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# Experimental and computational study of a reductive elimination mechanism in a methyl–Pd(II)–CNC carbene complex

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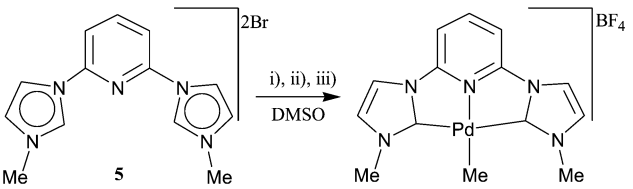
**Experimental and density functional studies on the decomposition of a novel palladium–methyl complex of the rigid CNC ligand 2,6-bis(1-alkylimidazolin-2-yliden-3-yl)pyridine show that reductive elimination to give 2-methylimidazolium species is a facile reaction.**

Isolation of stable nucleophilic heterocyclic carbenes by Arduengo *et al.*[1] provoked much interest in the use of these species as ligands for both main group and transition metals and comparisons were made with the ubiquitous phosphine ligands. Complexes of N-heterocyclic carbenes (NHC's) were found to outperform traditional phosphine-ligated systems in a number of transition metal catalysed reactions.[2–5] However, we observed that reductive elimination of 2-organylimidazolium salts from Ni(II) and Pd(II) NHC complexes can be a facile reaction, and the process represents a potentially important route to catalyst deactivation.[6,7] Subsequent experimental and theoretical evidence suggested that chelation may lessen the tendency towards decomposition. Consistent with this idea, decomposition by reductive elimination was not observed in Pd–hydrocarbyl complexes with chelating bis-NHC ligands.[8]

The inclusion of heteroatom functionality with NHC ligands, in particular pyridyl functionalised NHC's, has furnished extremely active and ostensibly stable catalysts for C–C coupling and amination reactions.[9–13] Significantly, under catalytic conditions, complex **1** shows long-term stability at temperatures above those traditionally used for the Heck reaction, and exhibits excellent catalytic activities and selectivities at low catalyst loadings.[11] Similarly, the Pd(II) complexes **2**[14] and **3** containing the related, but rigid tridentate (CNC) ligand have been shown to exhibit high activity in Heck coupling and to retain catalytic activity in air at 184 °C.[15]

However, the important Pd–hydrocarbyl complexes, of type **4**, which are of interest as a potentially convenient entry point to various catalytic cycles and as model compounds for the study of catalytic processes, have not previously been reported. Therefore, we have undertaken the synthesis of **4**, which was achieved in moderate yield by the sequential one-pot reaction of functionalised bis-imidazolium salt **5**, $Ag_2O$, $AgBF_4$ and PdClMe(cod) (Scheme 1).[11]† The $^1$H NMR and $^{13}$C NMR spectra of **4** in $d_6$-DMSO show the PdMe group signal at $\delta$ 0.32 in the proton NMR and at $\delta$ −13.29 in the $^{13}$C NMR spectrum, values that are slightly upfield and downfield, respectively, from the corresponding signals in **1**. The $_{im}C_2$ signal is at $\delta$ 174.65. The structure of **4** was established unequivocally by a single-crystal X-ray study‡ (Fig. 1), and shows the cation of **4** to be closely planar with the rigid ligand preventing puckering




**Scheme 1** Synthesis of **4**. *Reagents and conditions*: i) $Ag_2O$, ii) $AgBF_4$, iii) PdClMe(cod).

of the molecule about the $C_{Me}$–Pd–N axis.[13] As a result the C(22)–Pd–C(22′) angle, 156.6(2)°, is significantly distorted from an ideal square planar geometry about Pd. Pd–C(0) in **4** is 2.094(5) Å, increased from 2.044(1) Å in **1** due likely to the tight chelate; this is also evidenced by the decrease in Pd–N(1) to 2.021(4) Å in **4** from 2.1536(9) Å in **1**. However, Pd–N(1) is longer in **4,** 2.021(4) Å, than the 1.979(4) Å in **2**, reflecting the increased trans effect of the Me group compared to bromide.

Good solubility in highly polar organic solvents (*e.g.* DMSO, DMAc) enabled the decomposition of **4** to be followed by NMR. A $d_6$-DMSO solution of **4** maintained at 140 °C showed near complete loss of the PdMe signal within 6 h with formation of some Pd black. [Note: At this temperature the decomposition of **6**, the N$^t$Bu analogue of **1**, was too fast to be measured, with rapid deposition to Pd black. **1** requires up to 18 h at 150 °C for complete loss of the PdMe peak[11]]. Interestingly, attempts to prepare complex **7**, the N$^t$Bu analogue of **4**, were unsuccessful. Reaction of the Ag–NHC complex with PdClMe(cod) at room temperature gave only the reductive elimination product 2,6-bis(2-methyl-3-*tert*-butylimidazolium-1-yl)pyridine ditetrafluoroborate. The observed relative stabilities of the complexes **1**, **4** and **6** are in agreement with DFT calculations§ which suggest that the rigid planarity of complex **4** increases the

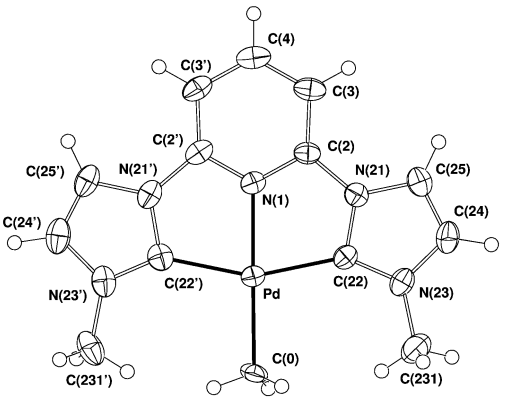
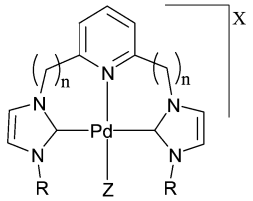



**Fig. 1** Projection of the closely planar $[PdMe(_{Me}CNC)]^+$ cation normal to its plane, showing 50% displacement ellipsoids for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. C(22)–Pd–C(22′) is 156.6(2)°, Pd–N(1),C(22,22′,0) are 2.021(4), 2.036(5), 2.041(5), 2.094(5) Å, inversion related cations stacking up the *a* direction in the lattice.




**1**: n = 1, R = Z = Me, X = $BF_4$
**2**: n = 0, R = Me, X = Z = Br
**3**: n = 0, R = $^n$Bu, X = Z = Br
**4**: n = 0, R = Z = Me, X = $BF_4$
**6**: n = 1, R = $^t$Bu, Z = Me, X = $BF_4$
**7**: n = 0, R = $^t$Bu, Z = Me, X = $BF_4$

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barrier to the reductive elimination process by 39 kJ mol$^{-1}$ when compared to **1**, and 60 kJ mol$^{-1}$ when compared to **6** (Fig. 2). However, excessive steric bulk can increase the propensity to reductive elimination, *vis-à-vis* **6** and **7**. Previous studies have suggested that methyl–NHC reductive coupling in **1** initially leads to a mono-NHC–Pd$^0$ complex with a pendant 2,3-dimethylimidazolium-1-yl group.[11] Experimental and theoretical evidence reported herein indicate that a similar route may be followed during the decomposition of **4**. A $^1$H NMR signal at $\delta$ 2.77 was observed in a $d_6$-DMSO solution of **4** within the first 10 min at 140 °C. Subsequently, several additional signals in the region $\delta$ 2.6–2.8 also became evident, indicating a mixture of products derived from the coupling of NHC and PdMe groups (*eg. cis* and *trans* isomers, and bridged species).¶ In the case of **4**, further decomposition of the mono-NHC–Pd$^0$ complex **V** with a pendant 2,3-dimethylimidazolium-1-yl group would generate Pd$^0$ and the free carbene 2,3-dimethyl-1-[6-(3-methylimidazol-2-ylidene)pyridin-2-yl]imidazolium tetrafluoroborate, however removal of Pd$^0$ from the encounter complex **III** (Fig. 2, R = Me, $n$ = 0) is calculated to require an additional energy input of 156 kJ mol$^{-1}$. The magnitude of this energy barrier suggests that further decomposition to give Pd$^0$ and the free carbene is less favoured. Thus a mono-NHC–Pd$^0$ complex of type **V** as shown in Fig. 2 may be a relatively stable intermediate in the decomposition process, particularly if additional stabilisation results from solvation of the metal centre. The nature of the final step, leading to complete loss of ligand is unclear at this stage.

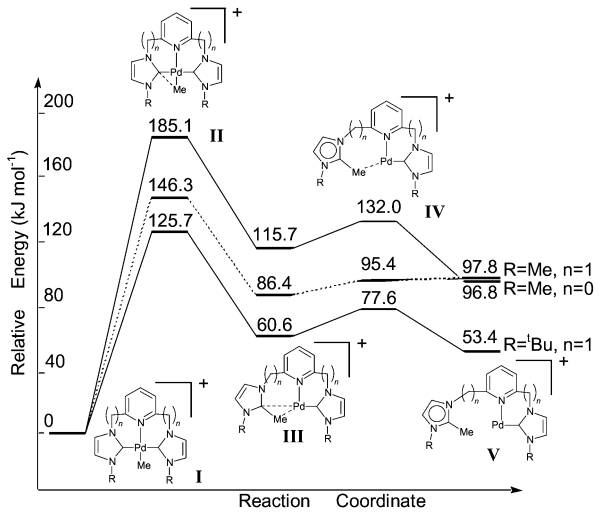


**Fig. 2** Potential energy profile for the reductive elimination of a 2-methylimidazolium-1-yl group from complexes **4** (top, unbroken line), **1** (broken line) and **6** (bottom, unbroken line).

Significantly, it may be noted that the barrier to reductive elimination in each system (185.1, 146.3 and 125.7 kJ mol$^{-1}$) appears to be linked to the out-of-plane carbene twist angles (calculated as 1, 41 and 50°) in complexes **4**, **1** and **6**, respectively. However, the relative stabilities of these complexes are governed by a number of interdependent factors both steric and electronic.

The decomposition behaviour of these systems appears to be influenced by the reaction conditions. At high temperatures and in the presence of excess substrate the catalytic process (migratory insertion and product elimination) is preferred over the reductive elimination (decomposition) pathway.[16] However, under stoichiometric reaction conditions, or when substrate in a catalytic reaction are consumed, or if attempts are made to recycle the catalyst, decomposition by reductive elimination can be rapid.

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## Notes and references

† *Synthesis* of [PdMe($_{Me}$CNC)]BF$_4$ ($_{Me}$CNC = *C,N,C′*-2,6-bis(3-methylimidazolin-2-yliden-1-yl)pyridine) (**4**): prepared from **5** (0.2270 g, 0.566 mmol), $Ag_2O$ (0.1311 g, 0.566 mmol), $AgBF_4$ (0.110 g, 0.566 mmol) and PdClMe(cod) (0.150 g, 0.566 mmol) in DMSO (10 mL), followed by filtration and addition of MeOH to precipitate the product (0.125 g, 49%). X-Ray quality colourless needles were obtained by vapour diffusion of $Et_2O$ into a DMSO/MeCN solution of **4**. Required for $C_{14}H_{16}N_5PdBF_4$: C, 37.57; H, 3.60; N, 15.65. Found: C, 37.52; H, 3.90; N, 15.71%. MS (ES): *m*/*z* 362.2 [M − BF$_4$]$^+$ (100%). $\delta_H$ (399.70 MHz, DMSO-$d_6$): 8.16 (t, *J* 8.0 Hz, 1H, $_{pyr}$C$_4$H), 8.06, 7.41 (2 × d, *J* 2.4 Hz, each 2H, $_{im}$C$_{4,5}$H), 7.57 (d, *J* 8.0 Hz, 2H, $_{pyr}$C$_{3,5}$H), 3.57 (s, 6H, NMe), 0.32 (s, 3H, PdMe). $\delta_C$ (100.51 MHz, DMSO-$d_6$): 174.65 ($_{im}$C$_2$), 148.04 ($_{pyr}$C$_{2,6}$), 144.56 ($_{pyr}$C$_4$), 125.00, 117.30, 107.66 ($_{im}$C$_{4,5}$ and $_{pyr}$C$_{3,5}$), 36.88 (NMe), −13.29 (PdMe).

‡ *Crystal data* for [PdMe($_{Me}$CNC)](BF$_4$) ≡ $C_{14}H_{16}BF_4N_5Pd$: $M$ = 447.5, monoclinic, $P2_1/c$, $a$ = 7.5226(6), $b$ = 20.093(2), $c$ = 11.0576(9) Å, $\beta$ = 104.141(2)°, $V$ = 1621 Å$^3$, $D_c$ ($Z$ = 4) = 1.83$_4$ g cm$^{-3}$. A full sphere of absorption-corrected CCD diffractometer data, 28189 reflections (*T ca.* 153 K; Bruker AXS instrument; monochromatic Mo-K$\alpha$ radiation, $\lambda$ = 0.7107$_3$ Å; $2\theta_{max}$ = 58°), merged to 4309 unique ($R_{int}$ = 0.045), 3781 with $F > 4\sigma(F)$ refining to conventional $R$, $R_w$ (weights: $(\sigma^2(F) + 0.0004F^2)^{-1}$) on $|F|$ 0.048, 0.076. CCDC reference number 190254. See http://www.rsc.org/suppdata/cc/b2/b207020k/ for crystallographic data in CIF format.

§ *Computational details*: B3LYP calculations were performed using the Gaussian 98 (Rev. A.9) suite of programs.[17] Full geometry optimisations employed the LANL2DZ basis set on palladium together with the 6-31G(d) basis set on other atoms. Harmonic vibrational frequencies were then calculated at the B3LYP level. Unscaled zero point vibrational energies and thermodynamic corrections were thus obtained. Single point energies for optimised geometries were calculated at the B3LYP/LANL2-augmented:6-311+G(2d,p) level.[18] Results are reported at this level with inclusion of thermodynamic corrections.

¶ 2,6-Bis(2,3-dimethylimidazolium-1-yl)pyridine, a possible reductive coupling product resulting from the decomposition of **4**, was synthesised as the dibromide salt and showed the characteristic signal of the $_{im}$C$_2$Me group at $\delta$ 2.80 in the $^1$H NMR, and $\delta$ 11.49 in the $^{13}$C NMR.


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