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Silver(I) complex of a new imino-*N*-heterocyclic carbene and ligand transfer to palladium(II) and rhodium(I)†

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Received 29th April 2003, Accepted 29th May 2003
First published as an Advance Article on the web 18th June 2003

A new imino-*N*-heterocyclic carbene ligand precursor [1-(2,4,6-$Me_3C_6H_2$)imidazolium-3-{$CH_2C(t\text{-Bu})=N(i\text{-Pr})$}] bromide has been synthesised and structurally characterised. The silver(I) complex $[Ag(C\text{^}imine)_2]AgBr_2$, where (C^imine) = 1-(2,4,6-$Me_3C_6H_2$)imidazol-2-ylidene-3-{$CH_2C(t\text{-Bu})=N(i\text{-Pr})$}, was readily prepared by reaction with Ag_2O. Transfer of the ligand from silver(I) to palladium(II) and rhodium(I) by reaction with $[PdCl_2(MeCN)_2]$ and $[Rh(cod)(THF)_2][BF_4]$ led to the tautomerisation of the imine moiety to the enamine affording the structurally characterised complex $[PdCl_2(C\text{^}enamine)]$ and $[Rh(cod)(C\text{^}enamine)][BF_4]$ respectively, where (C^enamine) = 1-(2,4,6-$Me_3C_6H_2$)imidazol-2-ylidene-3-{$CH=C(t\text{-Bu})NH(i\text{-Pr})$}.

Introduction

N-Heterocyclic carbenes have attracted considerable attention as a new class of ligand over the last few years.[1–10] Their ligating characteristics are comparable to the well-studied tertiary phosphines, which are ubiquitous in their role as ligands in transition metal catalyzed processes. *N*-Heterocyclic carbene ligands themselves are now finding more uses in catalysis and have been effective in hydrosilylation reactions,[11,12] ring opening and closing metathesis,[13–18] cross coupling reactions such as the Heck process[19–23] and carbon monoxide and ethylene copolymerisation.[24,25]

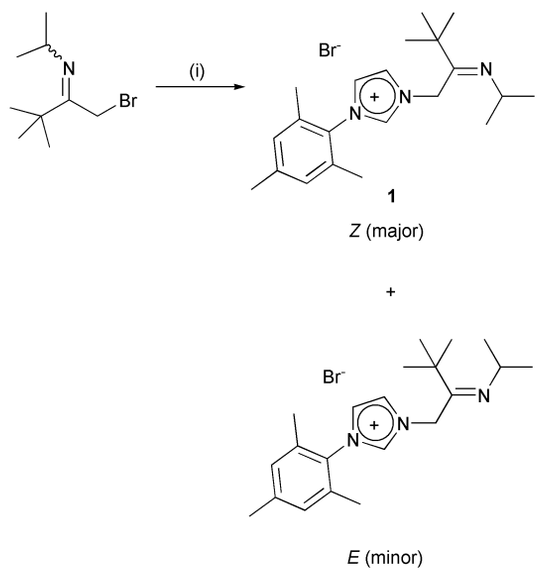
Our interests lie in heteroditopic ligands that incorporate N or O donor atoms along with strong donors such as tertiary phosphines and carbenes.[26] Such hybrid ligands can exhibit hemilabile behaviour which can be exploited in homogeneous catalysis and small molecule activation. A variety of P/N ligands have shown enormous potential in group 10 metal catalysed polymerisation of ethylene and propylene.[27] Similarly, Ni complexes containing P/O ligands have been shown to be of great importance in the oligomerisation of olefins, as in the Shell higher olefin process (SHOP).[28] Heteroditopic ligands containing *N*-heterocyclic carbene moieties are less numerous. Recently reported functionalised *N*-heterocyclic carbene ligands have included pyridine, ketone, ester, ether and oxazoline hemilabile groups.[12,19,21–23,25,29–32]

Herein we report the synthesis and reactivity of the first non-cyclic imino-*N*-heterocyclic carbene precursor and the corresponding Ag(I) complex and the transfer of the iminocarbene ligand to Pd(II) and Rh(I).

Results and discussion

Synthesis and characterisation of the ligand precursor [1-(2,4,6-$Me_3C_6H_2$)imidazolium-3-{$CH_2C(t\text{-Bu})=N(i\text{-Pr})$}] bromide (1)

The imine functionalised imidazolium salt (**1**), was prepared by reaction of the α-bromo imine $BrCH_2C(t\text{-Bu})=N(i\text{-Pr})$ with 1-mesitylimidazole in THF, Scheme 1. The reaction mixture was refluxed for 72 h during which time a precipitate formed which was washed with diethyl ether and recrystallised from a mixture of dichloromethane and diethyl ether. Compound (**1**) was characterised by elemental analysis, mass spectrometry (ES^+) and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy using gCOSY, NOESY, gHMQC and HMBC experiments. NMR spectroscopy showed the presence of two species in the ratio 2 : 1 which is attributed to the *Z* and the *E* isomers, respectively. Although no exchange broadening was detected at room temperature in the ^1H NMR spectrum, exchange peaks in the NOESY spectrum showed that the two isomers are in exchange in solution. Unfortunately, the rate of exchange was slow precluding any attempts to obtain an accurate value for the rate by NMR spectroscopy. Full ^1H and ^{13}C NMR assignments are given in the experimental section.



Scheme 1 Reagents: (i) 1-mesityl imidazole, THF, 72 h.

Crystals of (**1**) suitable for single-crystal X-ray diffraction were grown from a mixture of dichoromethane and diethyl ether. An ORTEP view of the molecular structure is shown in Fig. 1 and crystallographic data given in Table 1. Selected bond lengths and angles are listed in Table 2. In the solid state the imidazolium salt (**1**) adopts the *Z* isomer configuration, (also the major isomer in solution) presumably the more energetically favoured isomer for steric reasons. The mesityl group is found orthogonal to the imidazolium ring, probably to minimise interactions. The C(7)–N(10) bond is 1.267 Å, consistent with significant double bond character.[26] Similarly, the bond angles

† Electronic supplementary information (ESI) available: Fig. S1: ^1H-NOESY spectrum of imidazolium ligand (**1**). Fig. S2: $^1H/^{13}C$ gHSQC spectrum of palladium complex (**3**). Fig. S3: ^1H–^1H gCOSY spectrum of rhodium complex (**4**). See http://www.rsc.org/suppdata/dt/b3/b304474b/

DOI: 10.1039/b304474b

Table 1 Summary of crystallographic data for compounds **1** and **3**

	1	**3**
Empirical formula	$C_{21}H_{32}BrN_3$	$C_{21}H_{31}Cl_2N_3Pd{\cdot}n(CH_2Cl_2)$ ($n \sim 2.1$)
M_r	406.41	500.818 + 84.92n
T/K	150	150
λ/Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P\,2_1/c$	$P\,2_1/c$
a/Å	12.4006(4)	11.2224(2)
b/Å	12.5704(3)	19.2162(3)
c/Å	14.3606(5)	15.4168(2)
α/°	90	90
β/°	96.5002(11)	93.4326(7)
γ/°	90	90
V/Å^3	2224.1	3318.7
Z	4	4
D_c/Mg m^{-3}	1.214	1.358
μ/mm^{-1}	1.856	1.069
F_{000}	854.613	1378.561
Crystal size/mm	0.30 × 0.30 × 0.36	0.10 × 0.25 × 0.25
Description of crystal	Colourless block	Yellow block
Absorption correction	Semi-empirical from equivalent reflections	Semi-empirical from equivalent reflections
Transmission coefficients (min., max.)	0.51, 0.57	0.77, 0.90
θ Range for data collection/°	5.0–27.5	5.0–27.5
Index ranges, hkl	−16 to 15, 0 to 16, 0 to 18	−14 to 14, 0 to 24, 0 to 19
Reflections measured	16111	41359
Unique reflections	5271	7741
R_{int}	0.031	0.045
Observed reflections ($I > 3\sigma(I)$)	3987	5616
Refinement method	Full-matrix least-squares on F	Full-matrix least-squares on F
Parameters refined	226	344
Weighting scheme	Chebychev 3-term polynomial	Chebychev 3-term polynomial
Goodness of fit	1.0043	1.0273
R	0.0296	0.0464
wR	0.0392	0.0504
Residual electron density (min., max.)/e Å^{-3}	−0.43, 0.31	−0.86, 1.17

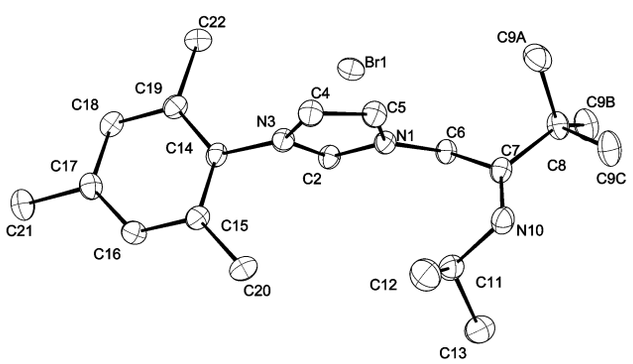


Fig. 1 ORTEP diagram of the molecular structure of (**1**). Thermal ellipsoids are set at 40%. Hydrogen atoms are omitted for clarity.

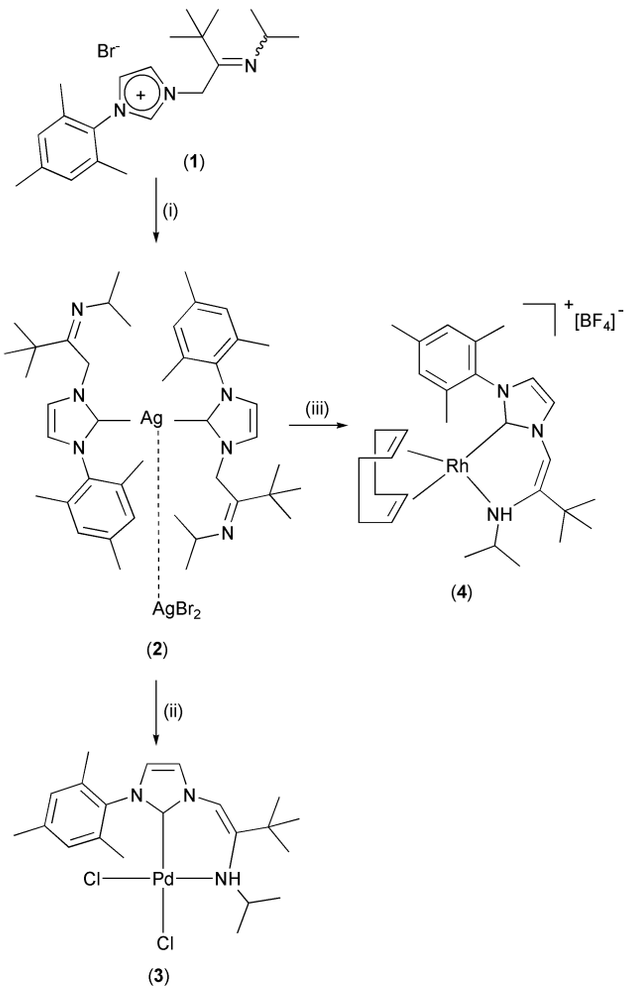
at both C(7) and N(10) are indicative of sp^2 centres. The internal bond lengths and angles of the imidazolium ring are unexceptional and lie within the range expected.[35]

Synthesis and characterisation of Ag(I), Pd(II) and Rh(I) carbene Ccomplexes

The Ag(I) complex [Ag(C^imine)$_2$]AgBr$_2$, (**2**) where (C^imine) = 1-(2,4,6-Me$_3$C$_6$H$_2$)imidazol-2-ylidene-3-{CH$_2$C(*t*-Bu)=N(*i*-Pr)}, was prepared, almost quantitatively by reaction of Ag$_2$O with (**1**), Scheme 2. Compound (**2**) is sensitive to air but can be readily characterised by elemental analysis, mass spectrometry (FAB$^+$) and ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. Silver(I) carbene complexes are known to adopt a variety of structures from mononuclear, with one or two carbene ligands coordinated to the metal centre, to bi- and polynuclear complexes.[33] Although it was not possible to obtain structural data for compound (**2**) the complexation of two carbene ligands to one Ag(I) centre was confirmed in this case by mass spectrometry with the peak at m/z = 759.8 corresponding to the parent cation of (**2**), [Ag(C^imine)$_2$]$^+$. Although there is a possibility of three isomers (*EE*, *ZZ* and *EZ*) of compound (**2**) NMR spectroscopy showed the presence of only two in a ratio of 15 : 1. The formation of the *EE* isomer is believed to be unfavourable due to steric crowding. The ^{1}H NMR spectrum (CDCl$_3$) of (**2**) is consistent with the coordination of the carbene moiety to the metal centre with the disappearance of the N*C*HN imidazolium

Table 2 Selected bond lengths (Å) and bond angles (°) for compounds **1** and **3**

Compound **1**			
N1–C2	1.327(2)	C2–N1–C5	108.46(14)
N1–C6	1.472(2)	C2–N1–C6	122.67(14)
N1–C5	1.308(2)	C5–N1–C6	128.68(14)
N3–C2	1.328(2)	C2–N3–C4	108.55(14)
N3–C4	1.379(2)	C2–N3–C14	123.75(14)
N3–C14	1.450(2)	N1–C2–N3	108.81(14)
C4–C5	1.349(3)	N1–C5–C4	107.18(15)
C6–C7	1.529(2)	N3–C4–C5	106.99(15)
N10–C7	1.267(2)	N1–C6–C7	113.09(13)
N10–C11	1.470(2)	N10–C7–C6	124.86(16)
Compound **3**			
N1–C2	1.366(4)	Cl2–Pd1–C2	93.6(1)
N1–C6	1.414(4)	Cl1–Pd1–Cl2	93.44(3)
N1–C5	1.388(4)	N10–Pd1–C2	85.93(13)
N3–C2	1.355(4)	C2–N1–C5	111.2(3)
N3–C4	1.392(4)	C2–N1–C6	124.29(3)
N3–C14	1.448(4)	C2–N3–C4	110.5(3)
C4–C5	1.346(5)	Pd1–N10–C7	108.3(2)
C6–C7	1.326(5)	N1–C2–N3	104.6(3)
N10–C7	1.455(5)	N3–C4–C5	107.6(3)
Pd1–N10	2.083(3)	N1–C5–C4	106.1(3)
Pd1–C2	1.966(3)	N1–C6–C7	123.0(3)
Pd1–Cl1	2.3506(9)	N10–C7–C6	118.5(3)
Pd1–Cl2	2.3089(8)		



Scheme 2 Reagents: (i) Ag_2O, CH_2Cl_2, 48 h; (ii) $PdCl_2(MeCN)_2$, CH_2Cl_2; (iii) $Rh_2Cl_2(COD)_2$, $AgBF_4$, THF, 24 h.

resonances in (**1**) at δ 10.74 (major isomer) and 9.62 (minor isomer). Similarly, the NC*HCH*N resonances were shifted to lower frequency, δ 6.88 and 6.86. Unfortunately the carbene carbon resonance in the ^{13}C NMR spectrum was not observed. ^1H NMR-NOE experiments confirmed that complex (**2**) exists mainly as the *ZZ* isomer in solution, as a large NOE was observed between the central isopropyl proton and the backbone CH_2 protons.

Silver carbene complexes are known to be effective reagents for the transfer of the carbene ligand to palladium,[19] gold[7] and more recently rhodium.[9] The use of transfer agents is particularly important when the imidazolium precursors contain functional groups that are sensitive to strong bases which are necessary to form the free carbene. To this end, the silver carbene (**2**) was reacted with $[PdCl_2(MeCN)_2]$ and $[Rh(cod)(THF)_2][BF_4]$ to form the corresponding Pd(II) and Rh(I) complexes. In general (**2**) was stirred at room temperature in CH_2Cl_2 with the appropriate metal precursor and the AgBr precipitate removed by filtration. The products were characterised by elemental analysis, mass spectrometry (ES^+) and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. Interestingly, tautomerisation of the carbene-imine ligand, (C^imine), occurred during the transfer reaction to afford the corresponding enamine complexes $[PdCl_2(C^enamine)]$ (**3**) and $[Rh(cod)(C^enamine)][BF_4]$ (**4**), where (C^enamine) = 1-(2,4,6-$Me_3C_6H_2$)imidazol-2-ylidene-3-{CH=C(*t*-Bu)NH(*i*-Pr)}, Scheme 2.

The ^1H NMR ($CDCl_3$) spectra show a doublet resonance at δ 5.15 and 3.17, assigned to the enamine N*H* proton which is coupled to the isopropyl proton, C*H*$(CH_3)_2$, for complex (**3**) and (**4**), respectively. This assignment was confirmed by deuterium exchange experiments. The =C*H* backbone resonance for complex (**3**) and (**4**) appears as a singlet resonance at δ 6.61 and 6.68, respectively. In the $^{13}C\{^1H\}$ NMR ($CDCl_3$) spectra the complexed carbene resonance is observed as a singlet at δ 152.0 for the palladium(II) complex (**3**) and as a doublet at δ 171.7 for the rhodium(I) complex (**4**), with a $^1J_{Rh-C}$ coupling constant of 56 Hz. Full ^1H and ^{13}C NMR assignments, using gCOSY, NOESY, gHSQC and gHMBC experiments, of complexes (**3**) and (**4**) are given in the Experimental section. Interestingly, for the palladium(II) complex (**3**) and the rhodium(I) complex (**4**) the *ortho*-methyl groups of the mesityl ring are magnetically inequivalent indicating restricted rotation as a result of steric congestion. The methyls of the isopropyl group in (**3**) and (**4**) are similarly inequivalent as they are attached to a now chiral nitrogen centre and are thus diastereotopic.

Typically in the tautomerism of imines to enamines the former dominates, particularly if there is a hydrogen on the nitrogen atom. This would explain the isolation of the imine form of (**1**) and (**2**). However, it has been observed in selected imino-phosphines that when the ligand is coordinated to palladium(II) there exists an equilibrium in solution between the imine and enamine form.[34] However, deuterium exchange experiments on complexes (**3**) and (**4**) show no hydrogen–deuterium exchange of the backbone –C*H* proton suggesting that in this particular case the carbene ligand rests in the enamine form when chelated to palladium(II) and rhodium(I). The initial tautomerism of the iminocarbene ligand is presumably triggered by the metal complexation.

The molecular structure of (**3**) determined by single crystal X-ray diffraction further supports enamine formation upon coordination. Crystals of (**3**) suitable for diffraction were grown by layering pentane onto a CH_2Cl_2 solution. The molecular structure is shown in Figs. 2 and 3 and selected bond lengths and angles listed in Table 2. A summary of crystallographic data are given in Table 1. Complex (**3**) is essentially square planar at palladium with the five-membered imidazol-2-ylidene ring of the carbene ligand tilted out of the Pd(1)–Cl(1)–Cl(2)–N(10)–C(2) plane by 38.5°, Fig. 3. The Pd-metallocycle displays a boat like conformation with a Pd(1)–N(10)–C(7)–C(6) torsion angle of 58.3(5)°. The tautomerisation of the iminocarbene ligand

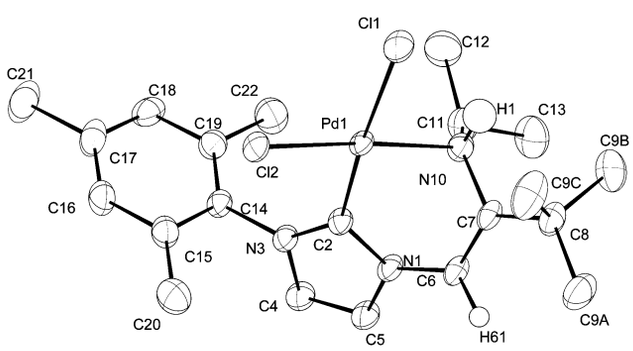


Fig. 2 ORTEP diagram of the molecular structure of (**3**). Thermal ellipsoids are set at 40%. Hydrogen atoms and solvent molecules are omitted for clarity.

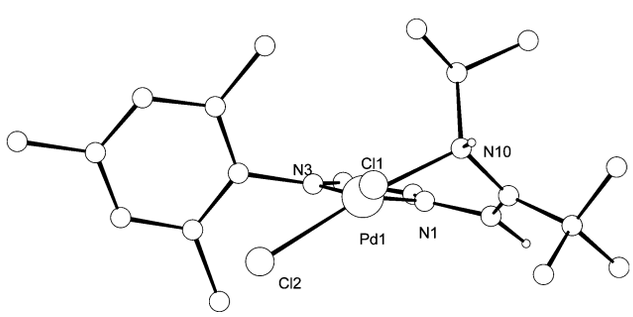


Fig. 3 Alternative view of the molecular structure of (**3**). Hydrogen atoms and solvent molecules are omitted for clarity.

coordinated to the silver complex, (**2**), to the enaminecarbene ligand when coordinated to palladium, (**3**), is clearly reflected in the molecular parameters, Table 2. The shorter carbon–carbon bond in the ligand backbone, C(6)–C(7), (1.326(5) Å *cf*. 1.529(2) Å for the imidazolium compound (**1**)) is consistent with the formation of a double bond and enamine formation. Similarly, the C(7)–N(10) bond length is lengthened to 1.455(5) Å when compared to compound (**1**) (1.267(2) Å). The Pd(1)–C(2) bond distance of 1.966(3) Å and the bite angle C(2)–Pd(1)–N(10) of 85.93(13)° are similar to those of numerous palladium(II) carbene complexes.[8,22] The Pd(1)–Cl(1) distance of 2.3506(9) Å and the Pd(1)–Cl(2) distance of 2.3089(8) Å are as expected for square planar Pd(II) complexes,[26] with the longer metal–halide bond *trans* to the carbene carbon, a consequence of the greater *trans* influence.

Conclusions

The synthesis of a new iminocarbene ligand coordinated to silver(I), $[Ag(C\text{^}imine)_2]AgBr_2$, where (C^imine) = 1-(2,4,6-$Me_3C_6H_2$)imidazol-2-ylidene-3-{$CH_2C(t\text{-}Bu)$=N(*i*-Pr)}, has been demonstrated by a simple reaction of the corresponding imidazolium compound with Ag_2O. The transfer of the iminocarbene to Pd(II) and Rh(I) results in the tautomerisation of the ligand to afford an enaminecarbene ligand complexed to the metal, $[PdCl_2(C\text{^}enamine)]$ and $[Rh(cod)(C\text{^}enamine)][BF_4]$, where (C^enamine) = 1-(2,4,6-$Me_3C_6H_2$)imidazol-2-ylidene-3-{CH=C(*t*-Bu)NH(*i*-Pr)}.

Experimental

General procedures

All manipulations were performed under dinitrogen using standard Schlenk techniques or in an inert atmosphere drybox. All solvents were dried over the appropriate drying agents and distilled under dinitrogen. NMR spectra were recorded on either a Varian Unity Plus 500 (^{1}H at 500 MHz, ^{13}C at 125.7 MHz) or on a Varian Mercury 300 (^{1}H at 300 MHz, ^{13}C at 75.5 MHz) spectrometer and are at room temperature unless otherwise stated. The spectra were referenced internally relative to the residual protio-solvent (^{1}H) and solvent (^{13}C) resonances and chemical shifts were reported with respect to δ = 0 for tetramethylsilane. Electrospray mass spectra were recorded in acetonitrile on a Micromass LC TOF and FAB spectra on a Micromass Autospec TOF using nitrobenzyl alcohol as the matrix. Microanalyses were performed by the microanalytical laboratory of the Inorganic Chemistry Laboratory, University of Oxford.

All reagents were purchased from Aldrich and used as received unless otherwise stated. The reagents 1-mesitylimidazole,[31] $PdCl_2(MeCN)_2$,[36] and the imine $BrCH_2C(t\text{-}Bu)$=N-(*i*-Pr)[37] were prepared using published procedures.

Preparations

1-(2,4,6-$Me_3C_6H_2$)imidazolium-3-{$CH_2C(t\text{-}Bu)$=N(*i*-Pr)}] bromide (1)

The α-bromo imine $BrCH_2C(t\text{-}Bu)$=N(*i*-Pr) (2.0 g, 0.009 mol) was added to a solution of 1-mesitylimidazole (1.7 g, 0.009 mol) in 200 ml THF. After refluxing at 70 °C for 72 h a white precipitate formed. The solution was filtered off and the precipitate washed with ether. The white solid was crystallised from CH_2Cl_2 and Et_2O. Yield: 2.80 g (77%).

***Z* Isomer (major).** ^{1}H NMR ($CDCl_3$): δ 10.74 (s, 1H, –NCHN–), 7.23 (m, 1H, –NC*H*CHN–), 7.19 (m, 1H, –NCHC*H*N–), 6.98 (s, 2H, -2,4,6-$Me_3C_6H_2$), 5.59 (s, 2H, –CH_2–), 3.75 (m, $^3J_{HH}$ = 6.7 Hz, 1H, –C*H*(CH_3)$_2$), 2.32 (s, 3H, -2,*4*,6-$Me_3C_6H_2$), 2.04 (s, 6H, -*2*,4,*6*-$Me_3C_6H_2$), 1.14 (s, 9H, –C(CH_3)$_3$), 1.10 (d, $^3J_{HH}$ = 6.5 Hz, 6H, –CH(CH_3)$_2$)

^{13}C{^{1}H} NMR ($CDCl_3$): δ 164.1 (–*C*=N^{i}Pr), 141.5 (-2,*4*,6-$Me_3C_6H_2$), 138.8 (–N*C*HN–), 133.9 (-*2*,4,*6*-$Me_3C_6H_2$), 130.5 (*ipso*-C of -2,4,6-$Me_3C_6H_2$), 129.9 (*meta*-*C*H of -2,*4*,6-$Me_3C_6H_2$), 123.1 (–N*C*HCHN–), 121.5 (–NCH*C*HN–), 51.8 (–*C*H(CH_3)$_2$), 43.1 (–*C*H_2–), 40.9 (–*C*(CH_3)$_3$), 27.7 (–C(CH_3)$_3$), 23.8 (–CH(CH_3)$_2$), 21.1 (-2,*4*,6-$Me_3C_6H_2$), 17.6 (-*2*,4,*6*-$Me_3C_6H_2$).

***E* Isomer (minor).** ^{1}H NMR ($CDCl_3$): δ 9.62 (s, 1H, –NC*H*N–), 7.48 (m, 1H, –NC*H*CHN–), 6.99 (m, 1H, –NCHC*H*N–), 6.96 (s, 2H, -2,4,6-$Me_3C_6H_2$), 5.70 (s, 2H, –CH_2–), 4.27 (m, $^3J_{HH}$ = 6.5 Hz, 1H, –C*H*(CH_3)$_2$), 2.32 (s, 3H, -2,*4*,6-$Me_3C_6H_2$), 2.06 (s, 6H, -*2*,4,*6*-$Me_3C_6H_2$), 1.34 (s, 9H, –C(CH_3)$_3$), 0.89 (d, $^3J_{HH}$ = 6.0 Hz, 6H, –CH(CH_3)$_2$).

^{13}C{^{1}H} NMR ($CDCl_3$): δ 163.3 (–*C*=N^{i}Pr), 141.1 (-2,*4*,6-$Me_3C_6H_2$), 138.7 (N*C*HN), 134.4 (-*2*,4,*6*-$Me_3C_6H_2$), 130.8 (*ipso*-*C* of -2,4,6-$Me_3C_6H_2$), 129.6 (*meta*-*C*H of -2,4,6-$Me_3C_6H_2$), 124.7 (–N*C*HCHN–), 120.9 (–NCH*C*HN–), 54.4 (–*C*H_2–), 49.7 (–*C*H(CH_3)$_2$), 38.8 (–*C*(CH_3)$_3$), 28.6 (–C(CH_3)$_3$), 23.7 (–CH(CH_3)$_2$), 21.1 (-2,*4*,6-$Me_3C_6H_2$), 17.5 (-*2*,4,*6*-$Me_3C_6H_2$).

MS (ES+) (CH_3CN): *m*/*z* = 326.5 $[M]^+$ (100%). Elemental analysis (%): found (calc.): C 61.71 (62.06), H 8.10 (7.94), N 9.93 (10.34). IR (KBr): ν_{CN} = 1650 cm^{-1}.

$[Ag(C\text{^}imine)_2]AgBr_2$, (2)

Silver oxide (0.134 g, 0.58 mmol) was added to (**1**) (0.313 g, 0.77 mmol), in CH_2Cl_2 (40 ml) in the presence of 4A activated molecular sieves and the reaction mixture refluxed for 48 h. The solution was then filtered and the solvent removed to leave a pale brown solid. Yield: 0.277 g (70%).

^{1}H NMR (CD_2Cl_2): δ 6.93 (s, 2H, -2,4,6-$Me_3C_6H_2$), 6.88 (d, $^3J_{HH}$ = 2.3 Hz, 1H, –NC*H*CHN–), 6.86 (d, $^3J_{HH}$ = 2.3 Hz, 1H, –NCHC*H*N–), 4.92 (s, 2H, –CH_2–), 3.68 (m, $^3J_{HH}$ = 5.7 Hz, 1H, –C*H*(CH_3)$_2$), 2.28 (s, 3H, -2,*4*,6-$Me_3C_6H_2$), 1.91 (s, 6H, -*2*,4,*6*-$Me_3C_6H_2$), 1.13 (s, 9H, –C(CH_3)$_3$), 1.02 (d, $^3J_{HH}$ = 5.7 Hz, 6H, –CH(CH_3)$_2$).

^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.2 (–*C*=N^{i}Pr), 139.9 (-2,*4*,6-$Me_3C_6H_2$), 134.6 (-*2*,4,*6*-$Me_3C_6H_2$), 129.7 (*meta*-*C*H of -2,4,6-$Me_3C_6H_2$), 123.0 (–N*C*HCHN–), 120.3 (–NCH*C*HN–), 52.1 (–*C*H(CH_3)$_2$), 45.9 (–*C*H_2–), 41.1 (–*C*(CH_3)$_3$), 28.6 (–C(CH_3)$_3$), 24.3 (–CH(CH_3)$_2$), 21.6 (-2,*4*,6-$Me_3C_6H_2$), 18.3 (-*2*,4,*6*-$Me_3C_6H_2$).

MS (FAB+): *m*/*z* = 759.8 $[M]^+$, (40%), Elemental analysis (%): found (calc.): C 48.79 (49.14), H 6.13 (6.09), N 7.55 (8.19). IR (KBr): ν_{CN} = 1644 cm^{-1}.

$[PdCl_2(C\text{^}enamine)]$ (3)

The silver complex (**2**) (0.513 g, 0.50 mmol) and $PdCl_2(MeCN)_2$ (0.260 g, 1.00 mmol) were placed in CH_2Cl_2 (50 ml) and the reaction mixture stirred for 24 h. During this time a brown precipitate formed. The yellow solution was filtered and the precipitate washed with two 10 ml portions of CH_2Cl_2, which were combined with the filtrate. The solvent was removed to yield a yellow–orange solid. The solid was purified by crystallisation from CH_2Cl_2 layered with pentane. Yield: 0.261 g (52%).

^{1}H NMR ($CDCl_3$): δ 7.38 (d, $^3J_{HH}$ = 2.4 Hz, 1H, –NC*H*CHN–), 6.84 (d, $^3J_{HH}$ = 2.4 Hz, 1H, –NCHC*H*N–), 6.80 (s, 2H, -2,4,6-$Me_3C_6H_2$), 6.61 (s, 1H, =C*H*–), 5.15 (d, $^3J_{HH}$ = 7.1 Hz, 1H, N*H*), 2.86 (m, 1H, –C*H*(CH_3)$_2$), 2.30 (s, 3H, -2,4,6-$Me_3C_6H_2$), 2.23 (s, 3H, -2,*4*,6-$Me_3C_6H_2$), 1.92 (s, 3H, -2,4,*6*-$Me_3C_6H_2$), 1.36 (s, 9H, –C(CH_3)$_3$), 1.30 (d, $^3J_{HH}$ = 6.6 Hz, 3H, –CH(CH_3)$_2$), 1.20 (d, $^3J_{HH}$ = 6.5 Hz, 3H, –CH(CH_3)$_2$).

^{13}C{^{1}H} NMR ($CDCl_3$): δ 152.0 (–N*C*N–), 145.7 (=*C*(*t*Bu)–), 139.3 (-2,*4*,6-$Me_3C_6H_2$), 136.4 (-*2*,4,6-$Me_3C_6H_2$), 135.2 (*ipso*-*C* of -2,4,6-$Me_3C_6H_2$), 133.0 (-2,4,*6*-$Me_3C_6H_2$), 129.2 (*meta*-*C*H of -2,4,6-$Me_3C_6H_2$), 129.1 (*meta*-*C*H of -2,4,6-$Me_3C_6H_2$), 127.0

(–N*C*HCHN–), 120.0 (–NCH*C*HN–), 118.6 (=*C*H–), 56.5 (–*C*H(CH_3)$_2$), 36.1 (–*C*(CH_3)$_3$), 30.0 (–C(*C*H_3)$_3$), 23.7 (–CH(*C*H_3)$_2$), 23.1 (–CH(*C*H_3)$_2$), 21.7 (-2,*4*,6-*Me*$_3$C$_6$H$_2$), 19.6 (-*2*,4,6-*Me*$_3$C$_6$H$_2$), 18.9 (-2,4,*6*-*Me*$_3$C$_6$H$_2$).

MS (ES+) (CH_3CN): *m*/*z* = 507.5 [M − Cl + MeCN]$^+$ (30%), Elemental analysis (%): found (calc.): C 47.91 (50.17), H 5.94 (6.21), N 7.66 (8.36).

[Rh(cod)(C^enamine)][BF_4] (4)

$Rh_2Cl_2(C_8H_{12})_2$ (0.197 g, 0.40 mmol) and $AgBF_4$ (0.160 g, 0.82 mmol) were placed in THF (20 ml) and the reaction mixture stirred for 2 h. The creamy white precipitate formed (AgCl) was removed to leave a clear yellow solution, [Rh(cod)(THF)$_2$][BF_4]. The silver complex (**2**) (0.410 g, 0.40 mmol) in THF (20 ml) was added to the reaction mixture and left to stir for a further 24 h. The precipitate was removed by filtration and washed with THF. The solutions were combined and the solvent removed to afford an orange solid. The solid was purified by crystallisation from CH_2Cl_2 layered with Et_2O. Yield: 0.224 g (45%).

^{1}H NMR ($CDCl_3$): δ 7.46 (d, $^3J_{HH}$ = 2.1 Hz, 1H, –NC*H*-CHN–), 7.05 (s, 1H, -2,4,6-Me$_3$C$_6$*H*$_2$), 6.90 (s, 1H, -2,4,6-Me$_3$C$_6$*H*$_2$), 6.83 (d,$^3J_{HH}$ = 2.1 Hz, 1H, –NCHC*H*N–), 6.68 (s, 1H, =C*H*), 4.68 (m, 1H, COD CH), 4.66 (m, 1H, COD CH), 3.88 (m, 1H, COD CH), 3.77 (d,$^3J_{HH}$ = 10.1 Hz, 1H, N*H*), 2.99 (m, 1H, –C*H*(CH_3)$_2$), 2.78 (m, 1H, COD CH), 2.36 (m, 2H, COD CH_2), 2.33 (s, 3H, -2,*4*,6-*Me*$_3$C$_6$H$_2$), 2.31 (s, 3H, -*2*,4,6-*Me*$_3$C$_6$H$_2$), 2.05 (m, 2H, COD CH_2), 1.96 (m, 1H, COD CH_2), 1.90 (s, 3H, -2,4,*6*-*Me*$_3$C$_6$H$_2$), 1.69 (d,$^3J_{HH}$ = 6.6 Hz, 3H, –CH(C*H*$_3$)$_2$), 1.60 (m, 2H, COD CH_2), 1.38 (s, 9H, –C(CH_3)$_3$), 1.37 (m, 1H, COD CH_2), 1.13 (d, $^3J_{HH}$ = 6.6 Hz, 3H, –CH(C*H*$_3$)$_2$).

^{13}C{^{1}H} NMR ($CDCl_3$): δ 171.7 (d, ^1J(^{103}Rh^{13}C) = 56.2 Hz, –N*C*N–), 146.2 (=*C*N(*t*Bu)–), 139.7 (-2,*4*,6-Me$_3$*C*$_6$H$_2$), 134.6 (-*2*,4,6-Me$_3$*C*$_6$H$_2$), 134.5 (*ipso*-*C* of -2,4,6-Me$_3$C$_6$H$_2$), 134.2 (-2,4,*6*-Me$_3$*C*$_6$H$_2$), 129.3 (*meta*-*C*H of -2,4,6-Me$_3$C$_6$H$_2$), 129.0 (*meta*-*C*H of -2,4,6-Me$_3$C$_6$H$_2$), 125.6 (–N*C*HCHN–), 120.9 (–NCH*C*HN–), 117.2 (=*C*H), 96.0 (d,^1J(^{103}Rh^{13}C) = 7.8 Hz, COD CH), 95.2 (d,^1J(^{103}Rh^{13}C) = 8.4 Hz, COD CH), 76.0 (d,^1J(^{103}Rh^{13}C) = 13.1 Hz, COD CH), 72.1 (d,^1J(^{103}Rh^{13}C) = 12.5 Hz, COD CH), 55.0 (–*C*H(CH_3)$_2$), 35.1 (–*C*(CH_3)$_3$), 34.2 (COD CH_2), 30.5 (COD CH_2), 30.3 (–C(*C*H_3)$_3$), 30.1 (COD CH_2), 27.2 (COD CH_2), 25.0 (–CH(*C*H_3)$_2$), 23.0 (–CH(*C*H_3)$_2$), 21.3 (-2,*4*,6-*Me*$_3$C$_6$H$_2$), 18.5 (-*2*,4,6-*Me*$_3$C$_6$H$_2$), 17.8 (-2,4,*6*-*Me*$_3$C$_6$H$_2$).

MS (ES+) (CH_3CN): *m*/*z* = 536.37 [M]$^+$ (100%), Elemental analysis (%): found (calc.): C 55.44 (55.88), H 6.63 (6.95), N 6.58 (6.74).

X-Ray crystallography

Crystals were isolated under dinitrogen, covered with a perfluoropolyether oil, and mounted on the end of a glass fibre. Crystal data are summarised in Table 1.

Data were collected at 150 K on an Enraf-Nonius Kappa CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073) as summarised in Table 1. The images were processed with the DENZO and SCALEPACK programs.[38] All solution, refinement, and graphical calculations were performed using the CRYSTALS program suite.[39] The crystal structures were solved by direct methods using the SIR92 program[40] and were refined by full-matrix least squares on *F*. All non-hydrogen atoms were refined with anisotropic displacement parameters. All carbon-bound hydrogen atoms were generated and allowed to ride on their corresponding carbon atoms with fixed thermal parameters.

For complex (**3**) three molecules of solvent (CH_2Cl_2) were located in a difference Fourier map. Refinement of the coordinates and anisotropic thermal parameters gave a model in which two of these had distorted geometries and unusually large thermal ellipsoids, suggesting these to be disordered. A further difference map showed additional peaks corresponding to a further solvent molecule occupying a site between these two. The site occupancies of the three sites were subsequently refined, together with coordinates and anisotropic thermal parameters of the two located in the initial Fourier map and coordinates and isotropic thermal parameters of the last molecule. Coordinates and anisotropic thermal parameters of all other non-hydrogen atoms were then also refined.

CCDC reference numbers 209030 and 209031.

See http://www.rsc.org/suppdata/dt/b3/b304474b/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank the Royal Society for a University Research Fellowship (K. S. C.) and the EPSRC for a studentship (S. T.). We also wish to thank Dr Nicholas Rees for helpful discussions.

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