Communication

N-heterocyclic carbenes: Reaction to give anilines

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Abstract

The attempted synthesis of bis(NHC)palladium complexes via the direct reaction of an imidazolium salt with palladium acetate results in the formation of a mixed NHC/aniline complex. The route by which the aniline is formed has not been completely elucidated, but it does originally derive from an imidazolium salt.
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1. Introduction

The nitrogen stabilised heterocyclic carbene (NHC) ligand has, in the past five years, progressed from being an academic curiosity to its present ubiquitousness: it is now considered as a versatile ligand that is often used in preference to the more usual phosphine [1]. Electronically, the NHC ligand is usually considered to be a better σ donor, and a weaker π acceptor, than the phosphine ligand, though evidence is not always clear cut [2]. Synthetic procedures leading to precursor imidazolium salts have been elucidated [3], and many routes that allow the introduction of an NHC ligand to a metal centre have been developed. The reaction of imidazolium salts with silver oxide giving an NHC complex of silver, which serves as a useful trans-metallating reagent, has proved particularly popular [4,5], though increasingly direct reaction of the imidazolium salt with the metal has been utilised [6]. More recently, NHC ligands have been shown not to be innocent spectators, but reactive intermediates themselves, with a number of new products being formed [7].

In the course of our research into platinum [8–10] and palladium [11–15] complexes, we sought to synthesise some NHC complexes of palladium via the direct reaction of an imidazolium chloride salt with palladium acetate. In the process we discovered a new reactivity of the NHC ligand, which we report here.

2. Results and discussion

Direct reaction of 2 equiv. of imidazolium salt **1** with palladium acetate under mild conditions results in the high yield of complex **2**. Complex **2** has a palladium atom to which is coordinated both the expected NHC ligand and an unexpected aniline, Scheme 1. Solution NMR provides strong evidence for the proposed structure (two signals in the ^{19}F NMR, in the ratio 2:1; the ^{1}H NMR containing two different types of phenyl ring, also in the ratio 2:1, a single signal for the NHC ring and a broad singlet at 4.27 ppm). This was also confirmed by a single crystal X-ray diffraction study.

A search of the Cambridge Crystallographic Database [16] shows no instances of metal complexes containing both an NHC and an aniline ligand, and a search of the chemical literature throws up no examples of anilines being generated in a similar fashion. The reaction conditions are not extreme, but still the product we obtained is unprecedented. This suggests that either we are doing something unique or, more likely, this type of reactivity has just not been recognised as such to date. Certainly we have observed this type of reactivity with other imidazolium salts (e.g., 1-methyl-3-(4-fluorophenyl)imidazolium chlo-

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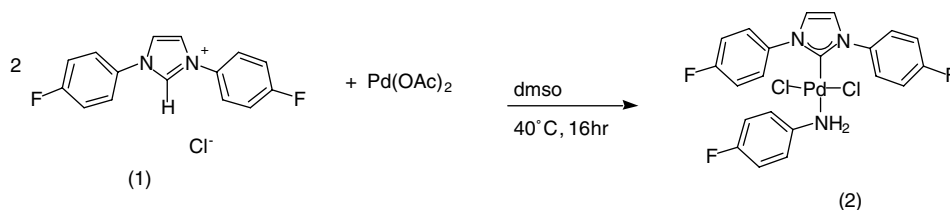
Scheme 1.

ride and 1-benzyl-3-(4-fluorophenyl)imidazolium chloride) palladium acetate, but the products have proved difficult to isolate in a pure form. In this communication we can do little other than speculate as to how complex **2** is formed, as further reactivity studies are underway.

The possibility that the aniline does not derive from the imidazolium salt, but comes from impurities in the imidazolium salt can be discounted on the grounds that the imidazolium salt was recrystallised to high purity, and no contamination could be detected via standard techniques (NMR, MS). The possibility of aniline being generated from the hydrolysis of the imidazolium salt can be discounted on the grounds that both starting materials and the solvent were anhydrous, and the reaction proceeded under an inert atmosphere. Thus there are three possible routes into the generation of the aniline from the imidazolium/NHC: an NHC coordinated to palladium reacts to give the aniline, a non-coordinated imidazolium salt reacts to give an aniline which then coordinates or, in the process of reacting with the palladium, the imidazolium salt reacts to give the aniline. The first two routes can be discounted on the grounds that we do not observe any similar reaction with a bis(NHC)palladium compound or of an uncoordinated imidazolium salt under such mild conditions. In addition, we can find no reports of similar behaviour in

the literature. Thus the formal oxidative addition reaction of the imidazolium with the palladium acetate would appear to be the likely source of the aniline. Two possibilities now arise: either an initial molecule of imidazolium salt reacts to give a mono(NHC)palladium species, which then reacts to generate the aniline or, the palladium acetate (or its DMSO adduct) reacts directly with a molecule of imidazolium salt to give an aniline complex which subsequently reacts with another molecule of imidazolium salt to give the observed complex. Implicit in this discussion is a recognition that the palladium starting material and the intermediates react differently with the imidazolium salts with a two step reaction process. Such behaviour has recently been documented to occur with bis(imidazolium) salts and rhodium and iridium precursors [17]. Of relevance to this issue is the question of quite what happens to the rest of the imidazolium salt that liberates the aniline. Unfortunately this is not clear as it proved impossible to identify any by-products from the reaction mixture. Potentially 1 equiv. of imidazolium could generate 2 equiv. of aniline, thus requiring only 1.5 equiv. of imidazolium per palladium for a 100% yield of the mixed NHC/aniline palladium compound. However this argument neglects the need for 2 equiv. of chloride to generate compounds such as **2**. Attempts to perform the reaction with only 1.5 equiv.
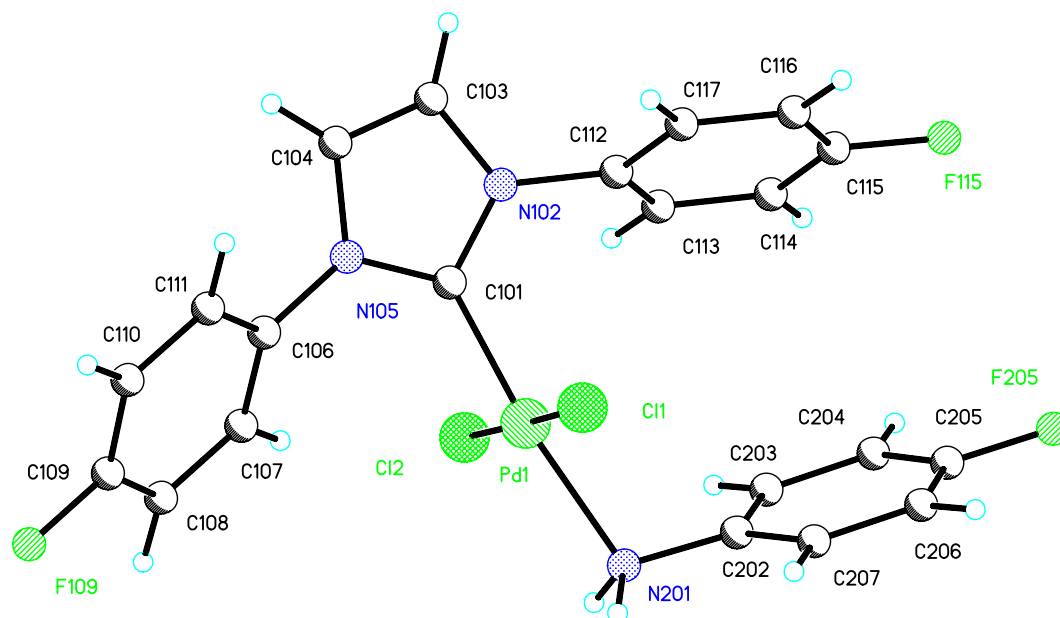

Fig. 1. The X-ray structure of **2**.

Table 1
Selected bond lengths (Å) and angles (°) for **2**

Pd(1)–C(101)	1.964(3)
Pd(1)–N(201)	2.118(2)
Pd(1)–Cl(1)	2.3008(7)
Pd(1)–Cl(2)	2.3114(7)
C(101)–N(102)	1.350(3)
C(101)–N(105)	1.355(3)
N(102)–C(103)	1.382(4)
N(102)–C(112)	1.447(3)
C(103)–C(104)	1.330(4)
C(104)–N(105)	1.399(3)
N(105)–C(106)	1.434(3)
N(201)–C(202)	1.447(4)
N(201)–H(201)	0.89(4)
N(201)–H(202)	0.90(4)
C(101)–Pd(1)–N(201)	173.58(9)
C(101)–Pd(1)–Cl(1)	87.20(7)
N(201)–Pd(1)–Cl(1)	91.12(7)
C(101)–Pd(1)–Cl(2)	91.71(7)
N(201)–Pd(1)–Cl(2)	90.04(7)
Cl(1)–Pd(1)–Cl(2)	178.64(2)
N(102)–C(101)–N(105)	104.9(2)
N(102)–C(101)–Pd(1)	122.72(19)
N(105)–C(101)–Pd(1)	132.25(19)
C(101)–N(102)–C(103)	111.0(2)
C(101)–N(102)–C(112)	124.5(2)
C(103)–N(102)–C(112)	124.1(2)
C(202)–N(201)–Pd(1)	109.19(16)

of imidazolium salt, with and without additional chloride, did not give a clear answer on this point, as isolated yields of **2** never exceeded 50%.

The X-ray structure of **2**, Fig. 1, clearly shows the square planar coordination at the palladium with the N–Pd–C and the Cl–Pd–Cl angles being 173.58(9)° and 178.64(2)°, respectively. The slight deviation from perfect square planar coordination is apparent in the nominally 90° angles of the ligands varying from 87° to 92°. Bond distances at palladium are usual, with Pd–Cl distances of 2.3008(7) and 2.3114(7) Å with the Pd–C distance at 1.964(3) Å and the Pd–N distance at 2.118(2) Å. The internal angle at the NHC carbon is 104.9(2)° and the Pd–N–C angle of the coordinated aniline is 109.19(16)°. Selected bond lengths and angles are included in Table 1. A further feature of the solid state structure is the presence of an extended hydrogen bonded network utilising the two *trans* chloride ligands on palladium and both NHs of the coordinated aniline. Chloride (Cl2) and N201-H201 on one side of the coordination plane act as acceptor and donor to the same NH and chloride of another complex related by an inversion centre with an NH...Cl distance of 2.64 Å and an donor-H-acceptor angle of 146°. A similar arrangement exists for the other *trans* chloride (Cl1) and N201-H202, again to an NH and chloride of a complex related by an inversion centre with an NH...Cl distance of 2.44 Å and an donor-H-acceptor angle of 169°. This extended ribbon like arrangement travels parallel to the *a* axis of the cell, Fig. 2. These ribbons are also connected by weaker aromatic CH...F (F103...C205 and F109...C116) and aromatic CH...Cl interactions (Cl1...C110) and a face to face π stacking interaction with one phenyl of the NHC (C112–C117) and a symmetry related phenyl (centroid–centroid distance
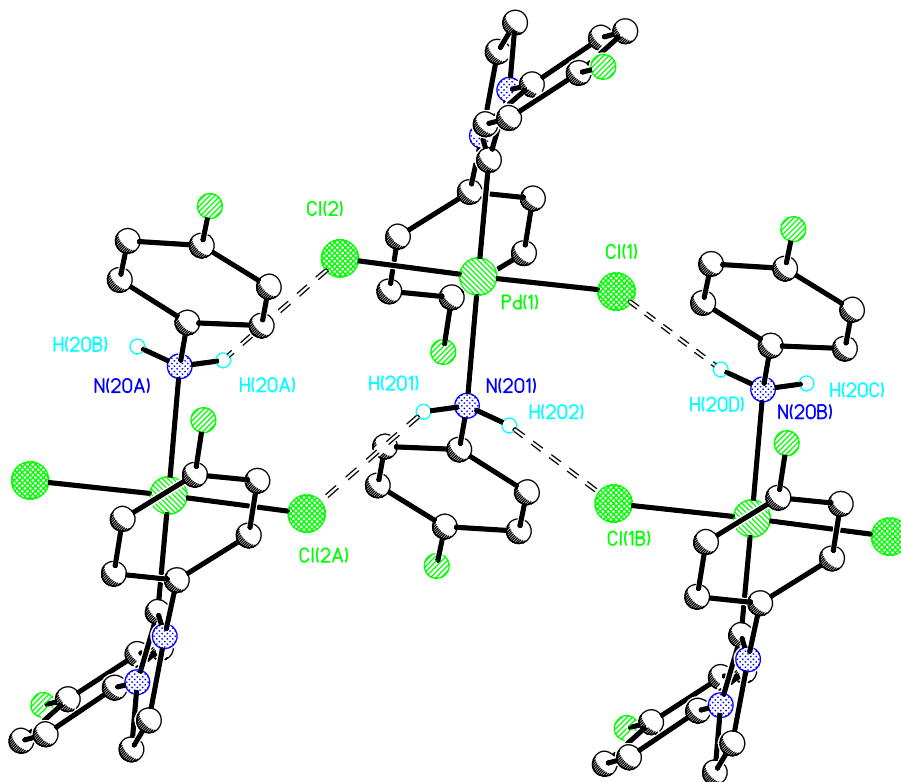

Fig. 2. The ribbon like hydrogen bonded network in the structure of **2**.

3.72 Å, closest interatomic contact 3.69 Å, planes parallel). Molecules of the crystallisation solvent chloroform lie in voids between the ribbons.

3. Conclusions

The attempted synthesis of bis(NHC)palladium complexes via the direct reaction of an imidazolium salt with palladium acetate results in the formation of a mixed NHC/aniline complex. Whilst the route by which the aniline is formed has not been completely elucidated, it is clear that it originally derives from an imidazolium salt.

4. Experimental

All chemicals were used as supplied, unless noted otherwise. All NMR spectra were obtained on a Bruker Avance 400 or 500 in CDCl$_3$ and are referenced to external TMS, assignments being made with the use of decoupling, nOe and COSY pulse sequences. Elemental analyses were performed by Warwick Analytical Services. NHC (1) was synthesised a literature route [18].

4.1. Palladium complex 2

Anhydrous 1,3-bis-(4-fluorophenyl)imidazolium chloride (48 mg, 1.64×10^{-4} mol) and palladium acetate (18 mg, 8.20×10^{-5} mol) were dissolved in dry DMSO (25 ml), and the mixture was heated at 40 °C for approximately 24 h. After cooling, water (150 ml) was added and the mixture was extracted with chloroform (3×20 ml). The yellow solid obtained was crystallised from chloroform to give yellow crystalline 2. Complex 2 rapidly lost a chloroform molecule of crystallisation to give an amorphous powder. Yield 21 mg (48%, 3.94×10^{-4} mol).

δ_H (CDCl$_3$): 7.84 (dd, 4H, $^3J_{HH}$ 7, $^4J_{HF}$ 2 Hz, NHC phenyl); 7.51 (dd, 2H, $^3J_{HH}$ 7, $^4J_{HF}$ 2 Hz, amine phenyl); 7.29 (s, 2H, NHC ring); 7.14 (t, 2H, $^3J_{HH}$ 7, $^3J_{HF}$ 7 Hz, amine phenyl); 7.06 (t, 4H, $^3J_{HH}$ 7, $^3J_{HF}$ 7 Hz, NHC phenyl); 4.27 (br s, 2H, NH$_2$). δ_F (CDCl$_3$): -111.9 (2F); -117.4 (1F). MS (LSIMS): m/z 543 (M$^+$). Elemental analysis: (C$_{21}$H$_{16}$Cl$_2$F$_3$N$_3$Pd requires): C, 46.2 (46.3); H, 2.7 (3.0); N, 7.9 (7.7).

Crystal structure data: yellow block $0.50 \times 0.30 \times 0.24$ mm, C$_{22}$H$_{17}$Cl$_5$F$_3$NPd, $M = 664.04$, triclinic, space group $P\bar{1}$; $a = 9.4501(6)$, $b = b = 10.6264(6)$, $c = 13.5207(8)$ Å, $\alpha = 104.7940(10)°$, $\beta = 97.8940(10)°$, $\gamma = 99.7610(10)°$. $D_{calc} = 1.736$ Mg m^{-3}. $U = 1270.28(13)$ Å^3 (by least squares refinement on 5156 reflection positions), $T = 180(2)$ K, $\lambda = 0.71073$ Å, $Z = 2$, $F(000) = 656$. μ(Mo Kα) = 1.295 mm^{-1}. Maximum theta was 29.20°. The hkl ranges were $-12/12$, $-14/13$, $-18/17$. 17131 reflections measured, 6253 unique [$R_{int} = 0.0280$]. Absorption correction semi-empirical from equivalents; minimum and maximum transmission factors: 0.4312; 0.7463.

No systematic absences; space group $P\bar{1}$ was chosen on the basis of intensity statistics and shown to be correct by successful refinement. The structure was solved in $P\bar{1}$ by direct methods using SHELXS [19] and additional light atoms were found by Fourier methods.

Refinement was by full matrix least-squares on F^2 for all reflection positions using SHELXTL. Hydrogen atoms were added at calculated positions and refined using a riding model except the ones on N201. Anisotropic displacement parameters were used for all non-H atoms apart from the disordered chain and some terminal chain atoms with high displacement parameters; H-atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for the hydrogen atoms on N201) times the equivalent isotropic displacement parameter of the atom to which the H-atom is attached. The weighting scheme was calculated using $w = 1/[\sigma^2(F_o^2) + (0.0762P)^2 + 0.2553P]$ where $P = (F_o^2 + 2F_c^2)/3$. Goodness-of-fit on $F^2 = 1.046$ R_1 [for 5491 reflections with $I > 2\sigma(I)$] = 0.0394, $wR_2 = 0.1102$. Data/restraints/parameters 6253/0/313. Largest difference Fourier peak and hole 0.940 and -0.523 e Å^{-3}. The largest peaks are all close to the Pd atom.

5. Supporting information

Full data for the structural analysis of 2 has been deposited with the Cambridge Crystallographic Data Centre, CCDC number 299613. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK, fax (int. code) +44 1223 336 033 or email: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk.

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