'Pincer' pyridine dicarbene complexes of nickel and their derivatives. Unusual ring opening of a coordinated imidazol-2-ylidene†‡

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The reaction of $NiBr_2(DME)$, DME = 1,2-dimethoxyethane, with the 'pincer' pyridine dicarbene ligands (C-N-C) (**2**) and (C-N^{Me}-C) (**2^{Me}**), (C-N-C = 2,6-bis-[(DiPP)imidazol-2-ylidene]pyridine, C-N^{Me}-C = 2,6-bis-[(DiPP)imidazol-2-ylidene]-3,5-dimethylpyridine, DiPP = 2,6-di*iso*propylphenyl) gave the square planar complexes $[Ni(C-N^{(Me)}-C)Br]Br$, **3·(Br)$^-$** and **3^{Me}·(Br)$^-$** respectively. Transmetallation from $[(C-N^{Me}-C)_2Ag_2](Ag_6I_8)$, **$6^{Me}$·(Ag$_6I_8$)$^{2-}$** to $NiBr_2(DME)$ gave $[Ni(C-N^{Me}-C)Br]$-(AgI_2), **3^{Me}·(AgI$_2$)$^-$**. Reaction of **3·(Br)$^-$** with KPF_6 resulted only in exchange of the ionic bromide, however the reaction of **3·(Br)$^-$** with $AgBF_4$ in MeCN or AgOTf in THF resulted in the exchange of both coordinated and ionic bromides, giving rise to the square planar **4·(BF$_4$)$^-_2$** and octahedral **5**, respectively. In contrast, the reaction of **3^{Me}·(AgI$_2$)$^-$**, with excess AgOTf resulted in an unusual 'reverse transmetallation' leading to **6^{Me}·(OTf)$^-$**. The substitution of tmeda in $Ni(CH_3)_2(tmeda)$, tmeda = N,N,N',N'-tetramethylethylenediamine, by **2** produced the complex **7**, in which ring opening of the heterocyclic imidazole ring of one of the NHC functional groups has taken place.

Introduction

The high interest in N-heterocyclic carbene (NHC) complexes of the late transition metals and their potential in homogeneous catalysis stems from the substitutional inertness of the M–C_{NHC} bond and consequent robust metal–ligand binding, leading to well defined coordination spheres.[1] Chelating NHC ligands are expected to amplify this feature. Furthermore, the chemical inertness and stability of the coordinated NHC heterocycle should suppress any unwanted catalyst deactivation initiated by ligand centered reactions. A simple and popular preparation of metal–NHC complexes involves transmetallation of an NHC ligand from silver to a transition metal with concomitant formation of insoluble silver halide.[2] In this paper we wish to describe the synthesis and characterisation of some new 'pincer' pyridine bis-NHC ligands and their complexes with Ag and Ni, some substitution reactions of the latter, including an unexpected 'reverse transmetallation' of coordinated NHC from Ni to Ag. We also report a ring-opening reaction of the coordinated NHC initiated by a methyl group migration from nickel to the coordinated C_{NHC}. The compounds described in this paper are summarised in Schemes 1–3.

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Results and discussion

Bis-imidazolium salts and dicarbene ligands

The novel pincer dicarbene ligand **2^{Me}** was prepared by an adaptation of the literature route to ligand **2**.[3] Quaternisation of 2,6-dibromo-3,5-lutidine with 2,6-DiPP imidazole yielded only the monosubstituted 2-(DiPP-imidazolium)-6-bromo-3,5-lutidine. However, reaction of 2,6-diiodo-3,5-lutidine[4] resulted in good yields of the bis(imidazolium) salt **1^{Me}·(I)$^-_2$** (Scheme 1). Unexpectedly, double deprotonation of **1^{Me}·(I)$^-_2$** with $KN(SiMe_3)_2$ afforded poor yields of the ligand **2^{Me}**. However, exchange of the iodides for bromides, followed by deprotonation of **1^{Me}·(Br)$^-_2$** gave **2^{Me}** cleanly and in good yield (*ca.* 77%).

Ligand **2^{Me}** was structurally characterised (Fig. 1), revealing the non co-planar geometry of the imidazol-2-ylidene and pyridine rings (*ca.* 30° angle between the planes of the NHC and pyridine rings). This is in contrast with the solid state structure of **2** which is planar.[3] The mutually *anti/gauche* orientation of the NHC and pyridine lone pairs is retained in **2^{Me}**. The C_{NHC}–N bond lengths [1.363(3)–1.375(3) Å] in **2^{Me}** are identical to those in **2**. The non-co-planar structure is also seen in the imidazolium salts **1^{Me}·(I)$^-_2$** and **1^{Me}·(Br)$^-_2$** (see ESI‡) and is presumably due to steric reasons.

Nickel NHC complexes

Pincer pyridine dicarbene nickel complexes were easily obtained by the reaction of the free ligands **2** and **2^{Me}** with $NiBr_2(DME)$ (Scheme 2).

The orange, air stable, square planar ionic complexes **3·(Br)$^-$** and **3^{Me}·(Br)$^-$** were isolated in good yield by slow diffusion of Et_2O into concentrated CH_2Cl_2 solutions. The ^1H NMR spectrum of **3^{Me}·(Br)$^-$** has characteristic features associated with the high
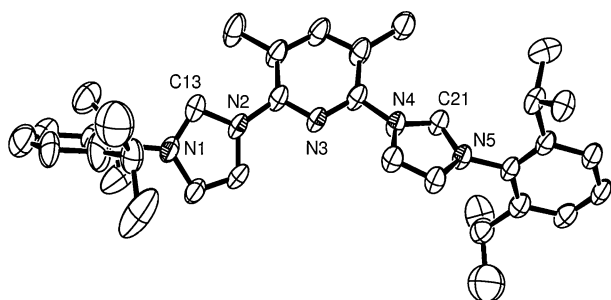
Fig. 1 ORTEP diagram of compound 2^{Me}; thermal ellipsoids at 50% probability, hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and angles (°): C(13)–N(1) 1.364(4); C(13)–N(2) 1.373(3); C(21)–N(4) 1.375(3); C(21)–N(5) 1.363(3); N(1)–C(13)–N(2) 101.7(2); N(4)–C(21)–N(5) 101.1(2).
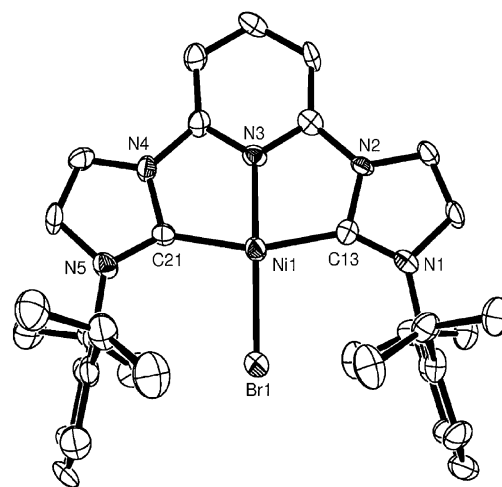
symmetry of the complex *i.e.* two doublets and one septet assignable to the isopropyl groups of the DiPP substituents and one sharp singlet from the methyl groups on the pyridine moiety. In contrast, the spectrum of $3 \cdot (Br)^-$ was uncharacteristically broad, possibly due to dynamic processes involving exchange of the ionic and coordinated bromide anions. Sharpening of the spectral features was not observed even at −70 °C. However, the structure of $3 \cdot (Br)^-$ in the solid state was confirmed crystallographically and is shown in Fig. 2.

The geometry around the Ni is distorted square planar, with a C_{NHC}–Ni–C_{NHC} angle of 161.1(3)° and a pincer ligand bite angle of *ca.* 81°. The Ni lies out of the coordination plane by 0.050(3) Å. The Ni–C_{NHC} bond lengths [1.914(7)–1.932(8) Å] are within

Fig. 2 ORTEP diagram showing one of two cations of $3 \cdot (Br)^-$ in the asymmetric unit with virtually identical metrical data; thermal ellipsoids at 50% probability, hydrogen atoms and one CH_2Cl_2 solvent molecule have been removed for clarity. Selected bond lengths (Å) and angles (°): C(13)–Ni(1) 1.920(7); N(3)–Ni(1) 1.872(5); C(21)–Ni(1) 1.914(7); Br(1)–Ni(1) 2.2813(11); C(48)–Ni(2) 1.927(8); N(8)–Ni(2) 1.873(5); C(56)–Ni(2) 1.932(8); Br(3)–Ni(2) 2.2591(11); C(13)–Ni(1)–C(21) 161.1(3); C(13)–Ni(1)–N(3) 80.3(3); C(48)–Ni(2)–C(56) 162.7(3); C(56)–Ni(2)–N(8) 81.6(3).

the range of previously observed [Ni^{II}–C_{NHC} bond lengths [1.835–2.019 Å].[5a,b] An analogue of $3 \cdot (Br)^-$ with methyl substituted NHC groups was recently reported.[6] The reaction of $3 \cdot (Br)^-$ with two
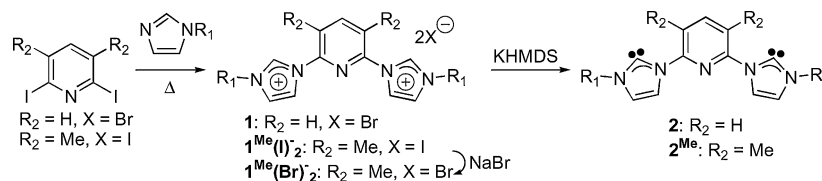
Scheme 1 Synthesis of pincer ligands **2** and 2^{Me} (R_1 = DiPP).
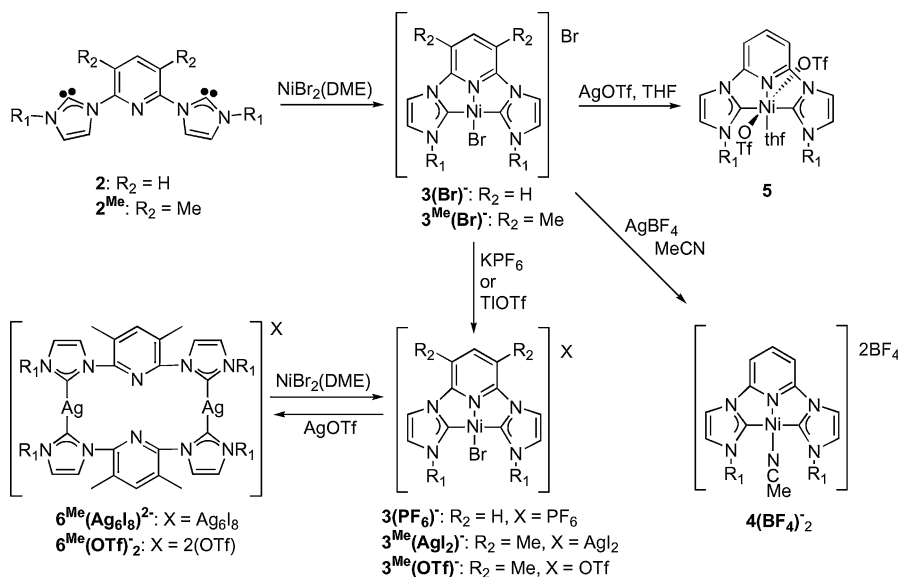
Scheme 2 Metal complexes described in this paper (R_1 = DiPP).

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equivalents of KPF_6 in THF (even in excess) yielded only complex $3 \cdot (PF_6)^-$, in which only the ionic bromide was exchanged by PF_6^-. Compound $3 \cdot (PF_6)^-$ was characterised by analytical, spectroscopic and diffraction methods (see ESI‡); all data revealed a 4-coordinate square planar monocationic complex, with the metrical data of the cation being identical to those observed in $3 \cdot (Br)^-$.

Reaction of $3 \cdot (Br)^-$ with two equivalents of $AgBF_4$ in MeCN resulted in substitution of both coordinated and ionic bromides. Compound $4 \cdot (BF_4)^-_2$ is a 4-coordinate square planar dication with one MeCN completing the coordination sphere of the nickel. The 4-coordinate structure is also suggested by a poor quality single crystal dataset; NMR and microanalytical data are also consistent with the proposed structure.

Both ionic and coordinated bromides in $3 \cdot (Br)^-$ can be exchanged for OTf^- by the reaction with two equivalents of AgOTf in THF, yielding green crystals of complex **5**. Interestingly, complex **5** is paramagnetic (μ_{eff} = 2.86 B.M.). It was characterised by analytical and diffraction methods. The structure of the molecule (Fig. 3) comprises an octahedral nickel centre which, in addition to the tridentate ligand, contains two monodentate mutually *trans* triflate ligands and one coordinated THF molecule.
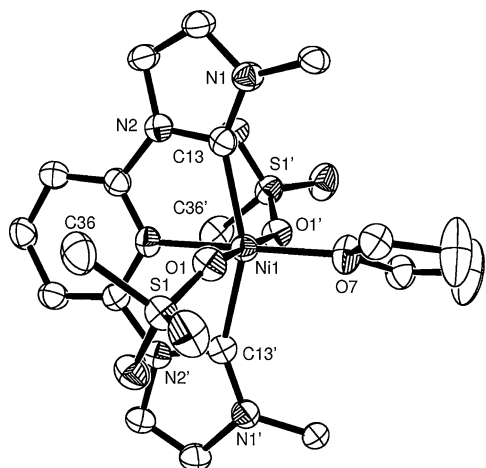

Fig. 3 ORTEP diagram of compound **5**; thermal ellipsoids at 50% probability, hydrogen atoms, DiPP rings (bar *ipso* carbons), fluorines from the OTf groups and two THF solvent molecules have been removed for clarity. Selected bond lengths (Å) and angles (°): C(13)–Ni(1) 2.103(4); N(3)–Ni(1) 2.017(4); O(1)–Ni(1) 2.190(3); O(7)–Ni(1) 2.069(4); C(13)–Ni(1)–C(13′) 155.3(2); C(13)–Ni(1)–N(3) 77.63(11); O(1)–Ni(1)–O(1′) 179.03(15) C(13)–Ni(1)–O(1) 87.49(12). The two halves of the molecule are related by the symmetry operation ($-x + 1, y, -z + 0.5$).

Complex **5** lies on a special position in the unit cell and has crystallographically imposed C_2-symmetry. The Ni–C_{NHC} bond length of 2.103(4) Å is substantially (*ca.* 0.084 Å) longer than the previous longest Ni–C_{NHC} bond length: interestingly, this was from the only other known octahedral nickel carbene,[5b] which indicates that the octahedral geometry contributes to the lengthening of the Ni–C_{NHC} bond. The pincer bite angle is *ca.* 77° and the Ni–N_{py} distance of 2.017(4) Å is much longer than the corresponding length in $3 \cdot (Br)^-$ [1.872(3) Å]. The dependence of the Ni geometry in NHC complexes on the nature of the co-ligands has been previously reported.[5b] Complex **5**, by virtue of the lability of the OTf^- and THF ligands, is an attractive starting material for further derivatisation which is currently under investigation.

Due to initial difficulties in isolating pure 2^{Me} in synthetically useful quantities, as described above, the silver NHC complex $6^{Me} \cdot (Ag_6I_8)^{2-}$ was synthesised from the reaction of $1^{Me} \cdot (I)^-_2$ with Ag_2O in dichloromethane. Based on analytical and structural data (Fig. 4), compound $6^{Me} \cdot (Ag_6I_8)^{2-}$ is dimeric with two (C-N^{Me}-C) ligands bridged by two Ag atoms forming a 16-membered ring lying on an inversion centre in the unit cell. Unlike the only previous structurally characterised example of a silver complex of a C-N-C pincer ligand,[5c] $6^{Me} \cdot (Ag_6I_8)^{2-}$ is not a helicate. Instead, it can be described as a mesocate due to the absence of a 'twist' in the molecule. The interplanar angles between the NHC and the pyridine rings are *ca.* 60°, roughly twice that observed in the free ligand 2^{Me}. The $(Ag_6I_8)^{2-}$ anion contains an unusual arrangement of Ag atoms in a planar 6-membered ring: this has only been observed once before.[7] There are iodides alternating above and below the ring as well as 'capping' iodides; one on each face of the ring.
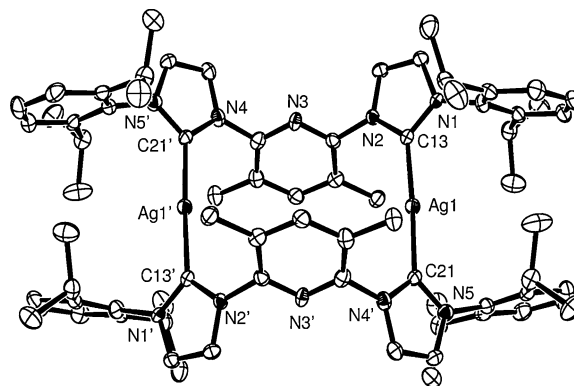

Fig. 4 ORTEP diagram of compound $6^{Me} \cdot (Ag_6I_8)^{2-}$; thermal ellipsoids at 50% probability, hydrogen atoms, the $(Ag_6I_8)^{2-}$ anion and two Et_2O molecules have been removed for clarity. Selected bond lengths (Å) and angles (°): C(13)–Ag(1) 2.079(7); C(21)–Ag(1) 2.082(7); C(13)–Ag(1)–C(21) 177.0(3).

Transmetallation of $6^{Me} \cdot (Ag_6I_8)^{2-}$ with $NiBr_2$(DME) gave complex $3^{Me} \cdot (AgI_2)^-$, which is analogous to $3^{Me} \cdot (Br)^-$ with $(AgI_2)^-$ rather than Br^- as the non-coordinating anion. This complex was characterised analytically, spectroscopically and crystallographically (Fig. 5). The compound contains a 4-coordinate square planar cation analogous to that in $3 \cdot (Br)^-$ and $3 \cdot (PF_6)^-$. The Ni–C_{NHC}, Ni–Br and Ni–N_{py} distances are unremarkable. The ^{1}H NMR spectrum of $3^{Me} \cdot (AgI_2)^-$ is in agreement with the high symmetry structure observed in the solid state.

When $3^{Me} \cdot (AgI_2)^-$, was reacted with two equivalents of AgOTf in THF, colourless crystals were isolated after workup. The complex obtained was characterised crystallographically: the structure indicated that a 'reverse NHC transmetallation' from the cation of $3^{Me} \cdot (AgI_2)^-$ to silver had taken place. Product $6^{Me} \cdot (OTf)^-_2$ contains an Ag-bridged bis(ligand) dication, as seen in the previous silver complex, with two triflate anions instead of $(Ag_6I_8)^{2-}$ (see ESI‡). The liberated Ni(II) stayed in solution, presumably in the form of solvated NiI_2.

The metrical data of $6^{Me} \cdot (Ag_6I_8)^{2-}$ and $6^{Me} \cdot (OTf)^-_2$ are not quite identical; although the C_{NHC}–Ag bond lengths are the same (within experimental error), the C_{NHC}–Ag–C_{NHC} bond angle is slightly smaller in $6^{Me} \cdot (OTf)^-_2$ [173.42(9)°] than in $6^{Me} \cdot (Ag_6I_8)^{2-}$ [177.0(3)°].
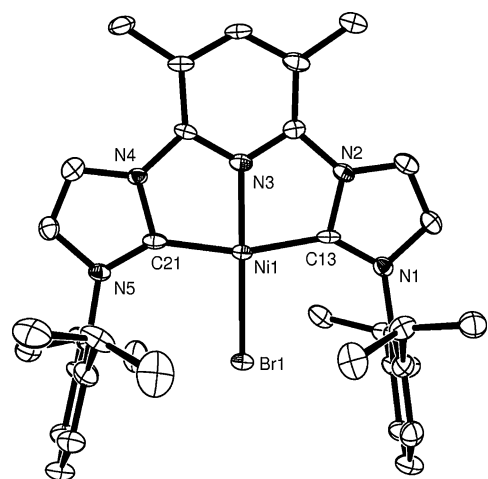
Fig. 5 ORTEP diagram of compound **3^Me·(AgI₂)⁻**; thermal ellipsoids at 50% probability, hydrogen atoms and the (AgI₂)⁻ anion have been removed for clarity. Selected bond lengths (Å) and angles (°): C(13)–Ni(1) 1.911(8); N(3)–Ni(1) 1.860(6); C(21)–Ni(1) 1.895(8); Br(1)–Ni(1) 2.2761(11); C(13)–Ni(1)–C(21) 163.3(3); C(13)–Ni(1)–N(3) 81.1(3); C(21)–Ni(1)–N(3) 82.2(3).

To prevent transmetallation, AgOTf was replaced by TlOTf and the reaction was rerun. Compound **3^Me·(Br)⁻** was reacted with two equivalents of TlOTf in THF, but after workup an orange solution remained. Complex **3^Me·(OTf)⁻** was characterised by structural (see ESI‡), spectroscopic and analytical methods. Structural features of the cation are identical to other square planar cations discussed above [**3^Me(X)⁻**].

The occurrence of 'reverse NHC transmetallation' is unexpected: It implies some degree of (hemi)lability of the pincer ligand in **3^Me·(AgI₂)⁻** and underlines the importance of the nature of the anions, in addition to the strengths of the M–C$_{NHC}$ bonds that are being broken and formed during the reaction, in determining the direction of the transmetallation. We have not been able to observe this reaction with other Ni complexes, even though the transformation described above is reproducible.

Attempts at alkylating **3·(Br)⁻** and **3^Me·(Br)⁻** with MeLi, AlMe₃ or PhMgCl gave intractable reaction mixtures. In an attempt to prepare a methyl complex stabilised by the pincer ligand, we reacted NiMe₂(tmeda) with **2**. The product **7** exhibited a complicated ¹H NMR spectrum with a broad resonance in place of the usual sharp doublets for the ^iPr methyl groups, three signals for the ^iPr CH groups (in a 1 : 1 : 2 ratio) and only one singlet assignable to methyl groups attached to Ni. In addition, a singlet and several other resonances in the olefinic region suggested possible decomposition of the ligand system. The identity of **7** was clearly established by single crystal X-ray diffraction (Scheme 3 and Fig. 6).
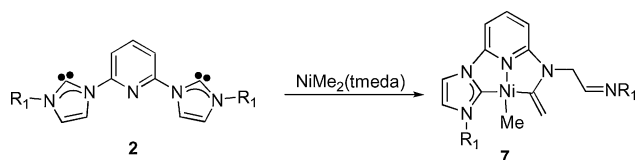
Scheme 3 Reaction between **2^Me** and NiMe₂(tmeda) (R₁ = DiPP).

The structure of the molecule revealed an unexpected ring opening of the NHC functional group, accompanied by migration
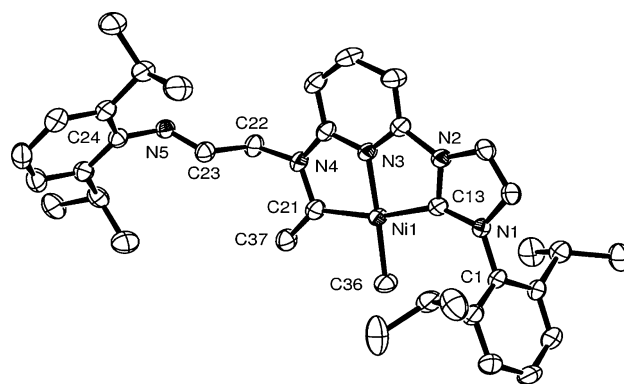

Fig. 6 ORTEP diagram of compound **7**; thermal ellipsoids at 50% probability, hydrogen atoms and one THF solvent molecule have been removed for clarity. Selected bond lengths (Å) and angles (°): C(13)–Ni(1) 1.912(2); N(3)–Ni(1) 1.8725(19); C(21)–Ni(1) 1.930(2); C(36)–Ni(1) 1.924(2); C(21)–C(37) 1.337(3); C(23)–N(5) 1.259(3); C(13)–Ni(1)–C(21) 164.05(10); N(3)–Ni(1)–C(36) 177.77(10); N(3)–Ni(1)–C(13) 81.50(9); N(3)–Ni(1)–C(21) 82.68(10); C(37)–C(21)–Ni(1) 132.2(2).

of a methyl group (crystallographic C37) from nickel to the C$_{NHC}$. The N(5)–C(23) bond length of 1.259(3) Å is consistent with an imine functionality, the C(21)–C(37) bond length of 1.337(3) Å is concordant with a C=C bond and is consistent with the olefinic resonances observed in the ¹H NMR spectrum. Assignment of C(22) as a methylene carbon was indicated by the geometry around the atom, along with the experimental location of the hydrogens in the difference Fourier map. The C(13)–Ni(1) and C(21)–Ni(1) bond lengths are different [1.912(2) Å and 1.930(2) Å respectively] but, surprisingly, the Ni–C$_{NHC}$ distance is shorter than the Ni–C$_{vinyl}$ distance. The bite angles in the NHC-pyridine and pyridine-σ-enyl-amine chelate rings of the non-symmetric pincer ligand are slightly different [81.50(9)° and 82.68(10)° respectively].

The study of complexes in which various organometallic functionalities (for example alkyls, alkylidenes *etc.*) share the same coordination sphere with a 'spectator' NHC ligand offers fundamental understanding of the reactivity of NHC complexes in homogeneous catalysis. The following transformations have been recently observed with late transition metal complexes which question the widely accepted view that NHCs are ideal 'innocent' ligands in organometallic chemistry: (i) the reductive elimination of alkyl- or aryl-imidazolium salts from alkyl- or aryl-imidazol-2-ylidene complexes;[8] (ii) the migration of CH₃ from Pd to the C$_{NHC}$ of a coordinated imidazol-2-ylidene;[9] (iii) the ring expansion in metathesis catalysts;[10] (iv) C–C and C–H activation of alkyl substituents;[11] (v) the ring opening of imidazolin-2-ylidenes coordinated on Ni phenyl leading to Fischer type carbene complexes[12] and (vi) the coupling of alkynes with imidazol-2-ylidenes on ruthenium.[13] It has been postulated that the transformations (v) and (vi) are initiated by the migration of σ-bound organometallic to the C$_{NHC}$ of a coordinated NHC; this reaction was first established in the 'pincer' pyridine dicarbene Pd complex (ii).[9,12,13]

The exact mechanism of the ring opening occurring in our system is not clear. However, based on the direct observation of Me migration from Pd to C$_{NHC}$ and the identity of **7**, we propose a plausible mechanism illustrated in Scheme 4.

The first step is coordination of ligand **2** to Ni with displacement of tmeda. The resultant 5-coordinate intermediate undergoes
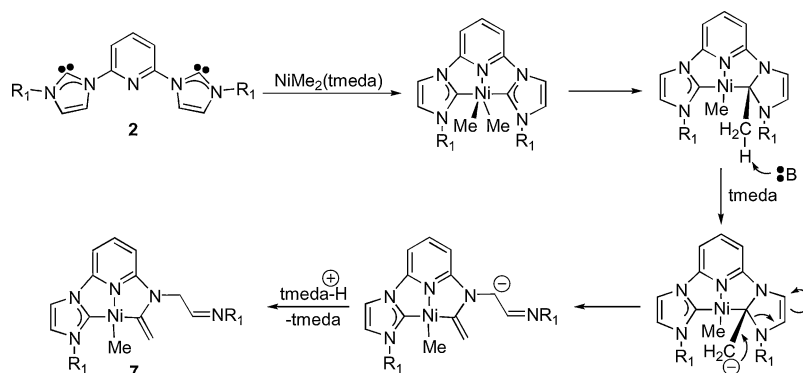
Scheme 4 Plausible mechanism of formation for **7** (R_1 = DiPP).

methyl migration to the C_{NHC}, followed by base (tmeda) catalysed deprotonation of the β-hydrogen bearing alkyl. In the resulting σ-vinyl group, ring-opening of the imidazol ring takes place, forming the imine. The resulting carbanion is then reprotonated by the ammonium cation (tmeda·H)[+] at C(22) affording product **7**.

Conclusions

The synthesis of the pincer pyridine dicarbene ligands (**2** and **2^{Me}**) provided access to a class of analogous nickel complexes and showed the influence of ligand steric and electronic factors and the counter anion on the nature of the products obtained. This was highlighted by the first observation of transfer of functionalised NHC ligand from nickel to silver. A ring opening of the coordinated imidazol-2-ylidene was also observed for the first time when methyl co-ligands shared the same coordination sphere with the rigid NHC pincer. A mechanism for this transformation has been proposed and is based on migratory insertion of the coordinated methyl to coordinated C_{NHC}.

The study of complexes of **2^{Me}** with other transition metals, especially where metallation of the pyridine ring of **2** has been observed, and the dependence of organometallic reaction products on the electronics of the pyridine ring is work currently in progress and will be reported shortly.

Experimental

General methods

Elemental analyses were carried out by the London Metropolitan University microanalytical laboratory. NMR data were recorded on Bruker AV-300 and DPX-400 spectrometers, operating at 300 and 400 MHz (^{1}H) respectively. The spectra were referenced internally using the signal from the residual protio-solvent (^{1}H), the signals of the solvent (^{13}C) or an external CFCl$_3$ sample (^{19}F). Magnetic data were recorded at room temperature on a Johnson Matthey balance. All manipulations were performed under nitrogen in a Braun glove box or by using standard Schlenk techniques, unless stated otherwise. Solvents were dried using standard methods and distilled under nitrogen prior to use. The light petroleum used throughout had a bp 40–60 °C. The starting materials DiPP imidazole,[14] 2,6-diiodolutidine[4] and NiMe$_2$(tmeda)[15] were prepared according to literature procedures.

2,6-Bis-[(3-(2,6-di*iso*propylphenyl)-imidazolium]-3,5-dimethyl-pyridine diiodide, 1^{Me}·(I)$^-_2$. 2,6-Diiodo-3,5-dimethylpyridine (5.0 g, 13.9 mmol) and 2,6-DiPP imidazole (9.5 g, 41.7 mmol) were heated to 190 °C under vacuum in a sealed ampoule and stirred for 7 days. After this time, the cooled solid was extracted into a minimum of dichloromethane and ether was added. The grey solid formed was filtered, washed with Et$_2$O and dried under Dean and Stark conditions affording 10.98 g (97%). Crystallisation occurred by slow diffusion of Et$_2$O into a concentrated dichloromethane solution. δ_H (400 MHz, CDCl$_3$): 10.83 (2H, s, imidazolium CH), 9.11 (2H, s, Ar), 8.02 (1H, s, Ar), 7.56 (2H, t, J = 8.0 Hz, Ar), 7.35–7.42 (6H, m, Ar), 2.67 (6H, s, py-Me), 2.42 (4H, septet, J = 7.0 Hz, ^{i}Pr CH), 1.20 and 1.27 (each 12H, d, J = 7.0 Hz, ^{i}Pr CH$_3$) ppm. δ_C (100.63 MHz, CDCl$_3$): 147.61 (CH, Ar), 145.10, 142.09 (C, Ar), 138.27, 132.15 (CH, Ar), 131.60, 129.73 (C, Ar), 125.10, 124.76, 124.15, 123.98 (CH, Ar), 28.82 (CH, ^{i}Pr), 24.49, 24.13 (CH$_3$, ^{i}Pr), 18.23 (CH$_3$, py-Me) ppm. Calc. for C$_{37}$H$_{47}$N$_5$I$_2$: C 54.49; H 5.81; N 8.59. Found: C 54.58; H 5.85; N 8.51%.

2,6-Bis-[(3-(2,6-di*iso*propylphenyl)-imidazolium]-3,5-dimethyl-pyridine dibromide, 1^{Me}·(Br)$^-_2$. Compound 1^{Me}·(I)$^-_2$ (20.0 g, 24.5 mmol) was dissolved in MeOH (300 cm^3) and a solution of NaBr (100.0 g, 980 mmol) in water (100 cm^3) was added. The reaction was stirred at room temperature for 6 h after which time the solvents were removed, the solid extracted into a minimum amount of dichloromethane, dried (MgSO$_4$) and filtered. Et$_2$O was added with vigorous stirring and the grey solid formed was filtered, washed with Et$_2$O and azeotropically dried, yielding 17.2 g of the title product (97%). Crystallisation occurred from slow diffusion of Et$_2$O into a concentrated dichloromethane solution. δ_H (400 MHz, CDCl$_3$): 10.95 (2H, s, imidazolium CH), 9.14 (2H, s, Ar), 7.97 (1H, s, Ar), 7.47 (2H, t, J = 6.0 Hz, Ar), 7.33 (2H, s, Ar), 7.24 (4H, br s, Ar), 2.62 (6H, s, py-Me), 2.33 (4H, septet, J = 6.5 Hz, ^{i}Pr CH), 1.18 and 1.12 (each 12H, d, J = 6.5 Hz, ^{i}Pr CH$_3$) ppm. δ_C (100.63 MHz, CDCl$_3$): 147.51 (CH, Ar), 144.79, 141.82 (C, Ar), 138.24, 131.83 (CH, Ar), 130.97, 129.53, 128.71, 127.91 (C, Ar), 124.90, 124.46, 124.01 (CH, Ar), 28.56 (CH, ^{i}Pr), 24.22, 23.82 (CH$_3$, ^{i}Pr), 18.06 (CH$_3$, py-Me) ppm. Calc. for C$_{37}$H$_{47}$N$_5$Br$_2$: C 61.58; H 6.56; N 9.71. Found: C 61.66; H 6.65; N 9.85%.

2,6-Bis[(3-(2,6-di*iso*propylphenyl)-imidazol-2-ylidene]-3,5-di-methylpyridine, 2^{Me}. KN(SiMe$_3$)$_2$ (580 mg, 2.91 mmol) and 1^{Me}·(Br)$^-_2$ (1.0 g, 1.38 mmol) were cooled to −78 °C and cold (−78 °C) petrol (30 cm^3) was added. The suspension was stirred at

−78 °C for 15 min then warmed to room temperature and stirred for 72 h. After this time the solution was filtered, the solid washed with petrol (20 cm³) and concentrated *in vacuo*, affording 600 mg of a pale yellow solid (77%). Crystallisation occurred by cooling a saturated petrol solution to −35 °C. δ_H (400 MHz, C_6D_6): 7.73 (2H, d, J = 1.5 Hz, imidazol-2-ylidine), 7.30–7.36 (2H, m, Ar), 7.19–7.23 (5H, m, Ar), 6.62 (2H, d, J = 1.5 Hz, imidazol-2-ylidine), 2.92 (4H, septet, J = 7.0 Hz, ^{i}Pr CH), 2.76 (6H, s, py-Me), 1.25 and 1.15 (each 12H, d, J = 7.0 Hz, ^{i}Pr CH₃) ppm. δ_C (100.63 MHz, C_6D_6): 221.70 (C, C_{NHC}), 148.81 (C, Ar), 146.66 (CH, Ar), 146.43, 138.90, 129.34 (C, Ar), 129.12 (CH, Ar), 128.57, 125.70, 125.03 (C, Ar), 123.79, 121.21, 119.83 (CH, Ar), 28.66, 24.63 (CH₃, ^{i}Pr), 23.88 (CH, ^{i}Pr), 20.42 (CH₃, py-Me) ppm. Calc. for $C_{37}H_{45}N_5$: C 79.39; H 8.10; N 12.51. Found: C 79.50; H 8.13; N 12.44%.

Nickel{2,6-bis-[(3-(2,6-di*iso*propylphenyl)-imidazol-2-ylidene]-pyridine}bromide bromide, 3·(Br)⁻. To a solution of NiBr₂(DME) (116 mg, 0.38 mmol) in THF (15 cm³) was added a solution of **2** (200 mg, 0.38 mmol) in THF (15 cm³) at 0 °C. The reaction was stirred for 15 min, then warmed to room temperature and stirred for 16 h. After this time, the solvent was removed under vacuum and the solid product was washed with light petroleum (20 cm³) and dried. Crystallisation occurred from slow diffusion of ether into a concentrated diclioromethane solution. Yield: 210 mg of an orange solid (74%). δ_H (300 MHz, CD_2Cl_2): 6.0–9.2 (13H, br m, Ar), 0.5–3.0 (38H, br m, ^{i}Pr CH/CH₃ + acetone) ppm. δ_C (75.5 MHz, CD_2Cl_2): 164.62, 150.88, 144.55, 134.00, 130.09, 127.86, 123.58, 118.41, 109.83 (C/CH, Ar), 28.60, 24.42, 22.91 (CH/CH₃, ^{i}Pr) ppm. Calc. for $C_{35}H_{41}N_5NiBr_2$: C 56.03; H 5.51; N 9.33. Found: C 55.97; H 5.41; N 9.41%.

Nickel{2,6-bis-[(3-(2,6-di*iso*propylphenyl)-imidazol-2-ylidene]-3,5-dimethylpyridine}bromide bromide, 3^{Me}·(Br)⁻. Compound **2^{Me}** (250 mg, 0.45 mmol) and NiBr₂(DME) (96 mg, 0.45 mmol) were suspended in THF (20 cm³) and stirred for 16 h at room temperature. After this time, solvents were removed *in vacuo*, affording 326 mg of the title compound as an orange powder (94%). δ_H (400 MHz, C_6D_6): 8.32 (1H, s, py-H), 8.28 (2H, br s, imidazol-2-ylidene), 7.35 (2H, t, J = 7.5 Hz, Ar), 7.11 (4H, br d, J = 7.5 Hz, Ar), 7.01 (2H, br s, imidazol-2-ylidene), 2.89 (6H, s, py-Me), 2.46 (4H, septet, J = 6.5 Hz, ^{i}Pr CH), 1.19 and 1.05 (each 12H, d, J = 6.5 Hz, ^{i}Pr CH₃) ppm. δ_C (100.6 MHz, C_6D_6): 182.18 (C, C_{NHC}), 167.10 (C, Ar), 152.86 (CH, Ar), 148.58, 145.21, 134.98 (C, Ar), 130.91, 128.55, 124.38 (CH, Ar), 120.91 (C, Ar), 119.63 (CH, Ar), 29.42 (CH, ^{i}Pr), 25.26, 23.68 (CH₃, ^{i}Pr), 19.50 (CH₃, py-Me) ppm. Calc. for $C_{37}H_{45}N_5NiBr_2$: C 57.10; H 5.83; N 9.00. Found: C 56.96; H 5.69; N 8.82%.

Nickel{2,6-bis-[(3-(2,6-di*iso*propylphenyl)-imidazol-2-ylidene]-pyridine}bromide hexafluorophosphate, 3·(PF₆)⁻. Compound **3·(Br)⁻** (150 mg, 0.20 mmol) and KPF₆ (171 mg, 0.66 mmol) were dissolved in THF (20 cm³) and stirred for 16 h. After this time the solution was filtered through Celite and the solvent was removed under vacuum. Crystallisation occurred by slow diffusion of ether into a concentrated dichloromethane solution. Yield: 150 mg of orange crystals, (92%). δ_H (400 MHz, CD_2Cl_2): 8.43 (1H, t, J = 8.0 Hz, py-4), 7.95 (2H, s, imidazol-2-ylidene CH), 7.69 (2H, d, J = 8.0 Hz, py-3,5), 7.36 (2H, t, J = 8.0 Hz, Ph-4), 7.13 (4H, d, J = 8.0 Hz, Ph-3,5), 7.00 (2H, s, imidazol-2-ylidene CH), 2.485 (4H,

septet, J = 7.0 Hz, ^{i}Pr CH), 1.21 and 1.07 (each 12H, d, J = 7.0 Hz, ^{i}Pr CH₃) ppm. δ_C (100.63 MHz, CD_2Cl_2): 165.22 (C, C_{NHC}), 150.76 (C, Ar), 146.53 (CH, Ar), 144.61, 133.94 (C, Ar), 130.36 (CH, Ar), 128.32 (CH, imidazol-2-ylidene), 123.75 (CH, Ar), 116.21 (CH, imidazol-2-ylidene), 108.32 (CH, Ar), 28.76 (CH, ^{i}Pr), 24.48, 23.03 (CH₃, ^{i}Pr) ppm. Calc. for $C_{35}H_{41}N_5BrF_6NiP$: C 51.56; H 5.07; N 8.59. Found: C 51.43; H 5.16; N 8.65%.

Nickel{2,6-bis-[(3-(2,6-di*iso*propylphenyl)-imidazol-2-ylidene]-pyridine} acetonitrile bis(tetrafluoroborate), 4·(BF₄)⁻₂. Compound **3·(Br)⁻** (250 mg, 0.33 mmol) and AgBF₄ (136 mg, 0.70 mmol) were dissolved in MeCN (25 cm³) and stirred for 16 h. After this time the solution was filtered through Celite, the solvent was removed under vacuum and the solid was kept. Crystallisation occurred from slow diffusion of Et₂O into a concentrated MeCN solution. Yield: 247 mg of green crystals (92%). δ_H (300 MHz, CD_3CN): 8.46 (1H, t, J = 8.5 Hz, py-4), 8.14 (2H, d, J = 2 Hz, imidazol-2-ylidene), 7.72 (2H, d, J = 8.5 Hz, py-3,5), 7.42 (2H, dd, J = 8.5, 7.0 Hz, Ar), 7.27–7.34 (6H, m, Ar), 2.54 (4H, septet, J = 7.0 Hz, ^{i}Pr CH), 1.94 (3H, s, MeCN), 1.19 and 1.08 (each 12H, d, J = 7.0 Hz, ^{i}Pr CH₃) ppm. δ_C (100.63 MHz, CD_3CN): 151.81 (C, Ar), 149.33 (CH, Ar), 145.92, 132,64 (C, Ar), 132.25, 128.32, 125.12, 118.67, 109.92 (CH, Ar), 28.72 (CH, ^{i}Pr), 23.90, 23.62 (CH₃, ^{i}Pr) ppm. δ_F (282.4 MHz, CD_3CN): −151.27. Calc. for $C_{37}H_{44}N_6NiB_2F_8$: C 55.20; H 5.51; N 10.44. Found: C 55.27; H 5.59; N 10.51%.

***trans*-Nickel{2,6-bis-[(3-(2,6-di*iso*propylphenyl)-imidazol-2-ylidene]pyridine}-bis-trifluoromethanesulfonate tetrahydrofuran, 5.** Compound **3·(Br)⁻** (250 mg, 0.33 mmol) and AgOTf (171 mg, 0.66 mmol) were dissolved in THF (25 cm³) and stirred for 4 h. After this time, the resultant green solution was filtered through Celite, the solvent was removed under vacuum and the solid product was dried under vacuum. Crystallisation occurred by slow diffusion of light petroleum to a concentrated THF solution. Yield: 300 mg of green crystals (94%). μ_{eff}: 2.86 B.M. Calc. for $C_{41}H_{49}N_5O_7F_6NiS_2$: C 51.26; H 5.14; N 7.29. Found: C 51.18; H 5.23; N 7.16%.

Bis-[2,6-bis-[(3-(2,6-di*iso*propylphenyl)-imidazol-2-ylidene]-3,5-dimethylpyridine disilver (hexasilver octaiodide), 6^{Me}·(Ag₆I₈)²⁻. Ag₂O (232 mg, 1.00 mol) and compound **1^{Me}·(I)⁻₂** (816 mg, 1.00 mmol) were mixed as powders, dissolved in dichloromethane (40 cm³) and stirred for 4 h with the exclusion of light. After this time, the solution was concentrated, filtered through Celite and ether (200 cm³) was added to complete precipitation. The white solid formed was filtered and dried *in vacuo*. Crystallisation occurred by slow diffusion of ether into a CDCl₃ solution. δ_H (400 MHz, C_6D_6): 7.66–7.87 (2H, m, Ar), 7.39–7.48 (2H, m, Ar), 7.18–7.32 (3H, m, Ar), 6.96–7.15 (4H, m, Ar), 2.51 (4H, br s, ^{i}Pr CH), 2.40 (6H, s, py-Me), 1.24, 1.14 (each 12H, br s, ^{i}Pr CH₃) ppm. δ_C (100.6 MHz, C_6D_6): 188.27 (C, C_{NHC}), 147.51, 147.25 (C, Ar), 146.58, 146.25 (CH, Ar), 145.82, 145.08, 134.80 (C, Ar), 130.82, 130.58, 124.34, 123.71, 122.41 (CH, Ar), 28.42 (CH, ^{i}Pr), 24.81, 24.49 (CH₃, ^{i}Pr), 19.01 (CH₃, py-Me) ppm. Calc. for $C_{74}H_{90}N_{10}Ag_8I_8$: C 29.65; H 3.03; N 4.67. Found: C 29.77, H 3.10; N 4.63%.

Nickel-{[2,6-bis-[(3-(2,6-di*iso*propylphenyl)-imidazol-2-ylidene]-3,5-dimethylpyridine}bromide (silver diiodide), 3^{Me}·(AgI₂)⁻. Compound **6^{Me}·(Ag₆I₈)²⁻** (450 mg, 0.44 mmol) and NiBr₂(DME)

(136 mg, 0.44 mmol) were both dissolved in thf (10 cm³). The solution of $6^{Me} \cdot (Ag_6I_8)^{2-}$ was added to the solution of the Ni complex *via* canula and stirred for 72 h. After this time, the solution was filtered through Celite, concentrated to dryness and crystallised by slow diffusion of PE into a concentrated THF solution. δ_H (400 MHz, d⁸-thf): 8.41–8.45 (3H, m, Ar), 7.36–7.46 (4H, m, Ar), 7.18–7.23 (4H, m, Ar), 3.02 (6H, s, py-Me), 2.76 (4H, septet, $J = 6.5$ Hz, ^{i}Pr CH), 1.36, 1.19 (each 12H, d, $J = 6.5$ Hz, ^{i}Pr CH₃) ppm. δ_C (100.6 MHz, d⁸-thf): 168.60 (C, Ar), 154.23 (CH, Ar), 150.09, 146.73, 137.12 (C, Ar), 131.70, 129.69, 125.36 (CH, Ar), 122.29 (C, Ar), 121.41 (CH, Ar), 30.60 (CH, ^{i}Pr), 26.39, 24.98 (CH₃, ^{i}Pr), 20.57 (CH₃, py-Me) ppm. Calc. for $C_{37}H_{45}N_5NiBrAgI_2$: C 41.92; H 4.28; N 6.61. Found: C 41.81, H 4.15; N 6.55%.

Nickel{2,6-bis-[(3-(2,6-di*iso*propylphenyl)-imidazol-2-ylidene]-3,5-dimethylpyridine}bromide trifluoromethanesulfonate, $3^{Me} \cdot$(OTf)⁻. Compound $3^{Me} \cdot$(Br)⁻ (250 mg, 0.32 mmol) and Tl(OTf) (226 mg, 0.64 mmol) were suspended in THF (20 cm³) and stirred for 16 h at room temperature. After this time, solvents were removed *in vacuo*, affording 326 mg of the title compound as an orange powder, (94%). δ_H (400 MHz, C₆D₆): 8.04 (2H, d, $J = 2.0$ Hz, imidazol-2-ylidene), 8.02 (1H, s, py-H), 7.35 (2H, t, $J = 7.5$ Hz, Ar), 7.09–7.16 (4H, m, Ar), 6.98 (2H, d, $J = 2.0$ Hz, imidazol-2-ylidene), 2.78 (6H, s, py-Me), 2.46 (4H, septet, $J = 7.0$ Hz, ^{i}Pr CH), 1.19 and 1.05 (each 12H, d, $J = 2.0$ Hz, ^{i}Pr CH₃) ppm. δ_C (100.6 MHz, C₆D₆): 167.22 (C, Ar), 152.44 (CH, Ar), 148.60, 145.23, 134.97 (C, Ar), 130.98, 128.55, 124.43 (CH, Ar), 120.77 (C, Ar), 119.08 (CH, Ar), 29.45 (CH, ^{i}Pr), 25.24, 23.68 (CH₃, ^{i}Pr), 18.90 (CH₃, py-Me) ppm. δ_F (282.4 MHz, C₆D₆): −78.89. Calc. for $C_{38}H_{45}N_5O_3F_3SNiBr$: C 53.86; H 5.35; N 8.26. Found: C 53.79; H 5.31; N 8.31%.

Methyl nickel{2-[(3-(2,6-di*iso*propylphenyl)-imidazol-2-ylidene]-6-[2-(2,6-di*iso*propylphenyl)iminomethyl vinyl amine]pyridine}, 7. Ligand 2 (250 mg, 0.47 mmol) and NiMe₂(tmeda) (96 mg,

0.47 mmol) were dissolved in cold (−78 °C) THF (20 cm³) and stirred for 16 h at room temperature. After this time, solvents were removed *in vacuo*, the solid was extracted into ether, filtered and cooled to −35 °C, affording 131 mg of the title compound as brown crystals (45%). δ_H (400 MHz, C₆D₆): 6.96–7.38 (11H, m, Ar), 5.97 (1H, dd, $J = 12.0$, 10.0 Hz, imine CH), 5.59 and 5.25 (each 1H, br s, olefin CH₂), 3.36 (1H, septet, $J = 6.5$ Hz, ^{i}Pr CH), 3.08 (1H, br s, ^{i}Pr CH), 2.85 (2H, br s, ^{i}Pr CH), 2.36 (2H, s, CH₂), 2.12 (3H, s, Ni–Me), 0.89–1.24 (24H, m, ^{i}Pr CH₃) ppm. δ_C (100.6 MHz, C₆D₆): 186.95 (C, C$_{NHC}$), 168.21 (C, imine), 157.48, 148.37, 145.68, 144.67, 138.61 (C, Ar), 137.15 (CH, Ar), 136.10 (C, Ar), 134.83, 130.22 (CH, Ar), 128.70, 127.40 (C, Ar), 126.07, 125.04, 124.61, 124.14, 123.95, 123.69 (CH, Ar), 104.41 (C, olefin), 100.01 (CH₂, olefin), 58.42 (CH₂, CH₂), 46.05 (CH, ^{i}Pr), 28.81, 28.28, 24.55, 23.93 (CH₃, ^{i}Pr), 15.62 (CH, ^{i}Pr), −7.63 (CH₃, Ni-Me) ppm. Calc. for $C_{37}H_{47}N_5Ni$: C 71.62; H 7.63; N 11.29. Found: C 71.71; H 7.70; N 11.33%.

X-Ray crystallography

A summary of the crystal data, data collection and refinement for compounds 2^{Me}, $3 \cdot$(Br)⁻, 5, $6^{Me} \cdot (Ag_6I_8)^{2-}$, $3^{Me} \cdot$(OTf)⁻ and 7 are given in Table 1.

All data sets (except those for 2 and 7) were collected on a Enraf-Nonius Kappa CCD area detector diffractometer with an FR591 rotating anode (Mo-Kα radiation) and an Oxford Cryosystems low temperature device operating in ω scanning mode with ψ and ω scans to fill the Ewald sphere. The programs used for control and integration were Collect, Scalepack, and Denzo.[16] The crystals were mounted on a glass fiber with silicon grease, from Fomblin vacuum oil. All solutions and refinements were performed using the WinGX package[17] and all software packages within. Refinements were carried out with all data on F^2 full matrix least-squares using SHELXL-97.[18] All non-hydrogen atoms were refined using anisotropic thermal parameters, and hydrogens were added using a riding model.

Table 1 Crystallographic data for the compounds described in this paper

Complex	2^{Me}	$3 \cdot$(Br)⁻	5	$6^{Me} \cdot (Ag_6I_8)^{2-}$	$3^{Me} \cdot$(OTf)⁻	7
Chemical formula	$C_{37}H_{45}N_5$	$C_{35}H_{41}N_5Br_2Ni$, (CH₂Cl₂)	$C_{41}H_{49}N_5O_7F_6S_2Ni$, 2(C₄H₈O)	$C_{74}H_{90}N_{10}Ag_8I_8$, 2(C₄H₁₀O)	$C_{37}H_{45}N_5NiBrAgI_2$	$C_{37}H_{47}N_5Ni$, (C₄H₁₀O)
Formula weight	559.78	835.18	1104.89	3145.96	1060.07	694.63
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$C2/c$	$P2_1/n$	$C2/c$	$P\bar{1}$
a/Å	15.058(3)	12.7728(5)	22.7194(19)	13.6353(4)	41.413(2)	9.907(2)
b/Å	24.920(6)	13.6700(5)	25.510(3)	22.1211(6)	8.1837(4)	13.813(3)
c/Å	10.967(3)	25.2292(10)	14.1716(13)	17.0640(5)	23.0900(11)	15.330(3)
α/°	90	87.286(2)	90	90	90	111.24(3)
β/°	91.360(3)	75.428(2)	125.520(4)	98.0900(10)	104.661(2)	93.82(3)
γ/°	90	71.776(2)	90	90	90	99.87(3)
V/Å³	4114.2(14)	4047.2(3)	6685.2(11)	5095.8(3)	1902.67(15)	1907.3(7)
Z	4	4	4	2	8	2
T/K	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)
μ/mm⁻¹	0.054	2.616	0.415	3.972	3.735	0.546
No. of data collected	22879	69924	28442	78859	42239	18662
No. of unique data	5879	18589	7590	11729	8691	9332
Goodness of fit on F^2	0.976	1.008	1.056	1.166	1.045	1.024
$R_{int.}$	0.0579	0.1227	0.0715	0.0516	0.0734	0.0377
Final $R(|F|)$ for $F_o > 2\sigma(F_o)$	0.0700	0.0900	0.0869	0.0560	0.0667	0.0498
Final $R(F^2)$ for all data	0.2125	0.1947	0.2181	0.1121	0.2119	0.1286

CCDC reference numbers 663954–663964.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b715769j

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