Trichloropalladate(II) Complexes with Pyridine Ligands − Molecular Structure and Conformational Analysis of [K(18C6)][PdCl$_3$(py)]

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Dedicated to Professor Karl-Heinz Thiele on the Occasion of his 75th Birthday

Abstract. [K(18C6)]$_2$[Pd$_2$Cl$_6$] (**1**) (18C6 = 18-crown-6) was found to react with pyridines in a strictly stoichiometric ratio 1 : 2 in methylene chloride or nitromethane to yield trichloropalladate(II) complexes [K(18C6)][PdCl$_3$(py*)] (py* = py, **2a**; 4-Bnpy, **2b**; 4-*t*Bupy, **2c**; Bn = benzyl; *t*Bu = *tert*-butyl). The reaction of **1** with pyrimidine (pyrm) in a 1 : 1 ratio led to the formation of the pyrimidine-bridged bis(trichloropalladate) complex [K(18C6)]$_2$[(PdCl$_3$)$_2$-(μ-pyrm)] (**3**). The identities of the complexes were confirmed by means of NMR spectroscopy (^{1}H, ^{13}C) and microanalysis. The X-ray structure analysis of **2a** reveals square-planar coordination of the Pd atom in the [PdCl$_3$(py)]$^-$ anion. The pyridine plane forms with the complex plane an angle of 55.8(2)°. In the [K(18C6)]$^+$ cation the K$^+$ lies outside the mean plane of the crown ether (defined by the 6 O atoms) by 0.816(1) Å. There are tight K···Cl contacts between the cation and the anion (K···Cl1 3.340(2) Å, K···Cl2 3.166(2) Å). To gain an insight into the conformation of the [PdCl$_3$(py)]$^-$ anion, DFT calculations were performed showing that the equilibrium structure (**6eq**) has an angle between the pyridine ligand and the complex plane of 35.3°. Rotation of the pyridine ligand around the Pd−N vector exhibited two transition states where the pyridine ligand lies either in the complex plane (**6TS**$_{\text{pla}}$, 0.87 kcal/mol above **6eq**) or is perpendicular to it (**6TS**$_{\text{per}}$, 3.76 kcal/mol above **6eq**). Based on an energy decomposition analysis the conformation of the anion is discussed in terms of repulsive steric interactions and of stabilizing σ and π orbital interactions between the PdCl$_3$$^-$ moiety and the pyridine ligand.

Keywords: Palladium; Trichloropalladate complexes; *N*-donor ligands; Crystal structure; Quantum chemical calculations

Introduction

In contrast to a large number of neutral palladium(II) complexes of the types [PdX$_2$L$_2$] (X = halogen, L = *N*-donor ligand) and [PdX$_3$L′] (L′ = zwitterionic ligand) [1, 2], only some anionic trihalogenopalladate(II) complexes of the type [PdX$_3$L]$^-$ were reported [1, 3−7]. Few complexes of the latter type have been structurally characterized so far, namely complexes with a benzamidine ligand (PPh$_4$)[PdCl$_3${PhC(NH)(NH$_2$)}] [8], with an *N*-substituted sulfimide ligand (PPh$_4$)[PdBr$_3$(Ph$_2$SNCH$_2$CH$_2$CN)] [9] and those with bridging N$_2$E$_2$ ligands (PPh$_4$)$_2$[{PdX$_3$}$_2$(μ-N$_2$E$_2$-κ^2*N*,*N′*)] (E = S, Se; X = Cl, Br) [10]. However, mono *N*-substituted anionic complexes with simple pyridine or pyrimidine ligands have not been structurally characterized as yet. They are also of interest with respect to their catalytic potential. Thus, the trichloro(pyridine)palladate(II) complex has received attention in view of its application in the catalytic oxidation of ethylene to acetaldehyde in the Wacker process and to 2-chloroethanol in syntheses of asymmetric chlorohydrins [11]. We present here the molecular structure of [K(18C6)][PdCl$_3$(py)] (18C6 = crown ether 18-crown-6) and a DFT study on the conformation of the [PdCl$_3$(py)]$^-$ anion.

Results and Discussion

The crown ether adduct of potassium hexachlorodipalladate(II) [K(18C6)]$_2$[Pd$_2$Cl$_6$] (**1**) [12] was found to react in methylene chloride or nitromethane with pyridines (py, 4-Bnpy, 4-*t*Bupy) in a strictly stoichiometric ratio 1 : 2 to yield the novel crown ether adducts of potassium trichloro(pyridine)palladate(II) complexes [K(18C6)][PdCl$_3$(py*)] (**2a−c**) as yellow-orange powders in yields between 53−69 %. The analogous reaction in a 1 : 1 ratio with a bidentate *N*-donor such as pyrimidine led to the formation of the pyrimidine-bridged bis(trichloropalladate) complex [K(18C6)]$_2$[(PdCl$_3$)$_2$(*μ*-pyrm)] (**3**) (Scheme 1). For comparison of NMR spectroscopic data, with excess of the ligands neutral complexes of the common type [PdCl$_2$L$_2$] (**4a−d**) were obtained. In accordance with data given in literature [13], the IR spectrum of the complex **4a** ($\nu_{\text{Pd-N}}$ = 471 cm^{-1}, m; $\nu_{\text{Pd-Cl}}$ = 356 cm^{-1}, s) gave proof for its *trans* configuration.

The constitution of complexes **2** was confirmed by means of microanalyses and NMR spectroscopy. Coordination of the pyridines to palladium gave rise to a down-field shift of the resonances for C2/C6 and H2/H6 by 3.0−3.8 ppm and by 0.23−0.29 ppm, respectively. Although there are only

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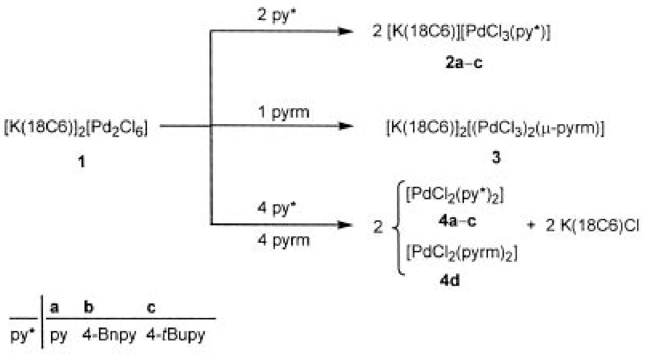

Scheme 1

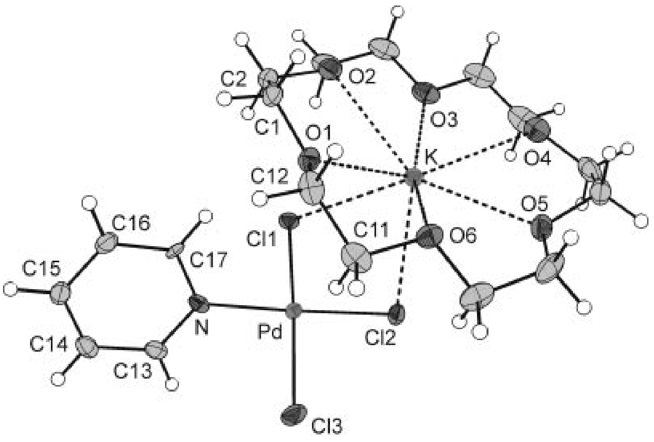

Figure 1 Molecular structure of [K(18C6)][PdCl$_3$(py)] (**2a**), H atoms are omitted for clarity, thermal ellipsoids are drawn with 30 % probability.

Table 1 Selected interatomic distances (in Å) and angles (in °) for [K(18C6)][PdCl$_3$(py)] (**2a**).

Pd−N	2.020(4)	Pd−Cl1	2.312(1)
Pd−Cl2	2.310(1)	Pd−Cl3	2.298(2)
K···Cl1	3.340(2)	K···Cl2	3.166(2)
Pd−N−C13	122.3(4)	Pd−N−C17	119.6(3)
K−Pd−Cl2	55.32(4)	K−Pd−Cl1	59.63(4)
Cl1−Pd−Cl3	176.17(5)	Cl2−Pd−N	176.4(1)
Cl3−Pd−N	88.4(1)	Cl1−Pd−Cl2	89.43(5)
Cl1−Pd−N	90.1(1)	Cl2−Pd−Cl3	92.34(5)

small differences between the NMR spectroscopic data of complexes **2** and the corresponding bis(pyridine)palladium complexes [PdCl$_2$(py*)$_2$] (py* =py, **4a**; 4-Bnpy, **4b**; 4-*t*Bupy, **4c**), a mixture of the complexes **2a** and **4a** exhibited in ^{1}H and ^{13}C NMR spectra two sets of signals. Thus, by means of NMR spectroscopy it can be clearly distinguished in a reaction solution between [K(18C6)][PdCl$_3$(py*)] (**2**) and a mixture of [PdCl$_2$(py*)$_2$] (**4**) with [K(18C6)]Cl.

The symmetric coordination of pyrimidine to two PdCl$_3$ moieties in the complex **3** is clearly established by only three resonances in ^{13}C and ^{1}H NMR spectra due to the chemical equivalence of H4/H6 and C4/C6. On the other hand, the monodentate coordination of pyrimidine in the complex **4d** gives rise to four resonances in ^{13}C and ^{1}H NMR spectra. The coordination induced shifts of H2/H6 and C2/C6 atoms are greater in **3** ($\Delta\delta$(C2/C6) = 3.8−4.3, $\Delta\delta$(H2/H6) = 0.45−0.74) than in **4d** ($\Delta\delta$(C2/C6) = 2.2−2.9, $\Delta\delta$(H2/H6) = 0.34−0.36) and also than in the case of complexes **2a-c**.

From the methylene chloride solution of [K(18C6)]-[PdCl$_3$(py)] (**2a**) well-shaped dark yellow crystals precipitated that proved to be suitable for single-crystal X-ray diffraction analysis. Complex **2a** crystallizes in the non-centrosymmetric monoclinic space group $P2_1$. Crystals of **2a** are composed of discrete molecules without any unusual intermolecular interactions; the shortest distance between non-hydrogen atoms is 3.338(5) Å (Pd···C14′). The molecular structure of complex **2a** is shown in Figure 1; selected structural parameters are given in Table 1.

The Pd atom is square-planar coordinated by three chloro atoms and the nitrogen atom of the pyridine ligand. Deviations from the square-planar coordination are small; the sum of angles around Pd is 360.0° and all angles between neighbored atoms are close to 90° (88.4(1)−92.34(5)°). The angle between the complex plane and the pyridine plane amounts to 55.8(2)°. The Pd−N bond length is 2.020(4) Å. It is only slightly shorter than the median value reported for square-planar palladium complexes with pyridine ligands (median: 2.044, lower/higher quartile: 2.027/2.072, n = 81, n − number of observations). The crown ether 18-crown-6 in the [K(18C6)]$^+$ cation has torsion angles (absolute values) in the ranges 170−179° for the C−O−C−C and 61−66° for the O−C−C−O units. The conformation of the macrocycle is characterized by an alternating sequence of the partial conformation of the O−C−C−O subunits (*ap*, +*sc*, *ap*) and (*ap*, −*sc*, *ap*). An analogous one has been found in the alkene and alkyne complexes of Zeise's salt type [K(18C6)][PtCl$_3$(*cis*-RHC=CHR′)] (R/R′ = Me/Me, Et/Me) [14] and [K(18C6)]-[PtCl$_3$(RC≡CR′)] (R/R′ = Me/Me, Et/Et, Ph/D) [15] as well as in the starting complex [K(18C6)]$_2$[Pd$_2$Cl$_6$] [12]. In contrast, the unhydrated solid 18-crown-6 has three conformationally different O−C−C−O subunits [(*ap*, *ap*, *ap*), (*ap*, +*sc*, *ap*), (*ap*, −*sc*, +*sc*)] [16]. The potassium cation is located 0.816(1) Å outside the mean plane of the crown ether (defined by the six O atoms). It is in a close contact with two chloro ligands of the [PdCl$_3$(py)]$^-$ anion. The K···Cl distances (K···Cl2 3.166(2) Å; K···Cl1 3.340(2) Å) are only slightly longer than those in the solid KCl (3.146 Å) [17]. The mean plane of the crown ether and the complex plane are nearly parallel to each other, with the interplanar angle being only 15.04(9)°. Likely, these cation−anion contacts give rise to a slight elongation of the Pd−Cl1 bond as revealed by the comparison with the Pd−Cl3 bond length (2.312(1) versus 2.298(2) Å).

To gain further insight into the molecular structure of **2a**, quantum chemical calculations on the DFT level of the theory were performed. The calculated equilibrium structure of the complex (**2a**$_{\text{calc}}$) is shown in Figure 2 with selec-

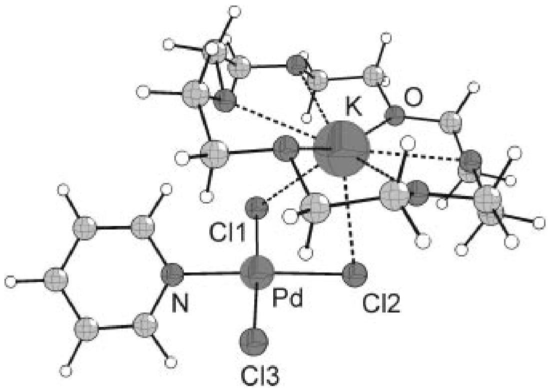

Figure 2 Calculated structure of $[K(18C6)][PdCl_3(py)]$ ($\mathbf{2a}_{calc}$). Selected parameters (distances in Å, angles in °): Pd−Cl1 2.421, Pd−Cl2 2.385, Pd−Cl3 2.404, Pd−N 2.053, K···Cl1 3.731, K···Cl2 3.214; N−Pd−Cl1 89.5, N−Pd−Cl2 176.8, N−Pd−Cl3 88.3, Cl1−Pd−Cl3 173.1.

ted parameters in the figure caption. All characteristic features of the experimental structure were also found in the calculated one. The pyridine ligand forms an angle of 49.7° (exp.: 55.8(2)°) with the complex plane. The conformation of the $[K(18C6)]^+$ cation in $\mathbf{2a}_{calc}$ is the same as that in **2a**. The potassium cation is located 0.558 Å (exp.: 0.816(1) Å) outside the mean plane of the six crown ether oxygen atoms and is in a close contact with two chloro ligands of the $[PdCl_3(py)]^-$ anion (K···Cl: 3.214/3.731 Å; exp.: 3.166(2)/ 3.340(2) Å). The angle between the complex plane and the mean plane of the crown ether is 17.4° (exp.: 15.04(9)°).

After calculating the equilibrium structures of the cation $[K(18C6)]^+$ (**5**) and the anion $[PdCl_3(py)]^-$ (**6**) on the same level of theory, the interaction energy (corrected for the basis set superposition error, BSSE) for the reaction

$$\begin{array}{ccccc} [K(18C6)]^+ & + & [PdCl_3(py)]^- & \rightarrow & [K(18C6)][PdCl_3(py)] \\ \mathbf{5} & & \mathbf{6} & & \mathbf{2a}_{calc} \end{array}$$

was shown to be −68.8 kcal/mol and −69.1 kcal/mol if the zero-point vibrational energies were taken into account.

The equilibrium structure of the anion $[PdCl_3(py)]^-$ (**6eq**) is shown in Figure 3a, selected structural parameters are given in Table 2. Similarly to **2a**/$\mathbf{2a}_{calc}$, the plane of the pyridine ligand is also declined to the complex plane; the interplanar angle was calculated to be 35.3°. This angle proved to be strongly dependent on the method used in the calculations; an angle of 40.7° was calculated in **6**. Differences of these angles between **6eq**/**6** (35.3/40.7°) and $\mathbf{2a}_{calc}$/**2a** (49.7/55.8(2)°) may be caused by the cation-anion interactions.

To gain an insight into this aspect of the structure, the conformational energy of the anion $[PdCl_3(py)]^-$ (**6eq**) in dependence on the $C2-N-Pd-Cl_{cis}$ coordinate (being a measure of the interplanar angle $py/PdCl_3N$, see Figure 3a) has been calculated. Rotation of the pyridine ligand around the Pd−N vector resulted in two different transition states where the pyridine ligand lies either in the complex plane (${\bf 6TS}_{pla}$, interplanar angle $py/PdCl_3N$: 0.4°) or is perpendicular to it (${\bf 6TS}_{per}$, interplanar angle $py/PdCl_3N$: 90.0°). The former one (${\bf 6TS}_{pla}$) is 0.86 kcal/mol above the equilibrium structure and the latter one (${\bf 6TS}_{per}$) 3.71 kcal/mol. These two structures are shown in the Figures 3b and 3c; selected structural parameters are given in Table 2. There was found a pronounced elongation of the Pd−N bond going from the structure with the pyridine ligand perpendicular to the complex plane ${\bf 6TS}_{per}$ (2.045 Å) via the equilibrium structure **6eq** (2.079 Å) to the planar structure ${\bf 6TS}_{pla}$ (2.116 Å). This indicates the presence of increasing (repulsive) steric interactions between the pyridine and the $PdCl_3^-$ moiety in the order ${\bf 6TS}_{per} < {\bf 6eq} < {\bf 6TS}_{pla}$.

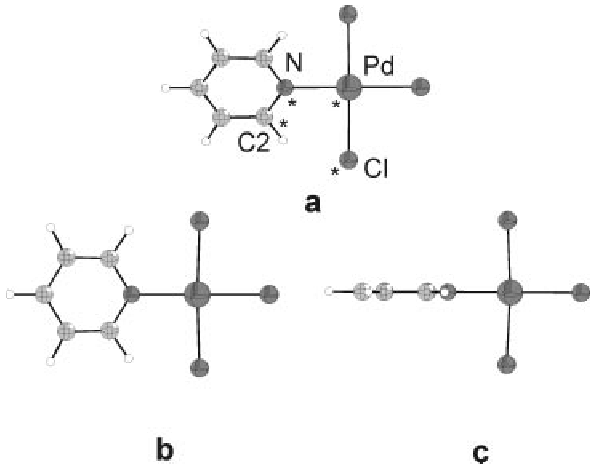

Figure 3 Calculated structures of $[PdCl_3(py)]^-$. a) Equilibrium structure **6eq** (atoms defining the dihedral angle for conformational analysis are marked with asterisks). b) Transition state ${\bf 6TS}_{pla}$. c) Transition state ${\bf 6TS}_{per}$.

Table 2 Calculated structural parameters for $[PdCl_3(py)]^-$: a) Equilibrium structure **6eq**. b) Transition state with pyridine in the complex plane ${\bf 6TS}_{pla}$. c) Transition state with pyridine perpendicular to the complex plane ${\bf 6TS}_{per}$. For comparison the values of the equilibrium structure of $[PdCl_3]^-$ are given.

	6eq	${\bf 6TS}_{pla}$	${\bf 6TS}_{per}$	$[PdCl_3]^-$
Pd−N	2.079	2.116	2.045	
$Pd-Cl_{trans}$	2.319	2.315	2.318	2.280
$Pd-Cl_{cis}$ [a]	2.372	2.376/2.377	2.370	2.311/2.312
$N-Pd-Cl_{trans}$	179.9	179.8	180.0	
$Cl_{cis}-Pd-Cl_{cis}$	178.9	176.5	175.1	165.5
$Cl_{cis}-Pd-Cl_{trans}$ [a]	90.6	88.3	92.5	97.1/97.4

[a] Identical values for the two *cis*-chloro ligands are given only once.

This argumentation is further confirmed by an energy decomposition analysis according to *Morokuma* [18] and *Ziegler* [19], see Ref. [20] for an explanation of the fundamental steps. The results shown in Table 3 suggest that the values of both ΔE_{Pauli} (repulsive) and ΔE_{elstat} (attractive) are in the order ${\bf 6TS}_{pla} < {\bf 6eq} < {\bf 6TS}_{per}$. Although the orbital contribution ΔE_{orb} remains to be approximately constant, the breakdown into energy contributions from σ (A symmetry) and π (B symmetry) interactions makes the follow-

Table 3 Energies and energy decomposition analyses of equilibrium structure and transition states of $[PdCl_3(py)]^-$. All energies are given in kcal/mol

	$6TS_{pla}$	6eq	$6TS_{per}$
Angle (in °) py/$PdCl_3^-$	0.4	35.3	90.0
Energy (rel.)	0.86	0	3.71
ΔE_{prep} ($PdCl_3^-$)	4.63	2.92	1.92
ΔE_{prep} (py)	0.54	0.51	0.35
ΔE_{int}	−26.77	−26.03	−21.07
ΔE_{Pauli}	108.17	115.29	120.51
ΔE_{elstat}	−90.01	−95.40	−97.45
ΔE_{orb} ($\Delta E_\sigma/\Delta E_\pi$)[a]	−44.93 (−32.43/−12.52)	−45.92 (−34.42/−11.50)	−44.13 (−34.98/−9.14)
ΔE[b]	−21.60	−22.60	−18.80

[a] Energy contributions from σ (A symmetry) and π interactions (B symmetry), respectively.

[b] Total bond energy (Pd−N).

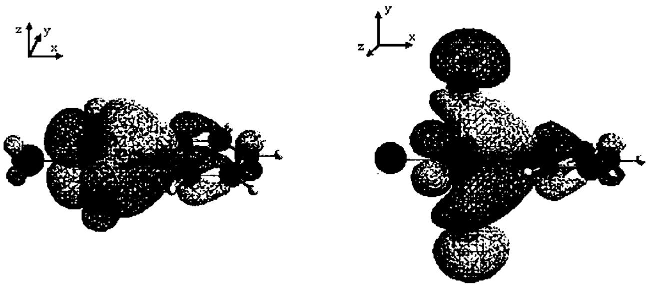

Figure 4 Localized orbitals for $\mathbf{6TS_{pla}}$ (left) and $\mathbf{6TS_{per}}$ (right) showing π-type back-donation into virtual pyridine fragment orbital.

ing clear: *i)* The σ contributions amount to 72−79 %. *ii)* As expected, the shorter the Pd−N distances are, the stronger are the energy contributions from σ interactions ($\mathbf{6TS_{pla}}$ < **6eq** < $\mathbf{6TS_{per}}$). *iii)* The reverse order was found for the π contributions, likely, due to stronger participation of the Pd d_{xy} orbital into π-type interaction with the chloro ligands than the d_{xz} orbital (Figure 4). Thus, the overall stabilizing contribution ΔE_{int} is greater for $\mathbf{6TS_{pla}}$ (−26.77 kcal/mol) and **6eq** (−26.03 kcal/mol) than for $\mathbf{6TS_{per}}$ (−21.07 kcal/mol). On the other hand, the energies to promote the equilibrium structures of the fragments to the geometries and electronic states which they have in the compound $[PdCl_3(py)]^-$ (ΔE_{prep}) show the opposite dependence: $\mathbf{6TS_{per}}$ (2.27 kcal/mol) < **6eq** (3.43 kcal/mol) < $\mathbf{6TS_{pla}}$ (5.17 kcal/mol). The major contribution comes from the distortion of the $PdCl_3^-$ fragment. Overall, the twist between the pyridine ligand and the complex plane in the equilibrium structure seems to be an energetic compromise between repulsive steric interactions (lowest in $\mathbf{6TS_{per}}$) and attractive π interactions (greatest in $\mathbf{6TS_{pla}}$). It remains to be speculative, whether weak C−H···Cl hydrogen bonds [21] between the 2/6-C−H groups (*„ortho"*) and the *cis*-chloro ligands play a significant role in stabilizing the equilibrium structure **6eq** and the planar transition state $\mathbf{6TS_{pla}}$.

Upon inspection of the Cambridge structural database (CSD) it was revealed that other structurally characterized square-planar transition metal complexes of the types $[MCl_3(py^*)]^z$ (**8**) and $[MCl_2(py^*)_2]^z$ (**9**) (py* = pyridine derivative) show in most cases an analogous ligand position, except that the pyridine ligands are 2- or 2/6-substituted. Such pyridine ligands tend to be approximately perpendicular to the complex plane, most likely, owing to steric hindrance caused by the substitution in 2- or 2/6-positions. Thus, in three type **8** complexes, $Q[PtCl_3(py)]$ (Q = NEt_4^+, PPh_3Bn^+) [22] and $[AuCl_3(py)]$ [23], interplanar angles (pyridine/complex plane) between 44 and 58° were observed. About 80 % of all complexes (total 38 entries) of the type $[MCl_2(py^*)_2]^z$ (**9**, M = Pd^{II}, Pt^{II}, Cu^{II}, Cd^{II}, z = 0; Au^{III}, z = 1+) exhibited interplanar angles between 40 and 65°. Only four complexes were found to have the pyridine ligands perpendicular to the complex plane (interplanar angle > 80°). In general, we have to take into consideration that the conformation of the complexes in the crystals may be strongly influenced by packing effects and also by specific intermolecular interactions. Such specific intermolecular interactions can be − depending on the coordination pattern of the pyridine ligands − hydrogen bonds or π−π stacking between aromatic rings and in charged complexes also the cation-anion interactions.

Concluding, novel trichloropalladate(II) and bis(trichloropalladate) complexes with simple mono- and bidentate heterocyclic *N*-donor ligands have been presented. The complex with the pyridine, $[K(18C6)][PdCl_3(py)]$ (**2a**), is the first structurally characterized representative of that type. The quantum chemical analysis of the anion $[PdCl_3(py)]^-$ (**6eq**, $\mathbf{6TS_{pla}}$, $\mathbf{6TS_{per}}$) reveals the factors upon which the conformation of the pyridine ligand with respect to the complex plane is dependent. Most likely, this can be generalized, because similar conformations as in **2a**/**6eq** were found in most of the other square-planar chloro complexes of transition metals with pyridine ligands.

Experimental

Syntheses of complexes were carried out under argon using standard Schlenk techniques whereas the work-up procedures were performed on air. Methylene chloride, nitromethane and diethyl ether were dried (CH_2Cl_2 over CaH_2, CH_3NO_2 over molecular sieve A4, Et_2O over Na−benzophenone) and distilled prior to use. $[K(18C6)]_2[Pd_2Cl_6]$ (**1**) was obtained according to the literature [12]. Microanalyses (C, H, N, Cl) were performed by the microanalytical laboratory of the University of Halle using CHNS-932 (LECO) and Vario EL (elementar Analysensysteme) elemental analyzers. ^1H and ^{13}C NMR spectra were recorded on Varian Gemini 200, VXR 400 and Unity 500 NMR spectrometers. Chemical shifts are relative to C*H*Cl$_3$ (δ 7.24), C*H*DCl$_2$ (δ 5.32) and *C*DCl$_3$ (δ 77.0), *C*D$_2$Cl$_2$ (δ 53.8) as internal references. IR spectra were recorded on a Galaxy FT-IR spectrometer Mattson 5000 using CsBr pellets.

Preparation of [K(18C6)][PdCl₃(py)]* (**2a**−**c**). To a suspension of the crown ether adduct of potassium hexachlorodipalladate $[K(18C6)]_2[Pd_2Cl_6]$ (**1**) (103 mg, 0.1 mmol) in methylene chloride (6 ml) or to a solution of **1** in nitromethane (3 ml) the corresponding pyridine (0.2 mmol) was added. Within a minute a light orange solution was formed. The solution was concentrated (50 % of the volume) by evaporation of the solvent *in vacuo*. Diethyl ether (10 ml) was added resulting in the formation of a yellow-orange precipitate that was filtered off, washed with diethyl ether (15 ml) and dried.

py = py* (**2a**). Yield: 69 mg (58 %). Anal. Found: C, 34.18; H, 4.81; N, 2.05; Cl, 18.06 %. $C_{17}H_{29}Cl_3NO_6KPd$ (595.30). Calc.: C, 34.30; H, 4.91; N, 2.35; Cl, 17.87 %.

^{1}**H NMR** ($CDCl_3$, 400 MHz): δ 3.67 (s, 24H[1], 18C6), 7.18−7.22 (m, 2H, *H3*/*H5*), 7.61−7.66 (m, 1H, *H4*), 8.86−8.88 (m, 2H, *H2*/*H6*). ^{13}**C NMR** ($CDCl_3$, 50 MHz): δ 70.1 (18C6), 124.4 (*C3*/*C5*), 137.5 (*C4*), 153.5 (*C2*/*C6*).

py = 4-Bnpy* (**2b**). Yield: 75 mg (55 %). Anal. Found: C, 41.34; H, 5.41; N, 1.75; Cl, 15.88 %. $C_{24}H_{35}Cl_3NO_6KPd$ (685.42). Calc.: C, 42.06; H, 5.15; N, 2.04; Cl, 15.52 %.

^{1}**H NMR** ($CDCl_3$, 400 MHz): δ 3.65 (s, 24H, 18C6), 3.90 (s, 2H, *CH*$_2$), 6.98−6.99 (m, 2H, *H3*/*H5* of py), 7.07−7.09 (m, 2H, *o-H* of Bn), 7.22−7.30 (m, 1H, *p-H* of Bn, 2H, *m-H* of Bn), 8.69−8.71 (m, 2H, *H2*/*H6* of py). ^{13}**C NMR** ($CDCl_3$, 50 MHz): δ 40.9 (*C*H$_2$), 70.1 (18C6), 124.8 (*C3*/*C5* of py), 127.0 (*p-C* of Bn), 128.9/129.1 (*o*/*m-C* of Bn), 137.6 (*i-C* of Bn), 152.3 (*C4* of py), 153.0 (*C2*/*C6* of py).

py = 4-tBupy* (**2c**). Yield: 90 mg (69 %). Anal. Found: C, 38.53; H, 5.72; N, 2.14; Cl, 16.03 %. $C_{21}H_{37}Cl_3NO_6KPd$ (651.40). Calc.: C, 38.72; H, 5.73; N, 2.15; Cl, 16.33 %.

^{1}**H NMR** ($CDCl_3$, 400 MHz): δ 1.23 (s, 9H, *CH*$_3$), 3.66 (s, 24H, 18C6), 7.15−7.17 (m, 2H, *H3*/*H5*), 8.69−8.71 (m, 2H, *H2*/*H6*). ^{13}**C NMR** ($CDCl_3$, 100 MHz): δ 30.2 (*C*H$_3$), 34.9 (*C*(CH$_3$)$_3$), 70.1 (18C6), 121.7 (*C3*/*C5*), 152.8 (*C2*/*C6*), 162.0 (*C4*).

Preparation of $[K(18C6)]_2[(PdCl_3)_2(\mu\text{-}pyrm)]$ (**3**). $[K(18C6)]_2[Pd_2Cl_6]$ (**1**) (103 mg, 0.1 mmol) was suspended in methylene chloride (3 ml). Then pyrimidine (8.0 mg, 0.1 mmol) was added. Within a few minutes of stirring the brown suspension turned to a dark orange solution. After adding diethyl ether (4 ml) the solution was stored at −40 °C for one day. After that time a yellow-orange microcrystalline precipitate was formed that was filtered off, washed with diethyl ether (15 ml) and dried. Yield: 80 mg (72 %).

Anal. Found: C, 29.96; H, 4.63; N, 2.60; Cl, 18.80 %. $C_{28}H_{52}N_2O_{12}Cl_6K_2Pd_2$ (1112.48). Calc.: C, 30.23; H, 4.71; N, 2.52; Cl, 19.12 %.

^{1}**H NMR** (CD_2Cl_2, 400 MHz): δ 3.70 (s, 48H, 18C6), 7.30 (dt, 1H, ^3J(H5,H4/6) = 5.7 Hz, ^5J(H2,H5) = 1.1 Hz, *H5*), 9.15 (dd, 2H, ^3J(H5,H4/6) = 5.6 Hz, ^4J(H2,H4/6) = 0.6 Hz, *H4*/*H6*), 9.91 (dd, 1H, ^5J(H2,H5) = 1.1 Hz, ^4J(H2,H4/6) = 0.5 Hz, *H2*). ^{13}**C NMR** (CD_2Cl_2, 100 MHz): δ 70.6 (18C6), 121.2 (*C5*), 161.0 (*C4*/*C6*), 163.6 (*C2*).

Preparation of $[PdCl_2(py^*)_2]$ (**4a−d**). To a suspension of **1** (103 mg, 0.1 mmol) in methylene chloride (3 ml) or to a solution of **1** in nitromethane (4 ml) the corresponding pyridine or pyrimidine (0.4 mmol) was added. Within a few minutes of stirring a yellow solution was formed and a yellow precipitate was observed. Diethyl ether (5 ml) was added to accomplish the precipitation and the yellow product was filtered off, washed with diethyl ether (15 ml) and dried.

py = py* (**4a**). Yield: 53 mg (79 %).

^{1}**H NMR** ($CDCl_3$, 400 MHz): δ 7.30−7.34 (m, 4H, *H3*/*H5*), 7.74−7.79 (m, 2H, *H4*), 8.81−8.83 (m, 4H, *H2*/*H6*). ^{13}**C NMR** ($CDCl_3$, 100 MHz): δ 124.9 (*C3*/*C5*), 138.5 (*C4*), 153.3 (*C2*/*C6*). **IR** (CsBr): ν(Pd−Cl) 357, ν(Pd−N) 471 cm^{-1}.

py = 4-Bnpy* (**4b**). Yield: 72 mg (70 %).

^{1}**H NMR** ($CDCl_3$, 400 MHz): δ 3.97 (s, 4H, *CH*$_2$), 7.08−7.12 (m, 4H, *H3*/*H5* of py, 4H, *o-H* of Bn), 7.23−7.33 (m, 2H, *p-H* of Bn, 4H, *m-H* of Bn), 8.63−8.65 (m, 4H, *H2*/*H6* of py). ^{13}**C NMR** ($CDCl_3$, 100 MHz): δ 41.0 (*C*H$_2$), 125.2 (*C3*/*C5* of py), 127.2 (*p-C* of Bn), 129.0/129.1 (*o*/*m-C* of Bn), 137.2 (*i-C* of Bn), 152.8 (*C4* of py), 153.6 (*C2*/*C6* of py).

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

Empirical formula	$C_{17}H_{29}Cl_3NO_6KPd$
Formula weight	595.26
Crystal system/space group	monoclinic/$P2_1$
a/Å	11.530(5)
b/Å	8.453(1)
c/Å	12.705(3)
β/°	101.26(4)
V/Å^3	1214.4(6)
Z	2
ρ/g cm^{-3}	1.628
μ(Mo-Kα)/mm^{-1}	1.296
F(000)	604
Scan range/°	$2.18 < \theta < 25.85$
Reciprocal lattice segments h, k, l	$-14 \rightarrow 14$, $-9 \rightarrow 10$, $-15 \rightarrow 15$
Reflections collected	9433
Reflections independent	4413 (R_{int} = 0.0570)
Data/restraints/parameters	4413/1/262
Goodness-of-fit on F^2	1.000
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0324, 0.0691
$R1$, $wR2$ (all data)	0.0414, 0.0749
Largest diff. peak and hole/e Å^{-3}	0.476 and −0.833

py = 4-tBupy* (**4c**). Yield: 64 mg (72 %). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.28 (s, 18H, *CH*$_3$), 7.27−7.29 (m, 4H, *H3*/*H5*), 8.65−8.67 (m, 4H, *H2*/*H6*). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 30.2 (*C*H$_3$), 35.1 (*C*(CH$_3$)$_3$), 122.2 (*C3*/*C5*), 152.6 (*C2*/*C6*), 163.4 (*C4*).

py = pyrm* (**4d**). Yield: 61 mg (88 %).

^{1}**H NMR** (CD_2Cl_2, 400 MHz): δ 7.32−7.35 (m, 2H, *H5*), 8.69−8.71 (m, 2H, *H4*), 9.05−9.07 (m, 2H, *H6*), 9.51 (s, 2H, *H2*). ^{13}**C NMR** (CD_2Cl_2, 100 MHz): δ 121.7 (*C5*), 158.0 (*C4*), 160.1 (*C6*), 161.5 (*C2*).

X-ray structure determination

Single-crystal X-ray diffraction analysis of **2a** was performed at 220(2) K on a STOE-IPDS diffractometer for a single crystal of **2a** with dimensions 0.42 × 0.09 × 0.02 mm, using Mo−K$_\alpha$ radiation (λ = 0.71073 Å, graphite monochromator). A summary of the crystallographic data, the data collection parameters, and the refinement parameters is given in Table 4. Absorption correction was applied numerically (T_{min}/T_{max} 0.86/0.98). The structure was solved by direct methods with SHELXS-97 [24]. The structure refinement was carried out by full-matrix least-squares procedures on F^2 (SHELXL-97 [24]) for all reflections. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were added to the model in their calculated positions (riding model) and refined isotropically. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Center (CCDC) as Supplementary Publication No. CCDC-261953 (**2a**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. (fax, (internat.) +44-1223-336033; e-mail, **deposit@ccdc.cam.ac.uk**.

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[1] The number of protons for 18C6 was found to be slightly higher in all cases.

Computational Details

DFT calculations of the compounds **$2a_{calc}$**, **5** and **6** were carried out by the Gaussian98 program package [25] using the hybrid functional B3LYP [26] and the basis sets SDD as implemented in the Gaussian program. All systems have been fully optimized without any symmetry restrictions. The resulting geometries were characterized as equilibrium structures by the analysis of the force constants of normal vibrations [27]. The interaction energy was corrected for basis set superposition errors (BSSE) that were estimated with counterpoise type calculations [28]. The conformational analysis of the $[PdCl_3(py)]^-$ anion was performed by means of the Amsterdam Density Functional package ADF (Release 2004.01) [29] using a generalized gradient approximation (GGA; mPWx + PW91c) in addition to the local density approximation (LDA) [30, 31]. Use was made of the frozen core approximation (coretyp = small) and triple-zeta basis sets extended with a polarization function. Relativistic effects have been considered by the zero order approximation (ZORA) as implemented in the ADF program package. These optimizations were also performed without any symmetry restrictions. The resulting geometries were characterized as equilibrium structure (**6eq**) and transition states (**$6TS_{pla}$**, **$6TS_{per}$**), respectively, by the analysis of the force constants of normal vibrations. The energy decomposition analysis was performed as implemented in the ADF program package. The breakdown of the ΔE_{orb} into energy contributions from σ symmetry (A symmetry, neglecting a small contribution from δ symmetry) and π (B) symmetry was done in the symmetry group C_2. Orbitals were localized as implemented in the ADF package according to the Boys-Foster-Method [32]. The canonical orbitals of different irreducible representations were localized seperately (symmetry group C_{2v}).

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