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The synthesis of a di-*N*-heterocyclic carbene-amido complex of palladium(II)†

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A diimidazolium salt incorporating a secondary amine moiety has been used to prepare a palladium(II) di-*N*-heterocyclic carbene amino complex that can be deprotonated with NaH to give the first example of a transition metal NHC–amide.

Metal complexes of hybrid ligand sets derived from a mixture of electronically diverse donor atoms have been extensively investigated for their application to catalysis and activation of small molecules. Of the hybrid ligand sets known, phosphorus–nitrogen complexes possibly exhibit the most diverse range of reactivities. These include N_2 activation,[1] polymerizations[2] and various catalytic coupling reactions.[3]

N-Heterocyclic carbenes (NHC) have often been compared to tertiary phosphines and have come to prominence mainly because of their application to catalysis.[4] However there is also growing interest in using NHC as a basis for new ligand platforms that display unusual reactivity. Several hybrid ligand sets based on NHC have been prepared[5] including those of N-donors.[6] However a notable exception is that an NHC–amido complex has not been reported. We have recently been interested in developing the chemistry of NHC–amine ligands and an initial goal was to prepare an example of an NHC–amido complex. Here we wish to report the synthesis and characterisation of a di-NHC–secondary amino complex of palladium(II) and its transformation to the corresponding di-NHC amide.

Our initial target ligand set was based on a di-NHC secondary amine shown in Fig. 1, because it was envisaged that chelating NHC moieties would favour metal–nitrogen interaction.

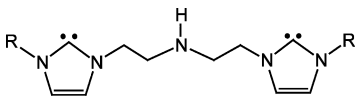


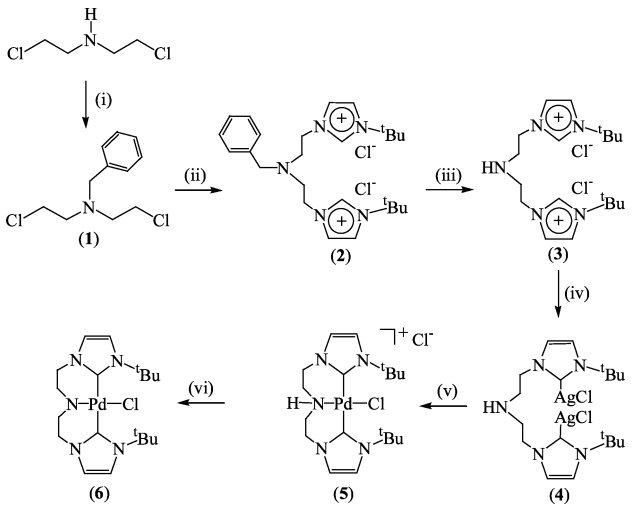
Fig. 1 Target ligand.

However preliminary experiments showed that preparation of the NHC-precursor diimidazolium salt from reaction between bis(2-dichloroethyl)amine and two equivalents of *tert*-butyl imidazole were largely thwarted by competitive oligomerisation of the amine. It was therefore found necessary to protect the secondary amine with a benzyl moiety giving the tertiary amine **1** as shown in Scheme 1.† Subsequent reaction between **1** and two equivalents of *tert*-butyl imidazole proceeded smoothly to give the diimidazolium tertiary amine salt ($^{t\mathrm{Bu}}$C(H)N(Bn)C(H)$^{t\mathrm{Bu}}$)2Cl$^-$ (**2**). Removal of the benzyl group could then be achieved by palladium catalysed hydrogenation to give the dimidazolium secondary amine salt ($^{t\mathrm{Bu}}$C(H)N(H)C(H)$^{t\mathrm{Bu}}$)2Cl$^-$ (**3**).

Silver(I) halide complexes of NHC have been shown to be useful as NHC ligand transfer agents to metals,[7] particularly palladium, and therefore we prepared ($^{t\mathrm{Bu}}$C(AgCl)N(H)C(AgCl)$^{t\mathrm{Bu}}$) **4** from reaction between **3** and Ag_2O in dichloromethane. Characteristic ^{1}H and ^{13}C NMR data for complex **4** include two triplet signals at δ 3.02 and 4.23 ppm for the CH_2 protons and in the ^{13}C NMR spectrum, a single NHC carbon signal at δ 178.0 ppm.

Reaction between **4** and $[PdCl_2(MeCN)_2]$ in dichloromethane at room temperature gives the sparingly soluble complex [($^{t\mathrm{Bu}}$CN(H)C$^{t\mathrm{Bu}}$) PdCl] Cl$^-$ (**5**). Crystals of complex **5**‡ suitable for an X-ray diffraction study were grown from dichloromethane and diethyl ether and the molecular structure of the cationic fragment is shown in Fig. 2.

The geometry at the palladium atom is square planar with the NHC moieties in a *trans* configuration. The proton H(3) is calculated but its existence is inferred from the presence of a chloride counter anion and the ^{1}H NMR spectrum (*vide infra*). In the solid state the cation of **5** is chiral by virtue of atropisomerism engendered by the 'S'-configuration of the CH_2 groups that link the amine and NHC nitrogen atoms. Related di-NHC complexes incorporating a bridging pyridine functionality exhibit similar



Scheme 1 i) BnBr, MeCN, 25 °C, 4 h; ii) *tert*-butyl imidazole, 1,4-dioxane, 120 °C, 18 h; iii) 10%Pd/C, 1 atm H_2, EtOH, 60 °C, 18 h; iv) Ag_2O, CH_2Cl_2, 25 °C, 18 h; v) $[PdCl_2(MeCN)_2]$, CH_2Cl_2, 25 °C, 1 h; NaH, CH_2Cl_2/THF, 25 °C, 24 h.

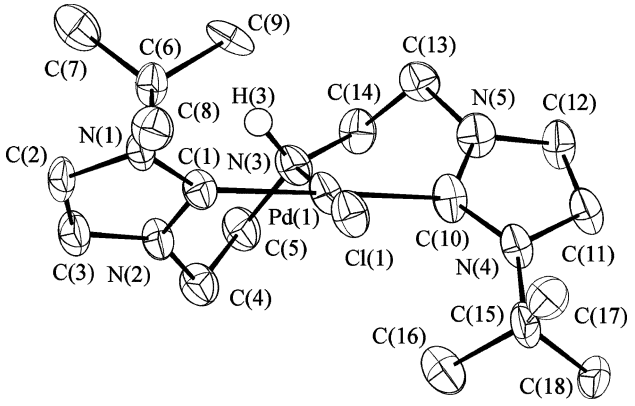


Fig. 2 Molecular structure of cation of **5**. Selected bond lengths (Å) and angles (°) Pd(1)–C(1) 2.057(15), Pd(1)–C(10) 2.087(15), Pd(1)–N(3) 2.058(12), Pd(1)–Cl(1) 2.341(4), C(1)–Pd(1)–C(10) 171.4(7), Cl(1)–Pd(1)–N(3) 173.4(4), C(1)–Pd(1)–N(3) 82.1(5), C(10)–Pd(1)–N(3) 89.7(6).

† Electronic supplementary information (ESI) available: synthesis and characterising data of compounds **1–6**. See http://www.rsc.org/suppdata/cc/b3/b314814a/

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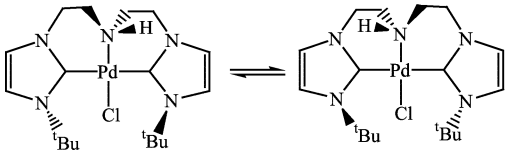
structures and have been shown to undergo atropisomerisation, interconverting between C_2 symmetric enantiomers.[8] In contrast the presence of H(3) renders the cationic fragment of **5** C_1 symmetric and this is reflected in the low temperature ^{1}H NMR spectrum. At 25 °C the only clearly discernable signals in the ^{1}H NMR spectrum are a single signal at δ 1.95 ppm attributable to the two ^{t}Bu groups, two signals at δ 7.02 and 7.09 ppm for the four NHC protons and a single broad signal at δ 8.50 ppm corresponding to the proton of the amine group. The protons of the CH_2 groups are broadened into the baseline of the spectrum. These observations are attributed to interconversion of the atropisomers *via* a 'H-windscreen wiper' motion as shown in eqn. (1) at a rate commensurate with the NMR timescale. On cooling to −40 °C the rate of interconversion is sufficiently slow to distinguish a complex set of 8 resolved signals for the CH_2 protons in addition to signals attributable to two ^{t}Bu, four NHC and an amine proton.



(1)

Reaction between **5** and various bases was then investigated in an attempt to prepare the corresponding di-NHC amido complex [($^{t\mathrm{Bu}}$CNC$^{t\mathrm{Bu}}$)PdCl] (**6**). We found that NEt_3 and Py gave no apparent reaction even on heating and KO^{t}Bu lead to decomposition. However in a mixture of THF and CH_2Cl_2 reaction between **5** and NaH gave **6** in 61% yield.‡ In contrast to **5**, compound **6** is readily soluble in aromatic and ether solvents, consistent with an uncharged molecule. Over the range 25 to −40 °C the ^{1}H NMR spectra of **6** differs significantly from **5** displaying signals consistent with atropisomerisation of a C_2 symmetric compound. At all temperatures a single ^{t}Bu resonance and two NHC protons are observed. The CH_2 protons appear as four very broad peaks at 25 °C resolving to four complex multiplets at −40 °C that do not change on further cooling and the resonance at δ 8.50 ppm attributed to the amine proton of **5** is absent. In addition the IR spectrum of **5** shows a stretch at 3152 cm^{-1} consistent with an N–H vibration, which is absent for **6**. Elemental analysis also confirmed the bulk composition. Unfortunately to date growth of a single crystal of **6** suitable for an X-ray diffraction study has not been successful.

Line shape analysis of the variable temperature ^{1}H NMR spectra over the range 25 to −40 °C allowed estimates of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for atropisomerisation of **5** and **6** and the data are shown in Table 1. Given the errors in $\Delta S^{\ddagger}$ the only meaningful conclusion is that the mechanism of interconversion between atropisomers for **5** and **6** is likely to be similar. Within the errors $\Delta H^{\ddagger}$ for **5** and **6** are lower than that obtained for a di-NHC pyridine complex[8b] in $CDCl_3$ (51.6 (1.9) kJ mol^{-1}) but are similar to those observed for the ring inversion of *N*,*N*,*N*′,*N*′-tetramethylpiperazinium dichloride (37.6 (5.0) kJ mol^{-1}).[9] For **5** and **6** the data are consistent with a mechanism where the nitrogen donor atom remains coordinated to the palladium atom as shown in eqn. (1) and also that the counter anion does not play a significant role in the interconversion mechanism.[8c]

Table 1 Thermodynamic parameters for atropisomerism of **5** and **6**

	5	**6**
$\Delta G^{\ddagger}$ (kJ mol^{-1})[a]	57.44 (0.37)	54.8 (0.41)
$\Delta H^{\ddagger}$ (kJ mol^{-1})	32.5 (4.9)	39.0 (5.4)
$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	−88 (18)	−56 (10)

[a] at 281 K.

In conclusion we have prepared the first example of a NHC–secondary amine complex and its corresponding amide by deprotonation of the metal coordinated amine. We are currently investigating the coordination chemistry of **2** and **3** and the synthesis of s-block amido–NHC complexes for ligand transfer to transition metals.

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Notes and references

‡ *Crystal data* for **5**: $C_{18}H_{31}Cl_2N_5Pd$, M = 494.78, monoclinic, space group $P2_1/c$, a = 12.5628(15), b = 10.3135(15), c = 17.2307(18) Å, β = 92.159(7)° U = 2230.9(5), Z = 4, D = 1.473 g cm^{-3}, T = 273(2), μ (Mo–K$_\alpha$) = 8.998 mm^{-1}, 4802 reflections measured, 1407 [R(int) = 0.1059] independent reflections, $wR(F^2_{\text{all data}})$ = 0.1820 and R ($F > 2\sigma(F)$) = 0.0905. CCDC 225003. See http://www.rsc.org/suppdata/cc/b3/b314814a/ for crystallographic data in .cif or other electronic format.

Synthesis and spectroscopic data for **6**: To a dichloromethane solution (10 ml) of **5** (62 mg, 0.125 mmol) was added a THF solution (5 mL) of sodium hydride (30 mg, 1.25 mmol) and the mixture stirred for 24 h at 25 °C. The volatiles were removed under reduced pressure and the resulting yellow solid extracted with toluene (2 × 20 ml). The volatiles were removed to give **6** as a pale yellow solid (Yield = 35 mg, 61%). ^{1}H NMR (300 MHz, CD_2Cl_2, −40 °C): 1.98 (18H, s, CH_3), 3.54 (2H, m, CH_2CH_2), 3.90 (2H, m, CH_2CH_2), 4.63 (2H, m, CH_2CH_2), 5.32 (2H, m, CH_2CH_2), 6.88 (2H, d, $^3J_{\mathrm{H-H}}$ = 2.59, C*H*=CH), 6.95 (2H, d, $^3J_{\mathrm{H-H}}$ = 2.59, CH=C*H*); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, 25 °C) 32.0 (CH_3), 58.4 ($C(CH_3)_3$), 58.5 (CH_2CH_2), 59.9 (CH_2CH_2), 118.1 (CH=*C*H), 119.8 (CH=*C*H), 120.8 (*C*H=CH), 122.5 (*C*H=CH), 165.7 (*C*Pd); MS (TOF ES$^+$) m/z 422 (100, [M − Cl]$^+$) ; Anal. [found (calc.)] for $C_{18}H_{30}N_5PdCl$: C 46.97 (47.17), H, 6.60 (6.40) N 15.00 (15.28)%.

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