Synthesis and catalytic properties of a heterocyclic–carbene complex of palladium

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The palladium N-heterocyclic carbene complex *trans*-[$PdCl_2$\{1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene\}(NC_5H_5)] has been prepared and its X-ray molecular structure is reported. The complex is highly catalytically active in the cross-coupling reaction of phenylhalides with phenylthiol to afford diphenyl sulfide and is efficient for the coupling of chlorobenzene.

Keywords: NHC carbene, palladium complex, X-ray structure, C–S coupling

Palladium-catalysed cross coupling has become the principal method for forming aromatic carbon–heteroatom bonds.[1] The reaction forming carbon–sulfur bonds has received less attention,[2] even though aryl thioethers are valuable synthetic intermediates frequently found in biologically- and pharmaceutically-active molecules.[3–5] Since the first isolation of a stable, free N-heterocyclic carbene (NHC) by Arduengo in 1991,[6] NHCs have emerged as an extremely useful class of ligands for transition-metal catalysis. NHC–palladium complexes have been successfully used in many processes.[7,8] We now report the synthesis and crystal structure of an NHC–ligated palladium (NHC–Pd–Py) complex and test its catalytic activity for the C–S coupling reaction.

The synthesis of NHC–Pd–Py complex (**1**) was achieved by refluxing 1,3-bis(2,6-diisopropylphenyl)imidazolinium chloride with palladium chloride in presence of K_2CO_3 in pyridine. This complex was characterised by NMR spectroscopy and gave satisfactory elemental analyses. The complex is air and moisture stable and can be stored in air in the solid state for more than 6 months without any noticeable decomposition.

The ^{1}H NMR complex of complex **1** shows two distinctive signals for the eight CH_3 groups, confirming that the molecule has binary symmetry. However, either the isopropyl groups or the phenyl rings cannot rotate freely, so there must be steric hindrance around the Pd centre. ^{13}C NMR provides direct evidence of the metalation of the ligand, as seen by the signal at 152.4 ppm, which is assigned to the Pd–$C_{carbene}$ resonance shifted upfield relative to that of the imidazolium N*C*HC peak of the starting ligand precursor (160.0 ppm).[11] The resonance of carbene carbon in **1** is significantly upfield compared to that in its analogue with a C4–C5 saturated imidazole ring namely, *trans*-[PdCl2{1,3-bis(2,6-diisopropylphenyl)imidazol in-2-ylidene}(NC_5H_5)] (**2**) (184.2 ppm),[8] which means that the carbene in unsaturated compound **1** is more electron rich than that in its saturated analogue **2** (Figure 1). The more electron rich carbene should lead to the shorter Pd–C (carbene) distance, which was confirmed by an X-ray diffraction study. The Pd–C (carbene) distance in **1** is 1.971(7) Å, shorter than that shown by its saturated analogue **2** (1.993(7) Å).[8]

The molecular diagram of **1** is shown in Figure 2. The structure of the complex consists of a pseudo-square-planar molecule with a palladium centre surrounded by imidazolylidene, two chloro-ligands in a *trans*-configuration, and a pyridine molecule. The Pd–N (pyridine) distance of **1** is 2.129(6) Å, which is longer than that shown for its saturated analogue **2** (2.106(6) Å),[8] indicating the strong *trans*-influence of the unsaturated N-heterocyclic carbene ligand. All other distances and angles lie in the expected range.[8]

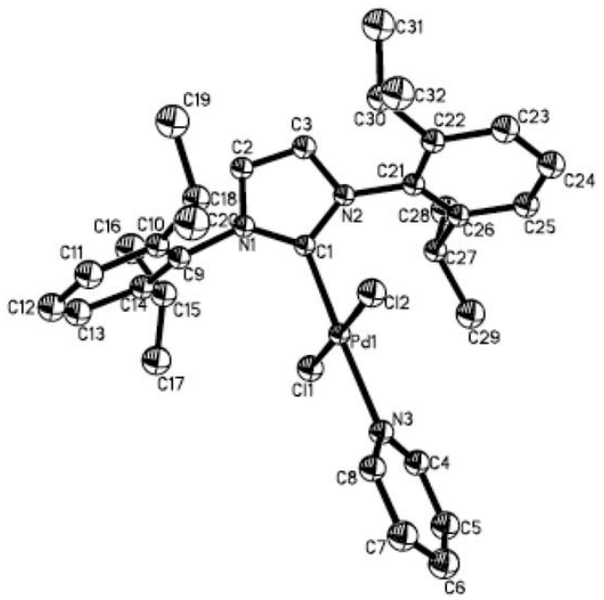
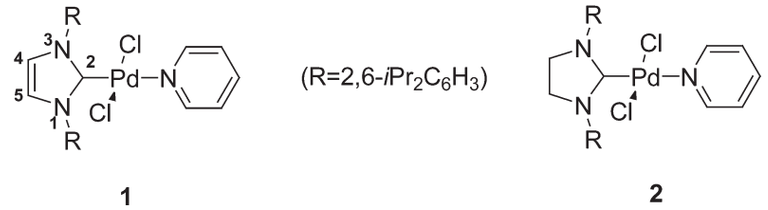


Fig. 2 ORTEP structure of complex **1** with the probability ellipsoids drawn at the 30% level.
(Hydrogen atoms have been omitted for clarity).



1 **2**

Fig. 1 Complexes of the C4–C5 unsaturated and saturated imidazole-based N-heterocyclic carbenes.

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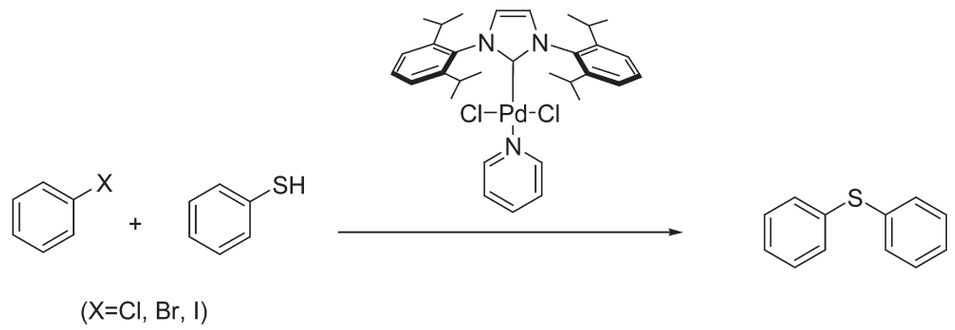


Scheme 1

The crystal is monoclinic, space group $P2_1/C$ with a = 1.491 7(3) nm, b = 1.714 9(3) nm, c = 1.490 5(3) nm, β = 102.20(3)°, V = 3.726 89(13) nm^3, Dc = 1.314 g/cm^3, Mr = 737.11, Z = 4, F(000) = 1536, R^1 = 0.0485, R^2 = 0.1225. Selected bond lengths (Å) and angels (deg): Pd(1)-C(1) 1.971(7), Pd(1)–N(3) 2.129(6), Pd(1)–Cl(1) 2.295(2), Pd(1)–Cl(2) 2.304(2), C(1)–Pd(1)–N(3) 175.5(3), Cl(1)–Pd(1)–Cl(2) 179.29(8), N(3)–Pd(1)–Cl(1) 89.69(18), C(1)–Pd(1)–Cl(2) 92.3(2).

The complex has been tested in the cross-coupling reaction of phenyl halides (iodide, bromide, chloride) with phenylthiol to afford the thioether (Scheme 1 and Table 1). It was found that **1** was highly catalytically active in this C–S reaction, the coupling reaction with chlorobenzene is also very efficient (isolated yield: 91%).

Experimental

Imidazolium salt was synthesised according to the literature procedure.[9,10] All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques. Toluene was distilled from sodium benzophenone ketyl under argon. Pyridine was distilled from calcium hydride under argon. All other chemicals were commercially available and used as received unless otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV400 spectrometer, using $CDCl_3$ or DMSO as solvents. GC-MS was performed on an Agilent 6890-5973N system with electron ionization (EI) mass spectrometry. Elemental analyses were performed on a EuroVektor Euro EA-300 elemental analyser. X-ray crystallography was conducted with a Bruker P4 CCD diffractometer using graphite-momnochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods and was refined using the SHELXTL 6.1 software package. The linear absorption coefficient was 0.671, and the range for collecting data (h, k, l and θ), $-19 \le h \le 16$, $-17 \le k \le 22$, $-19 \le l \le 19$, $3.04 \le \theta \le 27.47$. The total number of reflections that were collected were 25350, in which the independent reflections were 8519 and the number used in the structure determination were 7033.

Synthesis of palladium complex

To a mixture of 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (0.854 g, 2.0 mmol), $PdCl_2$ (0.390 g, 2.2 mmol), and K_2CO_3 (2.764 g, 20 mmol) in a 25 mL round bottom flask was added pyridine (10.5 mL). The reaction mixture was heated at 80 °C for 16 h, after which time the mixture was filtered through Celite and washed with CH_2Cl_2. The solvent was removed under vacuum and the crude product was washed with diethyl ether (15 mL). The pure compound was obtained as a yellow solid by recrystallization from CH_2Cl_2/ether in 81% yield (1.04 g). The single crystal for the X-ray study was obtained by diffusion of toluene into saturated solution of the complex in CH_2Cl_2.

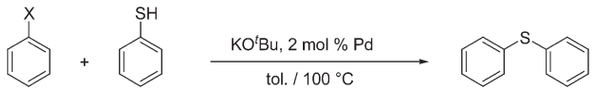
^{1}HNMR (400MHz, $CDCl_3$) δ: 8.56 (d, J = 5.2 Hz, 2H, o-NC_5H_5), 7.56–7.47 (m, 1H, p-NC_5H_5 and 2H, p-C_6H_3), 7.35 (d, J = 7.6 Hz, 4H, m-C_6H_3), 7.13–7.08 (m, 4H, 2H, m-NC_5H_5 and 2H, C*H*), 3.16 (sept, J = 6.4 Hz, 4H, C*H*$(CH_3)_2$), 1.49 (d, J = 6.4 Hz, 12H, CH_3), 1.12 (d, J = 6.8 Hz, 12H, CH_3). ^{13}C NMR (100MHz, DMSO) δ: 152.4 (N*C*N-Pd), 150.5, 146.2, 138.4, 135.0, 129.7, 126.3, 124.4, 123.5, 28.1, 25.8, 22.9. Anal. Found (Calcd for $C_{32}H_{41}Cl_2N_3Pd$): C 59.64 (59.59), H 6.55 (6.41), N 6.38 (6.51)%.

Procedure for the C–S coupling reaction

An oven-dried 4 mL vial containing a stirrer bar was charged with an aryl halides (0.5 mmol), **1** (2 mol %) and KO^{t}Bu (84.2 mg, 0.75 mmol) in a glove box and sealed with a cap containing a PTFE septum. After taking the vial out of glove box, toluene (1 mL) and thiols (0.60 mmol) were injected sequentially. The mixture was stirred at 100 °C for 1–36 h. The crude product was purified by column chromatography on silica gel with hexane giving diphenyl sulfide as a colourless liquid.

Diphenyl sulfide: ^{1}H NMR (400MHz, $CDCl_3$) δ: 7.21–7.35 (m, 10H); ^{13}C NMR (100MHz, $CDCl_3$) δ: 135.8, 131.0, 129.1, 127.0. EIMS m/z: 186 (M^+).

Table 1 C–S couping reaction with C_6H_5SH



Entry	X	Time/h	Isolated yield/%
1	Cl	24	91
2	Br	6	96
3	I	4	99

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