

# Migratory insertion in N-heterocyclic carbene complexes of palladium; an experimental and DFT study†

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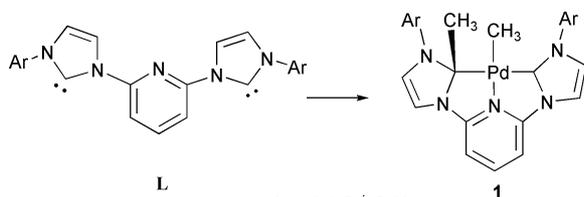
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**The first authenticated example of migration of a methyl group from palladium(II) to a coordinated N-heterocyclic carbene is described.**

The recent interest in the organometallic chemistry of coordinated N-heterocyclic carbenes (NHCs) originates from the remarkable activity of certain NHC complexes in catalytic reactions, especially C–C bond formation and metathesis.<sup>1</sup> Throughout the catalytic cycle the coordinated NHC is considered as the ideal spectator ligand, *i.e.* strongly bound to the metal, inert and not susceptible to any external attack by nucleophiles, electrophiles or participating in rearrangements at the metal coordination sphere. Experimental and theoretical studies have established that NHCs bind to Pd and Pt by  $\sigma$  donation; back-donation from the metal is minimal, thus the electronic properties of NHCs are comparable to trialkylphosphines.<sup>2</sup> Although catalytic studies with NHC complexes are now numerous, there are only a few attempts to understand the chemistry operating at the molecular level, for example by observation or isolation of reactive intermediates, labelling and product distribution studies *etc.* Recent reports are questioning the belief that the NHC–metal bond is inert. The substitution of a coordinated carbene by trialkylphosphines has been observed.<sup>3</sup> Reductive elimination of alkylimidazolium salts from NHC alkyl complexes by a concerted mechanism has also been studied experimentally and by theoretical methods in simple palladium model systems.<sup>4</sup> The microscopic reverse *i.e.* oxidative addition of imidazolium salts to NHC complexes has also been reported and used synthetically.<sup>5</sup> Insertions of NHCs into metal–alkyl bonds has not yet been observed directly, although recently insertion of an alkene into an Rh–NHC bond has been postulated as an elementary step in the catalytic intramolecular coupling of an alkene with benzimidazole.<sup>6</sup> In comparison, the isocyanide ligands, which are isoelectronic to NHCs, exhibit a rich insertion chemistry.<sup>7</sup> Herein, we report the first authenticated example of methyl migration from a Pd(II) centre to the carbene carbon of a NHC ligand.

Reaction of the ‘pincer’ bis-NHC, **L**,<sup>8</sup> with (tmed)Pd(CH<sub>3</sub>)<sub>2</sub> (tmed = *N,N,N',N'*-tetramethylethylenediamine)<sup>9</sup> at –78 °C in thf or toluene gave, after warming to room temperature, **1** as the only new, carbene containing product (by NMR) which can be isolated in 60–70% yield after repeated crystallisation from ether (Scheme 1).‡



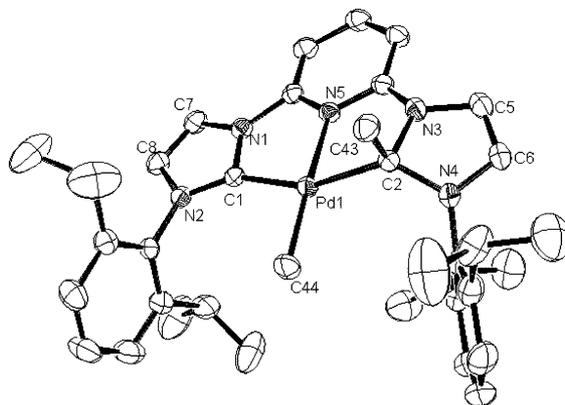
† Electronic supplementary information (ESI) available: experimental; structural data for **1**; computational data. See <http://www.rsc.org/suppdata/cc/b2/b212453j>

Compound **1** was characterized by spectroscopic methods. The <sup>1</sup>H NMR spectrum is consistent with the absence of any symmetry element in the molecule, featuring eight doublets and four septets, assignable to the diastereotopic isopropyl groups. The methyl protons on the palladium and the imidazolide groups are found at  $\delta$  –0.45 and 2.30, respectively.

The structure of **1** in the solid state was determined by single crystal X-ray diffraction. A diagram of the molecule is given in Fig. 1.‡ The metal centre is square planar; the coordination sphere comprises one pyridine nitrogen and three different types of carbon atoms.

Attempts to elucidate the reaction mechanism by detection of reaction intermediates preceding the formation of **1**, especially by <sup>1</sup>H NMR at low temperatures, were unsuccessful. Therefore, we decided to investigate plausible mechanistic models with the aid of density functional calculations. To save computational time the bulky aryl groups on the carbene functionalities were replaced by H atoms. All stationary points found were checked to see whether steric interaction by the replaced aryl groups would destabilise them, but this was not the case.

A plausible first step in the reaction is the replacement of the tmed by bidentate coordination of the ‘pincer’ ligand through a carbene carbon and the pyridine nitrogen. A search was carried out for possible intermediates of this type. An intermediate, **A**, was found in which the uncoordinated carbene was oriented so that one of its backbone hydrogens lay 2.67 Å from the Pd. Such hydrogens are acidic in character so there is the possibility of attraction between the positive H and the electron density associated with the Pd perpendicular to the coordination plane. When the uncoordinated carbene was rotated significantly from this position a second five coordinate intermediate, **B**, was characterized. All three functionalities of the pincer ligand were



**Fig. 1** ORTEP diagram of **1** showing 30% probability ellipsoids. A molecule of solvent (ether) as well as hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–C(1) 2.067(3), Pd(1)–C(2) 2.085(3), Pd(1)–C(44) 2.046(3), Pd(1)–N(5) 2.029(2), C(1)–N(2) 1.352(4), C(1)–N(1) 1.384(3), C(2)–N(3) 1.525(4), C(2)–N(4) 1.493(4), C(5)–C(6) 1.322(5), C(7)–C(8) 1.323(4); C(1)–Pd(1)–N(5) 77.79(10), C(1)–Pd(1)–C(44) 103.76(12), C(2)–Pd(1)–C(44) 97.59(12), C(2)–Pd(1)–N(5) 80.95(10), N(4)–C(2)–N(3) 98.49(2), Pd(1)–C(2)–C(43) 105.08(19).

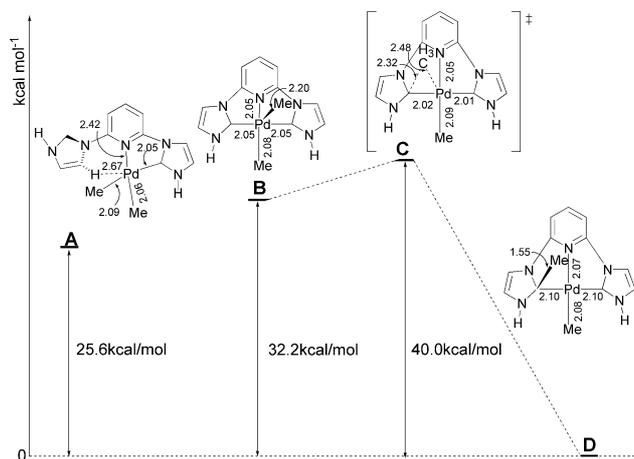
coordinated; one methyl group lay in the plane of the ligand and the other had moved to an axial position. This intermediate had  $C_s$  symmetry. Geometry optimisation<sup>10</sup> of the product analogue, **D**, gave a structure with distances and angles in good agreement with the experimental data. A search for a saddle point lying between **B** and **D** resulted in the transition state, **C**, which had one imaginary frequency of  $-289i$   $\text{cm}^{-1}$ . The imaginary vibration corresponds to motion of the methyl group between the Pd and the coordinated carbene. It also involves pyramidalisation of the adjacent nitrogens.

Energies of **A**, **B**, **C** and **D**, relative to the product **D**, are given in Fig. 2. Transfer of the Me from the Pd to the carbene carbon is strongly exothermic, 32.2  $\text{kcal mol}^{-1}$ , and the activation energy for this step is low, 7.8  $\text{kcal mol}^{-1}$ . The Mulliken charges of the methyl carbons are given in Fig. 2. The axial methyl carries a positive charge in intermediate **B** and becomes more positive on migration and formation of the product.

These studies demonstrate that formation of a five coordinate intermediate followed by migratory insertion is a realistic mechanism for the formation of **1**. It thus provides an interesting contrast with the reductive elimination proposed by Cavell *et al.* in cationic palladium pincer complexes which resulted in the formation of Pd(0) pyridine carbene species after concerted reductive elimination of 2-methylimidazolium groups.<sup>11</sup> The involvement of the high energy five coordinate intermediate in combination with the presence of the rigid chelating ligand inhibiting dissociation of the imidazolium group may account for the different behaviour observed here. The data shown here suggest that migratory insertion pathways should be considered in the formation of imidazolium products from N-heterocyclic carbenes.

It is also noteworthy that **1** can undergo further reactions including  $\beta$ -hydrogen elimination and reductive elimination of either the imidazolidine and methyl, or concerted NHC and methyl groups, giving rise to alkane or imidazolium salts, respectively. In fact, heating of a solution of **1** at 60 °C in  $C_6D_6$  results in the formation of a complex reaction mixture, in which 2-H imidazolium protons can be observed. The isolation and full characterisation of all products formed in this case is under way.

In summary, our experimental data and theoretical calculations provide strong support for facile migratory insertion reactions, which have not been observed before in N-heterocyclic carbene complexes. Consideration of this step in *in situ* formed catalytic systems could give rise to alternative mechanistic models, where NHCs are not acting as spectators.



**Fig. 2** Calculated reaction coordinate diagram for the migration reaction. The Mulliken charges of the in-plane and migrating carbons in the intermediates are as follows: **A**,  $-0.08$ ,  $-0.04$ ; **B**,  $0.02$ ,  $0.13$ ; **C**,  $-0.09$ ,  $0.31$ ; **D**,  $-0.09$ ,  $0.31$ .

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## Notes and references

† Preparation and spectroscopic data for **1**: To a cold ( $-78$  °C) solution of  $(\text{tmed})\text{PdMe}_2$  in thf (0.1 g, 0.4 mmol in 30  $\text{cm}^3$ ) was added by cannula a solution of carbene **L** (0.26 g, 0.5 mmol) in the same solvent (30  $\text{cm}^3$ ). The orange reaction mixture was allowed to reach room temperature and was stirred for 16 h. Evaporation of the volatiles under reduced pressure, washing of the residue with cold petroleum ( $3 \times 30$   $\text{cm}^3$ ), extraction into ether (50  $\text{cm}^3$ ), filtration, concentration and cooling of the ether extracts gave crude **1** which was contaminated by  $\text{Pd}(\text{tmed})\text{Me}_2$ . Repeated recrystallisations from ether gave the analytically and spectroscopically pure product as an orange crystalline material. Yield 60–70%. Found: C, 64.52, H, 7.50, N, 9.32. Calculated for  $C_{37}H_{47}N_5\text{Pd}\cdot C_4H_9O$ : C, 65.30, H, 7.87, N, 9.76%.  $^1\text{H NMR}$   $\delta(C_6D_6)$ :  $-0.45$ (s, 3H, Pd- $\text{CH}_3$ ), 1.05, 1.08, 1.22, 1.24, 1.32, 1.35, 1.45, 1.48 [doublets, total 24H,  $\text{CH}(\text{CH}_3)_2$ ], 2.30 [s, 3H,  $\text{NC}(\text{CH}_3)\text{N}$ ], 2.72, 2.85, 3.48, 4.38 [septets, 4H,  $\text{CH}(\text{CH}_3)_2$ ], 5.65 and 6.20 (doublets, 1H each, imidazolyl  $\text{CH}=\text{CH}$ ), 5.95 and 6.50 (doublets, 1H each, imidazol-2-ylidene  $\text{CH}=\text{CH}$ ), 7.05–7.40 (m, 9H, other aromatic protons).

§ Crystal data for **1**:  $C_{41}H_{57}N_5\text{OPd}$ ,  $M = 742.32$  g  $\text{mol}^{-1}$ , orange crystal, dimensions  $0.07 \times 0.04 \times 0.03$  mm, monoclinic  $P2(1)/n$  (no.14),  $a = 8.65920(10)$ ,  $b = 21.2788(3)$ ,  $c = 21.3929(4)$  Å,  $\beta = 93.5780(10)^\circ$ ,  $V = 3934.12(10)$  Å<sup>3</sup>,  $T = 150$  K,  $Z = 4$ ,  $\rho = 1.253$   $\text{mg m}^{-3}$ ,  $\mu(\text{Mo-K}\alpha) = 0.508$   $\text{mm}^{-1}$ ,  $\lambda = 0.71073$  Å, 44801 reflections measured, 8719 unique ( $R_{\text{int}} = 0.0968$ ) which were used in all calculations. The final  $wR2$  was 0.1004 (all data) and  $R1 = 0.0434$  [ $I > 2\sigma(I)$ ]. CCDC 200426. See <http://www.rsc.org/suppdata/cc/b2/b212453j/> for crystallographic data in CIF or other electronic format.

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