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Note

The first structurally characterized *N*-heterocyclic carbene complex with a ligand derived from pyrimidine

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ABSTRACT

Oxidative addition of *N*-alkyl-2-halopyrimidinium cations to $[Pd(PPh_3)_4]$ gives straightforward access to the cationic complexes $[(PPh_3)_2(NHC)PdX]BF_4$ (**3a,b**) with pyrimidine-derived NHC-ligands. The new complexes were fully characterized including X-ray crystallography.

1. Introduction

The chemistry of *N*-heterocyclic carbenes (NHCs) continues to be an attractive research area. The vast majority of known NHCs rely on the 5-membered ring structures of imidazole or imidazoline. However, NHCs based on heterocycles with other ring sizes have also been prepared, as well as acyclic derivatives [1]. We have recently reported on electronically differentiated bidentate hybrid ligands featuring one NHC donor (good σ-donor) together with a phosphaferrocene group (reasonable π-acceptor) [2]. This work inspired us to explore new NHCs derived from new interesting ring structures and 6-membered rings attracted our primary attention. Known derivatives include compounds based on, for example, tetrahydropyrimidine [3], 1,8-diaminonaphtaline [4], diboratriazine [5], and 1,1′-diaminoferrocene [6]. Interestingly, Crociani and coworkers reported as early as 1985 the first metal coordinated NHC based on the aromatic pyrimidine scaffold which was obtained by reversible N-protonation of the 2-metallated pyrimidine [7]. In 2008, the synthesis and coordination chemistry of anionic NHCs based on a pyrimidine-4,6-dione core were reported [8]. A related six-membered anionic diazadiborine ligand was prepared and characterized in 2006 [9]. Furthermore, dications resulting from the dialkylation of pyrimidines are known for a long time [10] but have not been used as precursors for NHCs, although theoretical work indicates that the resulting cationic carbenes should be stable species [11]. In addition, Driess and coworkers reported the synthesis and properties of the analogous silylene species [12] while Richeson and coworkers reported the preparation of a phosphenium cation as part of a six-membered ring system and its coordination properties towards a Rh(I) center [13]. In this contribution we wish to disclose our preliminary results concerning pyrimidine derived NHCs.

2. Results and discussion

Attempts to convert *N,N′*-dialkylated pyrimidinium dications into corresponding carbenes by deprotonation at C-2 under various conditions were unsuccessful. Therefore, we intended to build up the NHC by oxidative addition of monocationic *N*-alkyl-2-halopyrimidines to low-valent metal centers. Given the feasibility of the oxidative addition of the neutral 2-chloropyrimidine to Pd(0) resulting in the pyrimidinyl group acting formally as a carbanionic donor [7] we were interested in the reactivity of *N*-alkyl-2-halopyrimidinium cations towards a Pd(0) precursor. The cationic *N*-ethyl-2-halopyrimidinium species **2a** (Cl) and **2b** (I) were obtained in excellent yield by alkylation of the respective 2-halopyrimidines with triethyloxonium tetrafluoroborate in dichloromethane at room temperature (see Scheme 1).

Both halogen compounds reacted with $Pd(PPh_3)_4$ smoothly in DME at room temperature overnight to afford the cationic palladium complexes **3a** and **3b** in excellent yield featuring pyrimidinyl-based NHC-ligands. The compounds were fully characterized by NMR-spectroscopy, MS and elemental analysis. Interestingly, for the iodide complex **3b** the ^{31}P NMR spectrum of a freshly prepared sample showed two doublets in addition to the expected singlet which is due to the presence of the *cis*-isomer **4** with chemically non-equivalent P nuclei. Upon standing, the doublets

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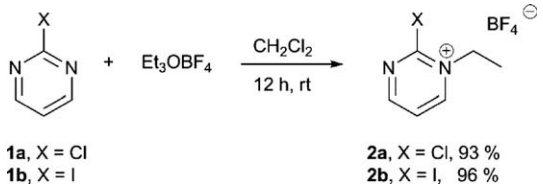


Scheme 1.

decrease in intensity while the *cis*-isomer is converted to the thermodynamically more stable *trans*-complex. For the Cl-complex **3a**, only the singlet for the *trans*-arrangement of PPh_3 ligands is observed (see Scheme 2).

Related oxidative additions to Pd(0) producing NHC complexes have been reported, for example, for other cyclic 2-haloamidinium salts by Fürstner et al. [14] and Cavell and coworkers [15] as well as for halogenated *N*-alkylpyridinium cations by Herrmann and coworkers [16] – the latter work dating back to early investigations by Stone and coworkers [17] –, and for 4-iodo-*N,N′*-diorganylpyrazolium salts by Huynh and coworkers [18].

Crystals of the *trans*-isomer **3b** suitable for X-ray diffraction were obtained from methanol. The complex crystallizes in the triclinic spacegroup $P\bar{1}$ with two independent molecules in the asymmetric unit, which show almost identical geometrical parameters. Therefore, relevant data will be discussed only for the molecule containing Pd1 (see Fig. 1). The structure features the Pd atom in a slightly distorted square-planar environment with *trans* angles for C–Pd–I of 174.87(13)° and P–Pd–P of 170.49(4)°, respectively, and *cis* angles for C–Pd–P of 87.50(12)° for P2 and 92.93(12)° for P1. The Pd1 atom is located 12.38(3) pm apart from the best plane containing the four ligating atoms. The pyrimidine ring is oriented almost perpendicular to the coordination plane of the Pd atom with an interplanar angle of 83.8(5)°. The relevant bond length values for C_{NHC}–Pd (201.2(4) pm), Pd–P (233.70(12) and 234.02(12) pm) and Pd–I (266.76(5) pm) are very close to the parameters found for other NHC palladium complexes with two PAr_3 ligands [4,16,18,19]. Interestingly, there seem to be only two other structurally characterized complexes with a [*trans*-$(PAr_3)_2$(NHC)PdI] core, in one of which the NHC an the phosphines are connected to a tridentate PCP-ligand [20], while the other features a rNHC-ligand based on a pyrazolyl-4-ylidene [18]. In addition, structurally characterized bis(phosphine)Pd-complexes with chloride instead of iodide and NHCs based on benzimidazolin-2-ylidene or benzoxazol-2-ylidene have been reported by Hahn et al. [21].

In complexes **3** the pyrimidine residue acts as a formally neutral NHC-ligand. We are currently exploring the synthesis of cationic NHCs derived from *N,N′*-dialkylated pyrimidinium dications.

3. Experimental

3.1. General

All reactions were carried out under an atmosphere of dry nitrogen by means of conventional Schlenk techniques. Solvents were dried and purified by standard methods. Alumina was heated at 200 °C for 12 h, cooled to room temperature under high vacuum, deactivated with 5% water and stored under nitrogen. NMR spectra were recorded on a Bruker Avance DRX 500 and a Bruker Avance DRX 200 spectrometer. ^1H and $^{13}C\{^1H\}$ spectra are referenced to the residual solvent signal and $^{31}P\{^1H\}$ spectra to external H_3PO_4 (85%). Mass spectra were recorded on a Finnigan MAT 8200 (FAB, EI). Elemental analyses were performed by the institute of pharmaceutical chemistry at the Heinrich-Heine-Universität Düsseldorf on a Perkin–Elmer elemental analyser 2400 Series II CHN. 2-Iodopyrimidine was prepared according to a published procedure [22].

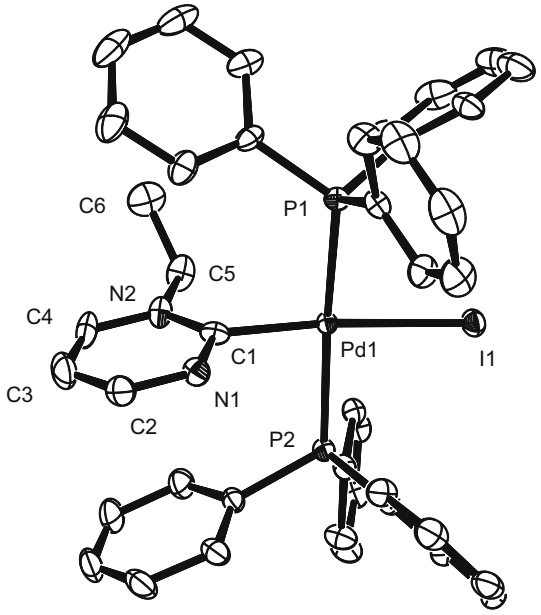
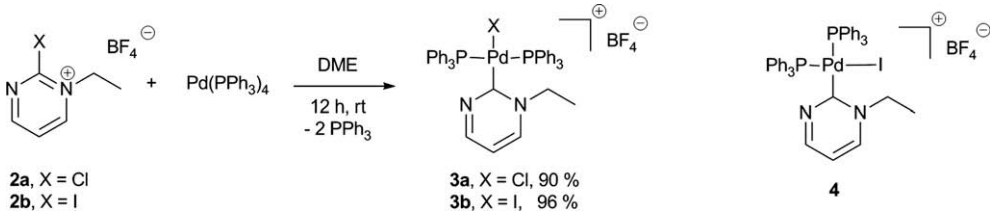


Fig. 1. Molecular structure of the cation of complex **3b** in the solid state. Only one of two independent molecules is shown. The BF_4^- anion is omitted for clarity. Selected bond lengths (Å) and angles (°): Pd1–C1 2.012(4), Pd1–P2 2.3370(12), Pd1–P1 2.3402(12), Pd1–I1 2.6676(5), C1–N1 1.335(6), C1–N2 1.344(5); C1–Pd1–P2 87.50(12), C1–Pd1–P1 92.93(12), P2–Pd1–P1 170.49(4), C1–Pd1–I1 174.87(13), P2–Pd1–I1 87.90(3), P1–Pd1–I1 91.24(3), N1–C1–N2 120.6(4), N1–C1–Pd1 115.6(3), N2–C1–Pd1 123.4(3).

4. Preparation of the pyrimidinium salts

4.1. 1-Ethyl-2-chloro-pyrimidinium-tetrafluoroborate (*2a*)

2-Chloropyrimidine (18.7 mmol, 1.2 equiv., 2.1 g) and triethyloxoniumtetrafluoroborate (15.4 mmol, 1 equiv., 3.92 g) were dissolved in 15 mL of dichlormethane. The solution was stirred over night. Instantaneously, a white solid started to precipitate. The solvent was decanted and the product was dried in high vacuum giving a colorless solid (14.4 mmol, 4.16 g, 93%). Anal. Calc. for $C_6H_8BF_4ClN_2$: C, 31.28; H, 3.50; N, 12.16. Found: C, 31.16; H, 3.43; N, 11.95%.). ^1H NMR (CD_3CN): δ = 1.60 (3H, t, $^3J_{HH}$ = 7.3 Hz, Me), 4.68 (2H, q, $^3J_{HH}$ = 7.3 Hz, CH_2), 8.10 (1H, dd, $^3J_{HH}$ = 6.2 and



Scheme 2.

4.9 Hz, C(5)H), 9.07 (1H, dd, $^3J_{HH}$ = 6.3 Hz, $^4J_{HH}$ = 2.1 Hz, C(4)H), 9.22 (1H, dd, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 2.1 Hz, C(6)H) $^{13}C\{^1H\}$ NMR (CD_3CN): δ_C = 14.2 (s, **C**H_3), 62.4 (s, **C**H_2), 123.3 (s, C5), 126.9 (s, C4), 154.2 (s, C6), 163.8 (s, C2) *m/z* (MALDI+) 143 $[M]^+$.

4.2. 1-Ethyl-2-iodo-pyrimidinium-tetrafluoroborate (**2b**)

2-Iodopyrimidine (10.4 mmol, 1.2 equiv., 2.0 g) and triethyloxoniumtetrafluoroborate (8.4 mmol, 1 equiv., 1.6 g) were dissolved in 10 mL of dichlormethane. The solution was stirred over night. After a few minutes a slightly yellow solid precipitated. The solvent was decanted and the product was dried in high vacuum giving a slightly yellow solid (7.98 mmol, 2.57 g, 96%). Anal. Calc. for $C_6H_8BF_4IN_2$: C, 22.39; H, 2.51; N, 8.70. Found: C, 23.47; H, 2.65; N, 8.59%. ^1H NMR (CD_3CN): δ = 1.58 (3H, t, $^3J_{HH}$ = 7.3 Hz, Me), 4.64 (2H, q, $^3J_{HH}$ = 7.3 Hz, CH_2), 8.05 (1H, dd, $^3J_{HH}$ = 6.2 and 4.8 Hz, C(6)H), 8.98 (1H, dd, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 2.1 Hz, C(4)H), 9.04 (1H, $^3J_{HH}$ = 6.3 Hz, $^4J_{HH}$ = 2.1 Hz, C(6)H) $^{13}C\{^1H\}$ NMR (CD_3CN): δ_C = 14.6 (s, **C**H_3), 62.8 (s, **C**H_2), 123.7 (s, C5), 127.4 (s, C4), 154.6 (s, C6), 164.2 (s, C2) *m/z* (ESI+) 235 $[M]^+$.

5. Preparation of the carbene complexes

5.1. trans-Chloro-bis-triphenylphosphine(1-ethyl-pyrimidin-2-ylidene)-palladium(II)-tetrafluoroborate (**3a**)

In a 100 mL Schlenk-flask 1-ethyl-2-chloropyrimidinium-tetrafluoroborate (**2a**) (397 μmol, 1.1 equiv., 115 mg) and $[Pd(PPh_3)_4]$ (365 μmol, 1 equiv., 422 mg) were dissolved in 20 mL of 1,2-dimethoxyethane. The olive-green solution was stirred over night and turned into a grey suspension. The precipitate was filtered and washed with a small amount of diethyl ether. The product **3a** was dried in high vacuum to give a white solid (138 μmol, 119 mg, 38%). Anal. Calc. for $C_{42}H_{38}BF_4ClN_2P_2Pd$: C, 58.56; H, 4.45; N, 3.25. Found: C, 58.47; H, 4.38; N, 3.25%. $^1H\{^{31}P\}$ NMR (CD_2Cl_2): δ = 1.32 (3H, t, $^3J_{HH}$ = 7.4 Hz, Me), 4.55 (2H, q, $^3J_{HH}$ = 7.4 Hz, CH_2), 7.06 (1H, dd, $^3J_{HH}$ = 6.3 and 4.5 Hz, C(5)H), 7.41–7.67 (30H, m, Ph), 8.17–8.26 (2H, m, C(4/6)H) $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 14.4 (s, Me), 56.3 (s, **C**H_2), 117.1 (s, C5), 128.7 (t, $^{1/3}J_{CP}$ = 25.0 Hz, C(1)–Ph), 129.0 (t, $^{3/5}J_{CP}$ = 5.3 Hz, C(3/5)–Ph), 131.6 (t, $^{4/6}J_{CP}$ = 1.1 Hz, C(4)–Ph), 134.2 (t, $^{2/4}J_{CP}$ = 6.3 Hz, C(2/6)–Ph), 149.6 (s, C4), 158.2 (s, C6), 197.1 (s, C2) $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 22.7 (s) *m/z* (MALDI+) 775 $[M]^+$, 513 $[M-PPh_3]^+$.

5.2. trans-Iodo-bis-triphenylphosphine(1-ethyl-pyrimidin-2-ylidene)-palladium(II)-tetrafluoroborate (**3b**)

In a 100 mL Schlenk-flask 1-ethyl-2-iodopyrimidinium-tetrafluoroborate (**2b**) (522 μmol, 1 equiv., 168 mg) and $[Pd(PPh_3)_4]$ (566 μmol, 1.1 equiv., 654 mg) were dissolved in 15 mL of 1,2-dimethoxyethane. The solution was stirred over night and turned its color from colorless to olive-green. After a few minutes a slightly yellow solid started to precipitate. The protruding solution was decanted. The yellow residue was washed with a small amount of diethyl ether and dried in high vacuum to give the yellow solid **3b** (500 μmol, 476 mg, 96%). Anal. Calc. for $C_{42}H_{38}BF_4IN_2P_2Pd$: C, 52.94; H, 4.02; N, 2.94. Found: C, 52.90; H, 4.29; N, 2.79%. $^1H\{^{31}P\}$ NMR (CD_2Cl_2): δ = 1.38 (3H, t, $^3J_{HH}$ = 7.4 Hz, Me), 4.58 (2H, q, $^3J_{HH}$ = 7.4 Hz, CH_2), 7.03 (1H, dd, $^3J_{HH}$ = 6.4 and 4.7 Hz, C(5)H), 7.40–7.66 (30H, m, Ph), 8.17–8.25 (2H, m, C(4/6)H) $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 14.3 (s, Me), 55.6 (s, **C**H_2), 117.1 (s, C5), 128.8 (t, $^{3/5}J_{CP}$ = 5.4 Hz, C(3/5)–Ph), 130.0 (t, $^{1/3}J_{CP}$ = 25.5 Hz, C(1)–Ph), 131.4 (s, C(4)–Ph), 134.5 (t, $^{2/4}J_{CP}$ = 6.1 Hz, C(2/6)–Ph), 149.4 (s, C4), 158.3 (s, C6), 199.5 (s, C2) $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 19.2 (s) *m/z* (MALDI+) 867 $[M]^+$, 605 $[M-PPh_3]^+$.

5.2.1. Crystal data for **3b**

$C_{42}H_{38}IPdN_2P_2BF_4$, M = 952.79 g/mol, triclinic, $P\bar{1}$, a = 14.5572(13) Å, b = 16.7770(15) Å, c = 17.6180(13) Å, α = 87.451(7), β = 74.403(7), γ = 77.766(7), V = 4049.9(6) Å^3, Z = 4, D_{calc} = 1.563 Mg/m^3, μ = 1.350 mm^{-1}, $F(0\,0\,0)$ = 1896, crystal size 0.30 × 0.25 × 0.20 mm^3, T = 293 K, Mo Kα (λ = 0.71073 Å), 4.15 < θ < 27.50°, total of 66 248 reflections, 18 310 independent reflections [R_{int} = 0.0446], completeness to θ = 27.50°: 98.5%, full-matrix least-squares refinement on F^2, 18 310 data, 955 parameters, goodness-of-fit on F^2 = 1.529, R_1 = 0.0595, wR_2 = 0.1344 [$I > 2\sigma(I)$], R_1 = 0.0944, wR_2 = 0.1466 (all data). Largest difference in peak and hole: 1.53/−1.70 e Å^{-3}.

6. Crystal structure determination

Crystals of compounds **3b** suitable for X-ray study were investigated with a Stoe CCD diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). Unit cell parameters were determined by least-squares refinements on the positions of 6041 reflections in the range 6.78° < θ < 16.50°. Lp corrections were applied to all intensity data. The structure was solved by direct methods in the space group $P\bar{1}$. The positions of all non-hydrogen atoms were found *via* Δ*F*-syntheses.

Difficulties during the crystal structure refinement arise from the fact, that there are two crystallographic independent ion pairs in the asymmetric unit. The two cations show only conformational differences in some of the phenyl groups of the triphenylphosphane ligand giving the typical pseudo-symmetry problems. Very strong reflections – suffering a blooding out effect of the CCD detector – are found side by side with weaker super structure reflections. The data collection and data integration strategy was therefore optimized toward a compromise for both groups of reflections. During the refinement process parameter correlations appear depending on which weighting scheme was used. Refinements by full-matrix least-squares calculations on F^2 converged to the indicators above. Anisotropic displacement parameters were refined for all atoms heavier than hydrogen. Idealized bond lengths and angles were used for the CH_3, CH_2 and CH groups; the riding model was applied for their H atoms. Isotropic displacement parameters of the H atoms were kept equal to 150, 120 and 120% of the equivalent isotropic displacement parameters of the parent primary, secondary and "aromatic" carbon atoms, respectively.

Appendix A. Supplementary material

CCDC 747909 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.10.049.

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