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Synthesis and characterization of a pyrazolium bearing *N*-heterocyclic carbene–palladium(II) complex

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ABSTRACT

3,5-Dichloro-1,2-diphenylpyrazolium tetrafluoroborate **1** reacts at 0 °C with 2,6-dimethylphenol in the presence of triethylamine to give the 5-chloro-3-aryloxy-1,2-diphenylpyrazolium tetrafluoroborate **2** (58% yield). Heterocycle **2** reacts with 1-methylimidazole affording 5-(1-methyl-1*H*-imidazolium-3-yl)-3-aryloxy-1,2-diphenylpyrazolium chloride tetrafluoroborate **3** in 83% yield. When half an equivalent of allylchloropalladium dimer $[Pd(allyl)Cl]_2$ is added to **3** in the presence of triethylamine, monocationic compound **4** featuring an *N*-heterocyclic carbene coordinated to allylchloropalladium(II) is isolated in 72% yield. All compounds have been fully characterized by multinuclear NMR spectroscopy. We also describe the X-ray crystal structure of **4**, which crystallizes in the monoclinic C2/c space group.

1. Introduction

Carbenes are neutral compounds featuring a divalent carbon atom with only six electrons in its valence shell [1]. Following the synthesis of the first stable phosphanyl(silyl)carbene in 1988 by our group [2], Arduengo reported the first structurally characterized free imidazol-2-ylidene (NHC) in 1991 [3]. NHCs are excellent ligands for transition metals and the corresponding complexes proved to be efficient catalysts for many organic reactions such as the Heck, Kumada, Stille, Suzuki–Miyaura, and Sonogashira coupling reactions, amination reactions, hydrosilylation, olefin metathesis, hydroformylation, polymerization, transfer hydrogenation etc [4]. Recently, another type of carbon-based ligand has been isolated. Named bent-allenes [5] or carbodicarbenes [6], they are not only stronger σ-donors but also less π-acceptor ligands than NHCs: consequently they are promising ligands for transition metals [7].

While searching for novel and effective ligands for new catalytic reactions, we chose to target heteroditopic ligands [8], featuring a bent-allene and an NHC, and here we report our preliminary results.

2. Result and discussion

The synthesis started from the readily available 3,5-dichloro-1,2-diphenylpyrazolium tetrafluoroborate **1** [9] (Scheme 1). Reaction of salt **1** with one equivalent of 2,6-dimethylphenol at room temperature, in presence of excess triethylamine as a base, cleanly gave **2** as indicated by ^{13}C and ^{1}H NMR spectroscopy. Indeed, in the ^{13}C NMR (in CD_3CN) spectrum, the CH carbon of the pyrazolium ring appeared at 92.5 ppm, and the ^{1}H NMR (in $CDCl_3$) spectrum showed the pyrazolium ring proton at 5.94 ppm.

In the next step, **2** was treated with *N*-methyl imidazole at room temperature. ^{13}C NMR spectroscopy of the reaction mixture revealed clean substitution, as shown by the CH carbon signal of the pyrazolium ring, which was slightly shifted from 92.5 to 92.3 ppm. Also distinctive, the signal of the CH carbon of the imidazolium group, which appears at 133.8 ppm. After workup, and recrystallization from a saturated acetonitrile solution at −30 °C, dicationic salt **3** was obtained as non-hygroscopic colorless crystals (83% yield). Unfortunately, deprotonation of the dicationic salt **3** with two equivalents of various bases (LDA, KHMDS, KO^{t}Bu, MesLi, and ^{n}BuLi) did not produce the desired free cyclic allene bearing an *N*-heterocyclic carbene (**3′**) (Scheme 2), but a complex mixture.

Although the initial goal to isolate the free cyclic allene bearing a metal-free NHC could not be achieved, reaction of **3** with half an equivalent of allylchloropalladium dimer $[Pd(allyl)Cl]_2$ and triethylamine in acetonitrile afforded cleanly the pyrazolium substituted NHC–Pd(II) complex **4** (Scheme 2). The ^{13}C NMR spectrum (in $CDC1_3$) showed the carbene signal at 184 ppm, which falls in the typical range for transition metal–NHC complexes [10]. The ^{1}H NMR spectrum revealed the disappearance of the

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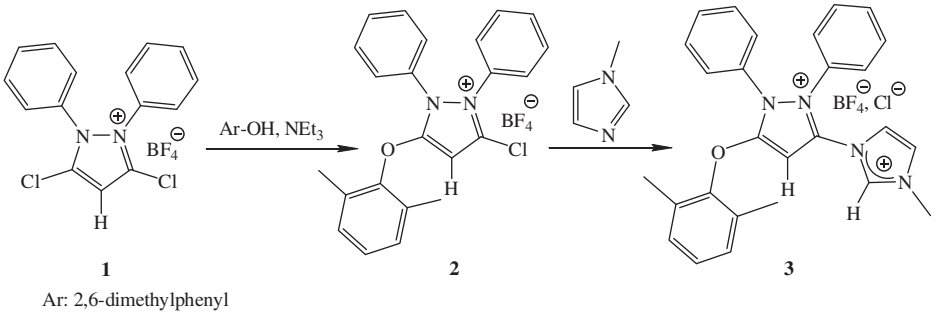


Scheme 1. Synthesis of compounds **2** and **3**.

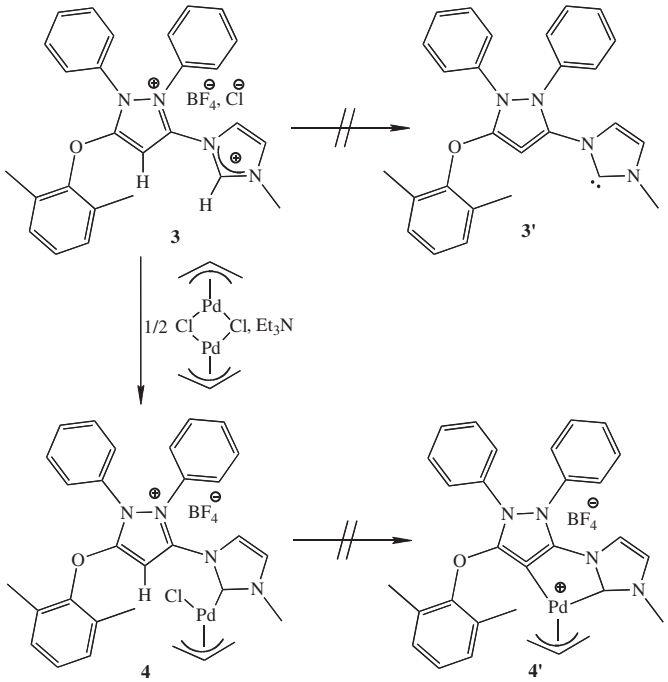
imidazolium CH proton and the region of the allyl moiety displayed a very characteristic pattern that indicates the coordination of the carbene to the palladium center (1 multiplet and 4 doublets) [11]. The ionic structure of **4** was indicated by its very low solubility in nonpolar solvents and by the presence of a sharp signal at −1.2 ($CDC1_3$) in the ^{11}B NMR spectrum, due to the tetrafluoroborate anion. Colorless crystals of **4** suitable for an X-ray diffraction study were obtained by slow evaporation of a chloroform solution at room temperature. The structure of **4** is illustrated in Fig. 1, and selected bond lengths and angles are given in Table 1.

The single crystal X-ray diffraction analysis unambiguously demonstrates the monocationic nature of **4**. The palladium atom is coordinated in a slightly distorted square planar geometry with the allyl moiety η^3-coordinated to the metal center. All the data for the allylpalladium complex **4** are comparable to those reported for others NHC–Pd(II) complexes [12]. The Pd–$C_{carbene}$, Pd–Cl and N2–C4 bond distance are 2.039(3) Å, 2.383(7) Å and 1.389(3) Å, while the C1–Pd1–C31, C1–Pd1–C29 and C29–Pd1–Cl1 angles are 98.29(13), 167.22(14) and 97.55(12), respectively. The internal angles of the heterocycles are 103.7(2) for N1–C1–N2 and 104.8(2) for C4–C5–C6. The relevant crystal data and experimental details along with the final parameters are summarized in Table 2.

All attempts to deprotonate the pyrazolium ring of the monocationic NHC–Pd(II) complex **4** with mild or strong bases failed to give the desired palladium complex **4′** featuring the heteroditopic cyclic bent allene–NHC ligand. This is a further demonstration of the extreme basicity of cyclic bent-allenes [5].

3. Conclusion

In conclusion, a novel pyrazolium bearing an *N*-heterocyclic carbene palladium(II) complex was synthesized and characterized by various spectroscopic techniques, and by a single crystal X-ray diffraction study. Unfortunately, all attempts to synthesize the free chelating ligand featuring both an *N*-heterocyclic carbene and a cyclic bent-allene failed. However, this work shows that the pyrazolium bearing an imidazol-2-ylidene Pd(II) complex is stable at room temperature even in air and water. The modifications of the



Scheme 2. Synthesis of complex **4**.

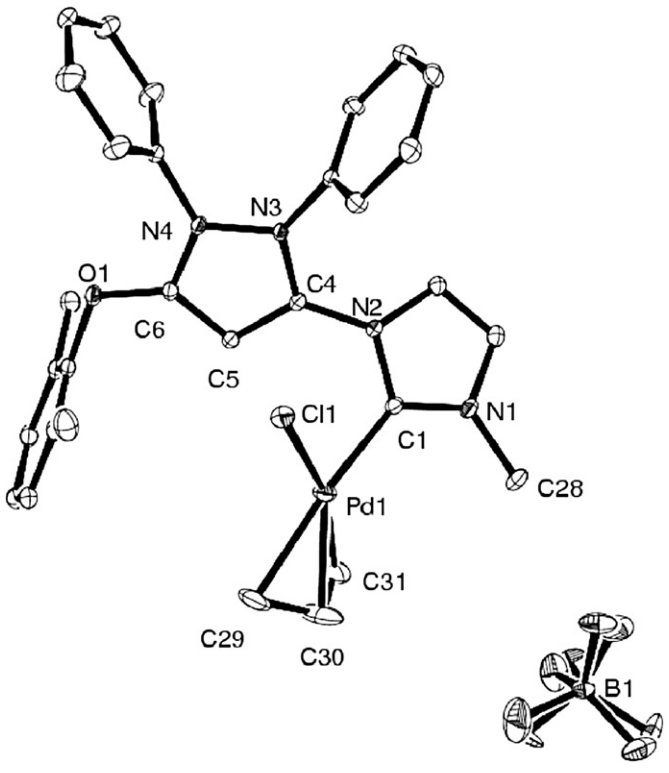


Fig. 1. Molecular structure of **4** in the solid state (hydrogen atoms are omitted for clarity; ellipsoids are drawn at 30% probability).

Table 1
Selected bond lengths (Å) and angles (deg) with esd's in parentheses, for complex **4**.

Pd(1)–C(1)	2.039(3)	Pd(1)–C(31)	2.110(3)
Pd(1)–Cl(1)	2.383(7)	N(2)–C(4)	1.389(3)
Pd(1)–C(29)	2.166(3)	O(1)–C(6)	1.335(3)
Pd(1)–C(30)	2.120(4)	N(1)–C(1)	1.331(3)
N(1)–C(2)	1.381(4)	N(3)–N(4)	1.386(3)
C(1)–Pd(1)–Cl(1)	95.12(7)	N(1)–C(1)–Pd(1)	129.23(19)
C(1)–Pd(1)–C(31)	98.29(13)	C(6)–C(5)–C(4)	104.8(2)
N(1)–C(1)–N(2)	103.7(2)	O(1)–C(6)–C(5)	132.4(2)
N(2)–C(1)–Pd(1)	126.82(18)	N(3)–C(4)–N(2)	121.5(2)
C(1)–Pd(1)–C(29)	167.22(14)	C(29)–Pd(1)–Cl(1)	97.55(12)

substituents on the pyrazolium and imidazolium rings and the possibility of introducing a spacer between the pyrazolium and imidazolium groups are under active investigation.

4. Experimental

4.1. General

All manipulations and reactions were performed under a purified argon atmosphere using standard Schlenk techniques. Dry, oxygen-free solvents were employed. Commercially available reagents were used without further purification. 3,5-Dichloro-1,2-diphenylpyrazolium tetrafluoroborate **1** was prepared according to the reported procedures [9]. Melting points were measured with an Electro thermal 9200 melting point apparatus and the values are uncorrected. ^{1}H, ^{13}C and ^{11}B NMR spectra were recorded on a Bruker Avance 300 spectrometer. Chemical shifts are reported in ppm downfield from Me_4Si and were referenced to solvent peaks. X-ray measurements were recorded on the Bruker X8-APEX [13] X-ray diffraction instrument with Mo-radiation. All data frames were collected at low temperatures ($T = 100$ K) using an ω, φ-scan mode (0.3° ω-scan width, hemisphere of reflections) and integrated using a Bruker SAINTPLUS software package [14]. The intensity data were corrected for lorentzian polarization. Absorption corrections were performed using the SADABS program [15]. The SIR97 [16] software was used for direct methods solution and phase determination, and Bruker SHELXTL [17] for structure refinement and difference Fourier maps. Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms of the compound were refined by means of a full matrix least-squares procedure on F^2. Drawings of the molecule were performed using Ortep 3.

Table 2
Crystal data and structure refinement for complex **4**.

Empirical formula	$C_{30}H_{30}BClF_4N_4OPd$
Formula weight	691.24
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
a, Å	37.0409(7)
b, Å	11.0088(2)
c, Å	16.9809(3)
α, deg	90
β, deg	105.7390(10)
γ, deg	90
V, Å^3	6664.8(2)
Z	8
d calc Mg m^{-3}	1.378
μ, mm^{-1}	0.687
Reflections collected	30,293
N_{measd}	5662
[R_{int}]	[0.0233]
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0319$, $wR2 = 0.0830$
R indices (all data)	$R1 = 0.0357$, $wR2 = 0.0858$
GOF	1.064
Largest diff. peak and hole [e Å^{-3}]	0.948, −0.655

4.2. 5-Chloro-3-phenoxy-1,2-diphenylpyrazolium tetrafluoroborate **2**

2,6-Dimethylphenol (1.86 g, 13.2 mmol) and triethylamine (33 mL, 23.5 mmol) were added at 0 °C to an acetonitrile (50 mL) solution of 3,5-dichloro-1,2-diphenylpyrazolium tetrafluoroborate **1** (5.0 g, 13.2 mmol). After stirring for 6 h at 0 °C, the reaction mixture was concentrated to 1/2 of its original volume and then diethyl ether (250 mL) was added to precipitate the product and ammonium salts. After filtration, the solid residue was washed with water (5 × 150 mL), and then with diethyl ether (3 × 40 mL). After recrystallization from ethanol, **2** was obtained as a colorless solid (3.55 g, 58%). m.p.: 138–141 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.34$ (s, 6H), 5.94 (s, 1H), 7.16–7.17 (m, 3H), 7.47–7.51 (m, 6H), 7.69–7.72 (m, 4H) ppm; ^{13}C NMR (75 MHz, CD_3CN): $\delta = 15.3, 92.5, 127.8, 128.0, 128.4, 129.4, 129.8, 130.2, 130.4, 132.1, 132.8, 133.3, 140.6, 150.1, 156.8$ ppm; ^{11}B NMR (96 MHz, $CDCl_3$): $\delta = -1.3$ ppm.

4.3. 5-(1-Methyl-1H-imidazol-3-ium-3-yl)-3-phenoxy-1, 2-diphenylpyrazolium chloride tetrafluoroborate **3**

1-Methylimidazole (0.45 g, 5.4 mmol) was added to a 5:1 $CHCl_3$/CH_3CN solution (25 mL) of **2** (2.5 g, 5.4 mmol) at room temperature. The solution was heated and stirred at 60 °C for 6 h. The reaction mixture was concentrated to 1/2 of its original volume and then diethyl ether (250 mL) was added to precipitate the product. After filtration, the solid residue was washed with diethyl ether, recrystallized from a saturated acetonitrile solution at −30 °C, and dried under vacuum to give **3** as colorless crystals (2.43 g, 83%). m.p.: 167 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.38$ (s, 6H), 3.90 (s, 3H), 6.22 (s, 1H), 7.08–7.10 (m, 3H), 7.30–7.49 (m, 8H), 7.88 (d, $J_{HH} = 6.6$ Hz, 2H), 8.19 (d, $J_{HH} = 7.34$ Hz, 2H), 10.37 (s, 1H) ppm; ^{13}C NMR (75 MHz, CD_3CN): $\delta = 16.2, 37.7, 92.3, 124.2, 125.7, 128.9, 129.6, 129.8, 130.4, 130.6, 130.9, 131.1, 131.2, 133.8, 133.9, 140.4, 151.0, 157.3$ ppm; ^{11}B NMR (96 MHz, $CDCl_3$): $\delta = -1.3$ ppm.

4.4. Allylchloro{1-[3-(2,6-dimethylphenoxy)-1, 2-diphenylpyrazoliumyl]-3-methyl-imidazol-2-ylidene} palladium(II) tetrafluoroborate **4**

A mixture of $[Pd(allyl)Cl]_2$ (0.23 g, 0.6 mmol), dicationic salt **3** (0.65 g, 1.2 mmol), and Et_3N (0.22 mL, 1.6 mmol), was dissolved in CH_3CN (20 mL) and the solution was stirred at room temperature for 2 h. After evaporation of the solvent the crude residue was washed with water (2 × 20 mL). Then the organic layer was extracted with CH_2Cl_2 (20 mL) and dried over anhydrous $MgSO_4$. After removal of the solvent under vacuum, **4** was obtained as a white solid (0.29 g, 72%). Crystals [m.p.: 205 °C (dec)] suitable for X-ray crystallography were obtained by slow evaporation of a chloroform solution of complex **4**. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.32$ (d, $J_{HH} = 13.6$ Hz, 1H), 2.39 (s, 6H), 3.14 (d, $J_{HH} = 13.6$ Hz, 1H), 3.56 (d, $J_{HH} = 6.6$ Hz, 1H), 3.71 (s, 3H), 4.22 (d, $J_{HH} = 6.6$ Hz, 1H), 5.03 (m, 1H), 5.98 (s, 1H), 7.11 (s, 2H), 7.27–7.34 (m, 5H), 7.43–7.60 (m, 4H), 7.74 (d, $J_{HH} = 7.34$ Hz, 2H), 8.02 (d, $J_{HH} = 7.34$ Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 15.9, 38.5, 50.8, 72.4, 90.26, 114.9, 122.9, 123.3, 127.6, 129.1, 129.3, 129.4, 129.6, 129.8, 130.5, 131.8, 132.2, 144.9, 150.3, 156.0, 184.0$ ($C_{carbene}$) ppm; ^{11}B NMR (96 MHz, $CDCl_3$): $\delta = -1.2$ ppm.

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Appendix A. Supplementary material

CCDC 882110 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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