Ni(I) and Ni(II) ring-expanded N-heterocyclic carbene complexes: C–H activation, indole elimination and catalytic hydrodehalogenation[†]

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Reaction of the bulky 6-membered N-heterocyclic carbene 6-Mes with $Ni(cod)_2$ gives a C-H activated 6-Mes nickel(11) complex, but the novel three-coordinate Ni(1) species $Ni(6-Mes)(PPh_3)Br$ if the reaction is performed in the presence of $Ni(PPh_3)_2Br_2$. The Ni(1) complex is a precursor for the catalytic hydrodehalogenation of aryl halides.

Nickel-N-heterocyclic carbene (NHC) complexes have been used in a wide range of catalytic transformations including cross-coupling reactions, cycloadditions and reductive coupling.1 Five-membered ring carbenes with bulky N-substituents are most commonly employed, as these appear to aid the stabilisation of low-coordinate Ni(0) species proposed to be active in the catalytic cycle. However, it is often far from clear even what the nickel-NHC starting complexes are, let alone any intermediates, as such species are typically generated in situ. We rationalised that 6- and 7-membered ring NHCs could allow the isolation of new, well-defined nickel complexes suitable for catalytic studies. These ring-expanded carbenes offer significantly different steric and electronic properties to their 5-membered counterparts,² but have so far received very little attention.³ We now describe reactions of the 6-membered NHC 6-Mes (Scheme 1) to give new ring-expanded carbene complexes of Ni.⁴ A Ni(II) complex has been isolated following carbene C–H activation, and found to degrade by a novel indole elimination pathway. A comproportionation of Ni(II) and Ni(0) has yielded a rare example of three-coordinate Ni(1), which has been investigated for the catalytic reduction of aryl halides.

The addition of 1 equiv. of the bulky 6-Mes ligand to a toluene solution of $Ni(cod)_2$ resulted in colour change over 1 h from yellow to deep red and formation of the C–H activated



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Fig. 1 Molecular structure of 1. Ellipsoids are shown at 30% probability with all hydrogen atoms (except those on C11) removed for clarity. Selected bond lengths (Å) and angles (°): Ni(1)–C(1) 1.8996(12), Ni(1)–C(11) 1.9796(14), Ni(1)–C(23) 2.0838(13), Ni(1)–C(24) 1.9547(14), Ni(1)–C(25) 2.0471(14), C(6)–C(11)–Ni(1) 94.32(8).

6-Mes Ni(II) species **1** (Scheme 1). The compound was isolated in 40% yield and characterised by NMR spectroscopy and X-ray crystallography.[†] Of most note in the ¹H NMR spectrum were two signals at δ 2.8 and 2.3 arising from the diastereotopic protons of the Ni–CH₂ moiety. These correlated by ¹H–¹³C HSQC to a low frequency ¹³C signal at δ 15.6.

The X-ray structure (Fig. 1)⁵ confirmed the presence of a metallated 6-Mes ligand and a cyclooctenyl group, arising presumably *via* hydrogen transfer from the transient Ni–H species formed upon C–H activation. The Ni– $C_{\rm NHC}$ and Ni–CH₂ distances (1.8996(12) and 1.9796(14) Å) are comparable to those reported by Caddick *et al.* in an analogous complex of the 5-membered 1,3-di-*tert*-butylimidazol-2-ylidene ligand, which is the only other known example of a C–H activated nickel carbene complex.⁶

Attempts to employ **1** as a latent source of 12-electron [Ni 6-Mes] for catalytic applications were thwarted by the instability of the complex in solution. Upon thermolysis at 70 °C (16 h), **1** decomposed to afford the *N*-alkyl indole **2**, which was isolated in 62% yield and characterised by a combination of NMR and X-ray techniques (Scheme 2).† Cyclooctene was also observed by NMR spectroscopy, consistent with a pathway involving hydrogen transfer from the activated methylene arm to the cyclooctenyl ligand and elimination of **2** from the nickel centre. A dark grey precipitate, presumed to be metallic Ni, was also deposited. Although there are a number of decomposition pathways for



metal–NHC complexes,⁷ we are unaware of any previous reports that describe products comparable to 2.

It seemed plausible to us that a short-lived Ni(0) 6-Mes complex must exist prior to the formation of 1. We thus adopted the approach employed by Sigman et al. of reacting Ni(0) with carbene in the presence of Ni(II) in an effort to generate a Ni(I) 6-Mes complex.⁸ To our delight, the reaction of Ni(cod)₂ with 6-Mes in the presence of Ni(PPh₃)₂Br₂ did indeed yield Ni(1) in the form of the 3-coordinate species Ni(6-Mes)(PPh₃)Br (3, Scheme 1).[†] The X-ray structure (Fig. 2)⁹ revealed a distorted trigonal planar geometry (sum of the bond angles 360.00°), in contrast to the T-shaped structure reported recently for the bis-carbene Ni(I) product $Ni(IPr)_2Cl$ (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2vlidene).¹⁰ The solution behaviour of **3** also differs from that of Ni(IPr)₂Cl, with no evidence of a monomer-dimer equilibrium involving either 6-Mes or PPh₃ dissociation. The ¹H NMR spectrum of 3 exhibited a series of broad, paramagnetically shifted resonances in the range +30 to -17 ppm, while we were unable to observe any signal at all for the PPh₃ ligand in the ³¹P{¹H} NMR spectrum. A solution magnetic moment (μ_{eff}) of 1.13 μ_{B} was measured in C₆D₆ (Evans method).

Well-characterised examples of Ni(1) species are rare¹¹ and, as a result, very little is known about their role in catalysis.^{10,12} We decided to target the hydrodehalogenation of aryl halides, which has been the subject of a number of reports using Ni/NHC combinations.¹³ Our initial findings on the activity of **3** for the hydrodehalogenation of disubstituted aryl halides are shown in Table 1. Thus, 1-bromo-4-fluorobenzene is completely reduced to fluorobenzene at room temperature within 30 min using NaOⁱPr as the hydrogen source

Fig. 2 Molecular structure of 3. Ellipsoids are shown at 30% probability with all hydrogen atoms removed for clarity. Selected bond lengths (Å) and angles (°): Ni(1)–C(1) 1.942(2), Ni(1)–P(1) 2.2187(6), Ni(1)–Br(1) 2.3332(3), C(1)–Ni(1)–P(1) 117.02(6), C(1)–Ni(1)–Br(1) 133.45(6), P(1)–Ni(1)–Br(1) 109.536(19).

Table 1 Hydrodehalogenation catalysed by 3⁺

	X $-$ F $\xrightarrow{4.5 \text{ mol} \% 3}{3 \text{ equiv. NaO}^{19}\text{r}}$ thf, RT or Δ	⟨ ¯ ⟩−F
Substrate	Product	% Conversion ^a (time/h)
p-BrC ₆ H ₄ F p-ClC ₆ H ₄ F C ₆ H ₅ F	$egin{array}{c} C_6H_5F\\ C_6H_5F\\ C_6H_6\end{array}$	> 99 $(0.5)^b$ 68 (4); 73 (48) ^b 18 $(22)^c$

^{*a*} Yields based on integrations of ¹⁹F NMR spectra relative to an internal standard of α, α, α -trifluorotoluene. ^{*b*} Reactions performed in thf at 25 °C with 4.5 mol% 3 and 3 equiv. of NaOⁱPr. ^{*c*} Reaction performed at 70 °C.

(NaOMe proved to be totally ineffective) in the presence of 4.5 mol% **3**. The Ni(1) complex also proved active for the reduction of 1-chloro-4-fluorobenzene to fluorobenzene at room temperature, although conversion was incomplete even after 48 h. When the reaction was repeated in the presence of 10 equivalents PPh₃, complete reduction was now achieved in the same period, suggesting that the phosphine helps to maintain the integrity of the catalyst. However, it also appears to hinder activity as a somewhat slower initial reaction rate (5% conversion after 1.5 h) was observed in comparison to the value found at the same time in the absence of PPh₃ (36%).

No hydrodefluorination was observed for either p-BrC₆H₄F or p-ClC₆H₄F. Moreover, we observed no reduction of fluorobenzene itself at room temperature. Under more forcing conditions (70 °C), we did achieve 18% conversion to benzene after 22 h, implying that **3** can bring about reduction of even the most unreactive of the carbon–halogen bonds.¹⁴

In summary, new Ni(II) and Ni(I) complexes incorporating ring-expanded N-heterocyclic carbene ligands have been prepared. The catalytic potential of the Ni(II) product, which contains a C-H activated NHC, is limited by a new decomposition pathway involving indole elimination. In contrast, the rare, three-coordinate Ni(I) species **3** proved to be a useful precursor for catalytic hydrodehalogenation. Further studies to investigate the potential of **3** in catalytic and stoichiometric transformations are ongoing.

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