[42] J.C. Garrisson, W.J. Youngs, Chem. Rev. 105 (2005) 3978.
[43] P. de Frémont, N.M. Scott, E.D. Stevens, T. Ramnial, O.C. Lightbody, C.L.B. Macdonald, J.A.C. Clyburne, C.D. Abernethy, S.P. Nolan, Organometallics 24 (2005) 6301.
[44] W. Li, H. Sun, M. Chen, Z. Wang, D. Hu, Q. Shen, Y. Zhang, Organometallics 24 (2005) 5925.
[45] J. Liu, J. Chen, J. Zhao, Y. Zhao, L. Li, H. Zhang, Synthesis (2003) 2661.
[46] A.A. Gridnev, I.M. Mihaltseva, Synth. Commun. 24 (1994) 1547.