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Bis(4-methylthiazolyl)isoindoline (4-Mebti) Complexes of Palladium: Cationic $[Pd^{II}(4\text{-Mebti})L]^+$ Species with a L = Neutral Group XIV or Group XV Donor Ligand

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In Memory of Professor Kurt Dehnicke

Keywords: BAI ligands; Palladium; Cationic complexes; Group 14 donors; Group 15 donors

Abstract. Ligand exchange has been studied on the chlorido palladium(II) complex of the bis(4-methylthiazolylimino)isoindoline ligand, [Pd(4-Mebti)Cl], with a number of neutral group XIV and group XV donor ligands in the presence of the sodium salt of tetrakis[3,5-bis(trifluoromethyl)phenyl]borate $NaB(Ar^F)_4$. Seven new cationic compounds with L = PMe_3, tBuNH$_2$, PhNH$_2$, py, 2,6-Me$_2$py, MeCN and MeNC were obtained as $B(Ar^F)_4^-$ salts, and were characterized by analytic, spectroscopic and crystallographic means. Further attempts to observe ligand exchange reactions with either the softer $AsMe_3$ or $SbMe_3$ donor ligands or with different carbenes were unsuccessful and led to decomposed material or to mixtures of different compounds. Most of the crystallographically characterized complexes have been found to reside in a pseudoplanar conformation regardless of the size or cone angle of the external donor ligand. The derivatives carrying an sp^2-type donor atom (L = py, 2,6-Me$_2$py), however, adopt helical forms in the solid state. ^{1}H NMR and UV/Vis spectroscopic data suggest that this helicity is also present in solution. The expected chirality, however, could not be observed due to the lack of diastereotopic ligand protons.

Introduction

Palladium(II) complexes with *N* donor chelate ligands have received much attention over the last decades. Cationic *N* donor chelate complexes and organometallics of divalent palladium have found many uses in academic as well as in applied chemistry. Prominent examples are found in the polymerization or oligomerization of alkenes[1] and in alkene/CO copolymerization reactions,[2] which are successfully catalyzed by activated palladium complexes with diimine or other *N*,*N* chelate ligands, and which yield a plethora of functional polymers with specialized and commercially interesting properties.

A *N*,*N*,*N* ligand with a planar and conjugated backbone in combination with steric encumbrance at the fourth position of a square may be considered to provide for a steric situation around a palladium(II) ion incompatible with an overall flat complex structure. In the course of our investigations on strained palladium compounds with such meridional tridentate ligands we have discovered, that the steric influence of α,ω-situated methyl groups leads to non-planar distortion modes and/or an increased reactivity, depending on the chelate ligand used. For α,ω-dimethyltri pyrrin (trpy) complexes of palladium[3] two different conformational states have been observed, denoted "pseudoplanar" and "helical", as shown in Figure 1. Neutral as well as anionic co-ligands, L and X, respectively, possess the ability to distort the complex in either of the two forms, and in one case an equilibrium between the two conformers has been observed. α,ω-Me$_2$bpi ligands (bpi = bis(pyridylimino)isoindoline[4]), on the other hand, are bound by palladium(II) in a strained manner only, if further alkyl groups block intramolecular reactions.[5] Otherwise the *N*,*N*,*N* coordination of the chelate ligand is observed in short-lived kinetic products. Within several minutes, and in particular in the presence of additional palladium acetate, these intermediates form thermodynamically stable products by rotation of one of the pyridine rings and C(sp^2)–H activation.[6] This process does not occur for α,ω-Me$_2$bti ligands (bti = bis(thiazolylimino)isoindoline[7]), which have so far been observed to form exclusively pseudoplanar structures with anionic and with neutral co-ligands. C(sp^3)–H activation and *S* coordination can, however, be enforced if sterically more demanding tert-butyl groups are introduced.[8] Figure 1 summarizes these different findings with the closely related trpy, bpi and bti systems. We have now extended our study and investigated cationic 4-Mebti complexes of palladium(II) with group XIV and group XV donor co-ligands (4-Mebti = bis(4-methylthiazolylimino)isoindoline), and we describe here the preparation as well as the solid state and solution structures of seven new complexes.

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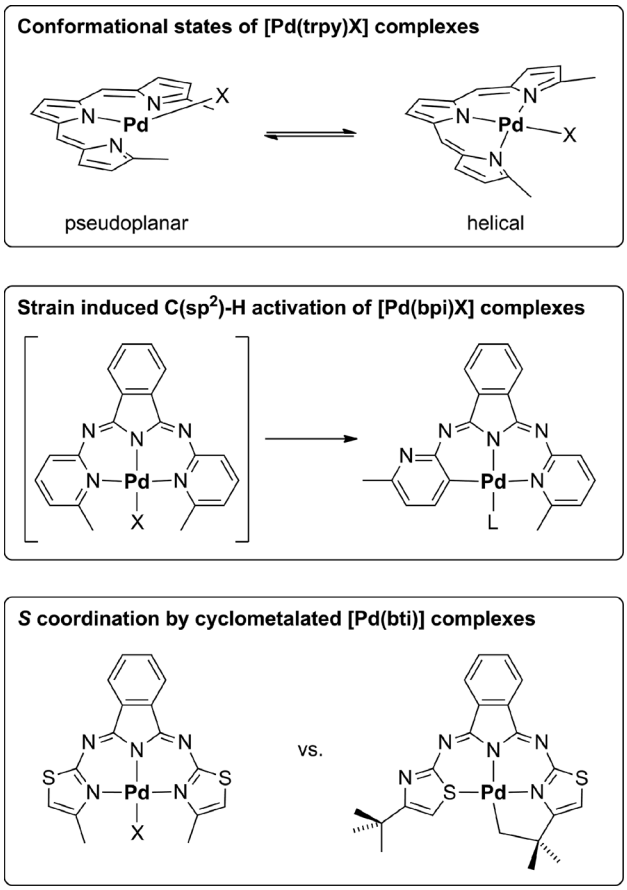
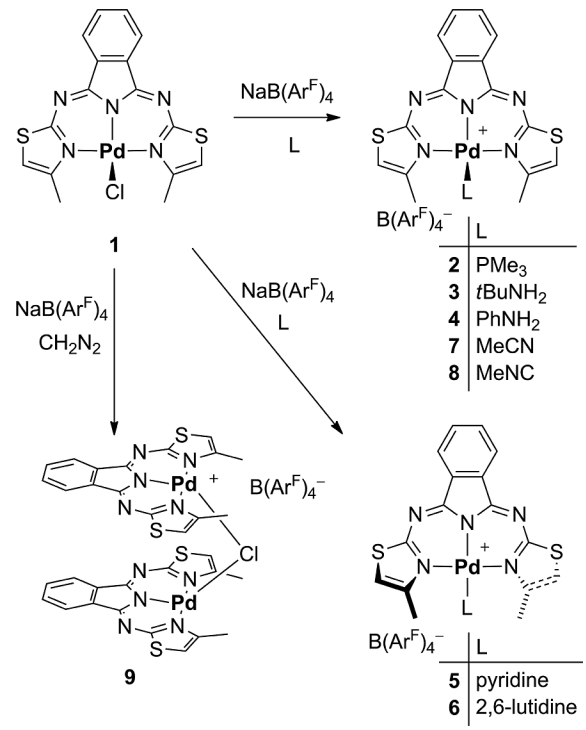


Figure 1. Schematic presentation of the behaviour of strained palladium(II) complexes with structurally-related *N*,*N*,*N* chelate ligands.

Results and Discussion

The preparation of cationic palladium(II) complexes with the 4-Mebti ligand can be carried out by a two-step procedure as described in the foregoing study.[7b] Starting from the chlorido complex [Pd(4-Mebti)Cl] (**1**)[9] (Scheme 1) the anion is partially exchanged by treatment with $NaB(Ar^F)_4$ (sodium salt of tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) in either dichloromethane or toluene solution for five minutes. Subsequently, this reaction mixture is treated with the donor ligand of choice. The amount of co-ligand and the choice of solvent are used to optimize the conditions in each case. Successful preparations were achieved with most of the small *N* donor ligands, and with the strong-field ligands PMe_3 and MeNC. Attempts with the larger and softer ligands NMe_3, PEt_3, *t*$BuPH_2$, $AsMe_3$ and $SbMe_3$ were unsuccessful und led to decomposed material, palladium metal deposition and/or product mixtures. The use of carbon donor ligands, i.e. of CO and of different carbenes or carbene precursors (1-*n*-butyl-3-methyl-imidazolin-2-ylidene, bis(4-methylphenyl)diazomethane ($(4\text{-}MeC_6H_4)_2CN_2$), and diazomethane ($CH_2N_2$)) results either in the formation of the dinuclear complex **9**[9] (Scheme 1), or in untraceable product mixtures. This result is in contrast to the successful preparation of palladium(II) diarylcarbene complexes with the tripyrrin ligand which we reported about some years ago. In addition, treatment with an excess of PMe_3 does not result in the formation of a pentacoordinate palladium(II) complex similar to the $[(trpy)Pd(PMe_3)_2]^+$-species observed earlier.[3c],[d],[e] All isolated products **2**–**8** thus display the typical flat, tetracoordinate structure expected for palladium(II) complexes with a $4d^8$ configuration, and could be analyzed and characterized spectroscopically by optical and magnetic resonance methods. Scheme 1 summarizes the outcome of the study.



Scheme 1. Overview of ligand exchange reactions performed in this study.

Single crystals for X-ray crystallographic investigations have been obtained at –20 °C from the seven substances **2**–**8** by the diffusion method, with **7** crystallizing in two different systems from toluene/*n*-pentane (**7**) and from dichloromethane/*n*-pentane (**7'**). The $B(Ar^F)_4^-$ anions present in the crystal lattices show occasional disorder with respect to the rotation of the CF_3 groups. These positions have been treated with restraints and refined in reasonable split-atom models. Crystallographic data and selected molecular parameters are summarized in Table 1, Table 2, and Table 3, respectively.

The PMe_3 complex **2** crystallizes free of solvent in the space group $P\bar{1}$ with $Z = 2$. The molecular structure of the cation of **2** reveals the expected pseudoplanar conformation of the coordination unit (Figure 2), with characteristic angles N1–Pd–N5 of 164.63(9)° and N3–Pd–P of 142.69(6)°. These angles are the steepest found in the whole series and reflect the steric repulsion and the large *van der Waals* radius of the third row phosphorus atom. The displacement of the *N*,*N*,*N*,*P* coordination environment of the palladium atom from a planar arrangement is also reflected in an enlarged Pd–N3 bond length of 2.036(2) Å, whereas the Pd–P bond shows no particular elongation. This observation is unique in the series of cationic

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Table 1. Selected crystallographic data for [Pd(4-Mebti)L][$B(Ar^F)_4$] complexes **2**–**5**.

L Compound	PMe_3 **2**	$tBuNH_2$ **3**	$PhNH_2$ **4**	py **5**
Formula	$C_{51}H_{33}BF_{24}N_5PPdS_2$	$C_{52}H_{35}BF_{24}N_6PdS_2$	$C_{54}H_{31}BF_{24}N_6PdS_2$	$C_{53}H_{29}BF_{24}N_6PdS_2$
M_r /g·mol^{-1}	1384.12	1381.23	1401.22	1397.19
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a /Å	13.400(2)	12.5785(9)	13.294(2)	16.764(2)
b /Å	14.435(2)	18.991(1)	13.803(2)	19.582(3)
c /Å	14.721(2)	23.321(2)	16.505(2)	20.554(3)
α /°	73.72(2)	90.00	67.13(1)	71.55(1)
β /°	86.04(2)	97.655(9)	87.45(1)	69.25(1)
γ /°	88.65(2)	90.00	88.55(2)	77.21(1)
V /Å^3	2726.6(7)	5521.3(6)	2787.7(6)	5940(1)
Z	2	4	2	4
$d_{calcd.}$ /g·cm^{-3}	1.686	1.662	1.669	1.530
Cryst. size /mm	0.40 × 0.32 × 0.23	0.19 × 0.15 × 0.13	0.19 × 0.19 × 0.14	0.33 × 0.30 × 0.17
μ /mm^{-1}	0.571	0.536	0.530	0.501
2θ limits /°	4.1–51.9	3.9–52.22	4–50	3.5–50
measured	26997	43452	24190	45264
independent	9964	10851	9240	20769
observed[a)]	7847	6090	5327	16042
parameters/ restraints	855/0	893/0	881/0	1683/78
$R1$[b)] all data	0.0470	0.0870	0.0857	0.0682
w$R2$[c)]	0.0850	0.0854	0.0774	0.1392
max./ min. peak /e·Å^{-3}	0.602 / –0.522	0.550 / –0.579	0.954 / –0.548	1.019 / –1.295

a) Observation criterion: $I > 2\sigma(I)$. b) $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. c) w$R2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 2. Selected crystallographic data for [Pd(4-Mebti)L][$B(Ar^F)_4$] complexes **6**–**8**.

L Compound	2,6-Me_2py **6**	MeCN[a)] **7**	MeCN[b)] **7'**	MeNC **8**
Formula	$C_{55}H_{33}BF_{24}N_6PdS_2$	$C_{50}H_{27}BF_{24}N_6PdS_2$	$C_{51}H_{29}BCl_2F_{24}N_6PdS_2$	$C_{51}H_{29}BCl_2F_{24}N_6PdS_2$
M_r /g·mol^{-1}	1415.24	1349.11	1434.07	1434.07
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a /Å	26.257(3)	12.94(1)	10.019(1)	10.021(1)
b /Å	36.732(3)	15.68(2)	14.511(2)	14.527(2)
c /Å	15.963(1)	17.85(1)	20.615(2)	20.684(2)
α /°	90	96.5(2)	104.90(1)	105.17(1)
β /°	114.61(1)	106.6(1)	103.47(1)	103.63(1)
γ /°	90	108.7(1)	90.89(2)	90.86(2)
V /Å^3	13997(2)	3202(6)	2807.8(6)	2814.8(6)
Z	8	2	2	2
$d_{calcd.}$ /g·cm^{-3}	1.343	1.401	1.696	1.650
Cryst. size /mm	0.43 × 0.32 × 0.07	0.29 × 0.15 × 0.04	0.33 × 0.24 × 0.21	0.47 × 0.31 × 0.11
μ /mm^{-1}	0.430	0.465	0.621	0.608
2θ limits /°	4–51.66	3.54–52.1	4.02–52.08	4.04–52.16
measured	66208	31672	27773	27967
independent	12790	11708	10250	10322
observed[c)]	8624	7149	7275	7129
parameters/ restraints	919/0	788/0	843/0	899/6
$R1$[d)] all data	0.0715	0.0801	0.0687	0.0661
w$R2$[e)]	0.1129	0.1122	0.1148	0.0952
max./ min. peak /e·Å^{-3}	0.479 / –0.338	0.760 / –0.402	0.941 / –0.568	0.813 / –0.618

a) From toluene. b) From dichloromethane. c) Observation criterion: $I > 2\sigma(I)$. d) $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. e) w$R2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

$[Pd(4\text{-Mebti})L]^+$ species from this and the foregoing study.[7b] In all other cases the bond to the central nitrogen donor atom is the shortest metal-*N* donor bond due to the localization of negative charge at the N3 position of the deprotonated 4-Mebti ligand. The situation is very similar to the findings earlier reported on related palladium tripyrrin chelates,[3c],[e] although the tripyrrin ligand is more capable of delocalizing the negative charge than the bti ligand. For two [(α,ω-Me_2trpy)Pd(PMe_3)] cations, Pd–P bond lengths of 2.314(1) Å and 2.3122(7) Å were observed, compared to 2.3087(8) Å for **2**, and the Pd–N bond lengths to the central and the peripheral nitrogen atoms are 2.053(2) Å/ 2.079(2) Å and 2.020 Å/ 2.043 Å (mean values) for the tripyrrin complexes, and 2.036(2) Å and 2.018 Å (mean value) for the bti derivative **2**, respectively. These data show that steric interactions govern the structure of these palladium chelates, rather than electronic ones.

Table 3. Selected bond lengths, distances /Å and angles /° for [Pd(4-Mebti)L][B(Ar^F)$_4$] complexes **2**–**8**.

L	PMe_3	$tBuNH_2$	$PhNH_2$	py		2,6-Me_2py	MeCN[a]	MeCN[b]	MeNC
Compound	**2**	**3**	**4**	**5**		**6**	**7**	**7'**	**8**
				cation I	cation II				
Pd–N1	2.026(2)	2.029(3)	2.028(3)	2.066(3)	2.048(3)	2.056(3)	2.041(5)	2.044(3)	2.038(3)
Pd–N3	2.036(2)	1.988(3)	1.974(3)	1.973(3)	1.969(3)	1.969(3)	1.961(4)	1.969(3)	2.000(3)
Pd–N5	2.010(2)	2.031(3)	2.034(4)	2.061(3)	2.056(3)	2.054(3)	2.046(4)	2.055(3)	2.057(3)
Pd–D[c]	2.3087(8)	2.097(3)	2.107(3)	2.023(3)	2.031(3)	2.064(3)	2.026(5)	2.040(3)	1.969(4)
N1–Pd–N3	88.75(9)	89.0(1)	89.2(1)	88.5(1)	88.1(1)	87.0(1)	88.6(2)	89.1(1)	88.6(1)
N1–Pd–N5	164.63(9)	164.9(1)	168.3(2)	175.8(1)	174.8(1)	174.3(1)	167.1(1)	166.6(1)	166.5(1)
N1–Pd–D[c]	97.19(6)	96.6(1)	89.8(1)	92.2(1)	91.2(1)	93.7(1)	92.8(2)	91.8(1)	92.4(1)
N3–Pd–N5	88.40(9)	89.4(1)	89.8(1)	87.3(1)	87.5(1)	87.3(1)	90.3(2)	89.6(1)	89.4(1)
N3–Pd–D[c]	142.69(6)	152.5(1)	157.3(2)	177.3(1)	179.0(1)	179.2(1)	158.1(1)	159.2(1)	159.3(1)
N5–Pd–D[c]	94.21(6)	91.7(1)	95.6(1)	92.0(1)	93.3(1)	92.0(1)	93.0(2)	94.2(1)	94.2(1)
C1···C16	4.327(6)	4.423(5)	4.561(7)	5.941(7)	5.964(8)	5.966(6)	4.53(1)	4.557(7)	4.607(6)
C1···D[c]	3.503(4)	3.216(5)	2.981(6)	2.973(6)	2.975(7)	2.982(5)	2.966(8)	2.955(6)	2.966(6)
C16···D[c]	3.403(4)	3.065(5)	3.027(7)	2.975(6)	2.995(7)	2.985(5)	2.932(8)	2.930(5)	2.925(5)

a) From toluene. b) From dichloromethane. c) D = P1 for **2**; D = N6 for **3**–**7**; D = C17 for **8**.

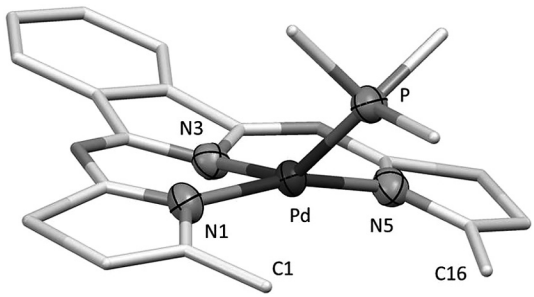
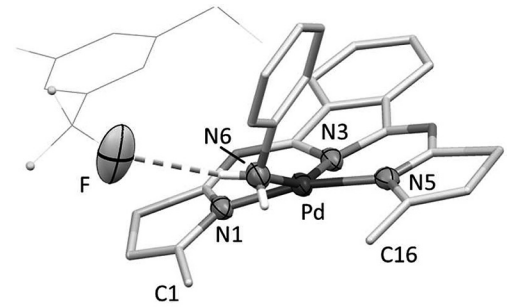


Figure 2. Molecular structure of the [Pd(4-Mebti)(PMe_3)]$^+$ cation of **2**.



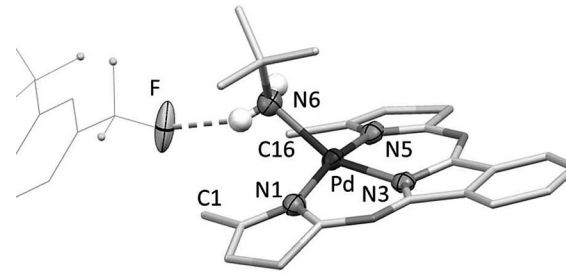


Figure 3. Molecular structures of the [Pd(4-Mebti)($tBuNH_2$)]$^+$ cation of **3** (bottom) and of the [Pd(4-Mebti)($PhNH_2$)]$^+$ cation of **4** (top). Weak hydrogen bonding to a fluorine atom of the B(Ar^F)$_4^-$ anion is indicated in both cases.

Two primary amines, *tert*-butylamine and aniline, were successfully coordinated to the [Pd(4-Mebti)]$^+$ fragment to yield the amine complexes **3** and **4**. Both compounds crystallize free of solvent molecules and were analyzed in the space group $P2_1/c$ with $Z = 4$ (**3**), and $P\bar{1}$ with $Z = 2$ (**4**). Both amine derivatives reside in the pseudoplanar conformation as depicted in Figure 3, and show the expected short central and long peripheral Pd–N bond lengths within the [Pd(4-Mebti)]$^+$ complex fragment (Table 3). The situation resembles the findings made earlier on a *tert*-butylamine complex of a (α,ω-Me_2trpy)Pd fragment,[3c] with the marked difference, that the polarized NH protons of **3** and **4** show weak hydrogen bonding to fluorine atoms of the B(Ar^F)$_4^-$ counterions. Such a behavior has not been observed so far within this class of palladium chelates. In all earlier instances,[3c,7b] the potential H-bridge donors of the palladium bound ligands have been isolated by encapsulation in non-polar confinements, which were build up either by the aryl rings of the anion, or by the co-ligand and ligand terminal methyl groups. The N–H···F hydrogen bonds found in **3** and **4** are, however, very weak as can be estimated from the rather long N···F distances of about 3.23 Å and 3.20 Å, respectively.

The compounds **5** and **6** with the *N* heterocyclic co-ligands pyridine (py) and lutidine (2,6-Me_2py) crystallized in the space group $P\bar{1}$ with $Z = 4$, and $C2/c$ with $Z = 8$, respectively, as solvates. Due to severe disorder these solvent molecules were removed using the SQUEEZE command in PLATON.[10] Two crystallographically independent cations with very similar structural parameters have been observed in the unit cell of the py derivative **5** (Table 3), of which only cation I is described further in detail. Figure 4 illustrates the molecular structures of the two complexes **5** and **6**, which are the first ever observed 4-Mebti species residing in the helical conformation.

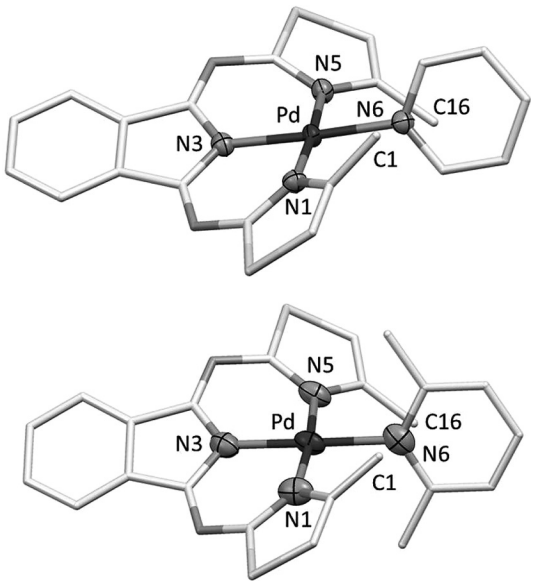


Figure 4. Molecular structures of one of the crystallographically independent forms of the $[Pd(4\text{-Mebti})(py)]^+$ cation of **5** (top) and of the $[Pd(4\text{-Mebti})(2,6\text{-}Me_2py)]^+$ cation of **6** (bottom).

The metrics of the PdN_4 coordination subunits of **5** and **6** deviate characteristically from those of the pseudoplanar derivatives. The Pd–N bonds to the peripheral N1 and N5 donor atoms are slightly elongated by about 0.02 Å, and the N3–Pd–N6 and N1–Pd–N5 angles are close to 180° with deviations of less than 6°. The helical conformation of the 4-Mebti ligand resembles much the ruffling conformation observed in many porphyrinoid macrocycles and leads to an increase of the accessible space between the terminal methyl groups. Therefore, the distance between these methyl group carbon atoms C1 and C16, as well as the angle between the mean-square planes of the juxtaposed C_3NS heterofivering moieties are meaningful measures for the degree of helicity in these compounds. For **5** and **6**, C1···C16 distances of 5.941(7) Å and 5.966(6) Å, and a rotational twist of about 51° and 55° are observed, respectively. Apparently these data are very similar and do not reflect the significant increase in steric bulk by the introduction of the 2,6-situated methyl groups in the pyridine co-ligand upon going from **5** to **6**. These methyl groups are obviously directed away from the $[Pd(4\text{-Mebti})]^+$ complex fragment and point into "free space", so that no significant changes in the intramolecular metrics are necessary to host the lutidine moiety.

An interesting comparison can be made to two examples of earlier described helical (trpy)Pd compounds. The degree of helical distortion of (trpy)Pd species with the bis(4-methylphenyl)carbene[3d] and the thiocyanate[7b] co-ligand is quantified by slightly longer C1···C16 distances of 6.34(1) Å and 6.05(1) Å, as well as by larger rotational twists of the C_4N heterofivering moieties of 76° and 71°, respectively. These values account for a more flexible ligand backbone of the trpy ligand, which contrasts the larger degree of electronic π-conjugation between the different heterocyclic substructures, but may be explained by the smaller imino bridges of the 4-Mebti ligand, as compared to the methine subunits of tripyrrins. As before, steric arguments appear more important for the description of the structural features of these systems than do electronic ones.

In solution, the cationic species **5** and **6** appear to retain the helical conformation. ^1H NMR spectroscopic measurements reveal resonance signals for the terminal methyl group protons of **5** and **6** at 1.02 and 1.08 ppm, respectively, whereas for the pseudoplanar derivatives typical values between 2.6 and 2.9 ppm are observed. The high-field shift of the former signals may be explained by the deshielding influence of the pyridine ring current if the pyridine moiety is located right inbetween the two methyl groups. In addition, the distorted ligand π-system of the helical conformation should induce a red-shift in the lowest energy absorption of the optical spectra. Such a shift of about 37 and 51 nm is in fact observed for **5** and **6**, respectively. In contrast, the optical absorption spectra of the pseudoplanar **2**, **3**, **4**, **7**, and **8** are almost indistinguishable and consist of broad and rather unstructured bands with maxima of 447–451 nm. The question, whether a racemization process transforms the two different helical enantiomers into each other in solution, could not be answered unambiguously, mainly due to the lack of diastereotopic protons at the 4-Mebti ligand.

The derivatives **7** and **8** with the isomeric acetonitrile and methylisocyanide co-ligands crystallize as solvates in the space group $P\bar{1}$ with $Z = 2$. The solvent molecules in crystals of **7** obtained from a toluene solution are highly disordered and were removed, as before, using the SQUEEZE command in PLATON.[10] From dichloromethane solutions, isomorphic crystals of **7'** and **8** grew with one molecule of dichloromethane per formula unit. The molecular structures of cationic $[Pd(4\text{-Mebti})L]^+$ complexes **7**, **7'** and **8** are of very similar shape. Figure 5 illustrates these results.

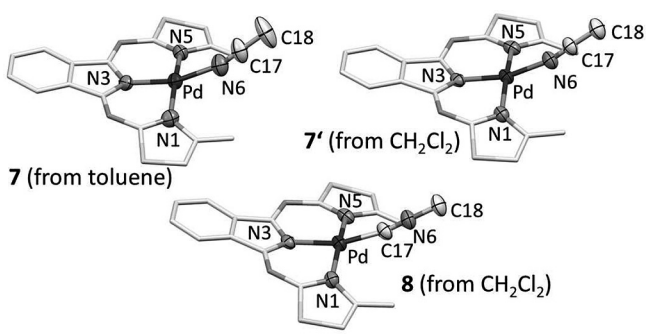


Figure 5. Molecular structures of the $[Pd(4\text{-Mebti})(MeCN)]^+$ cation of **7** (top; left side: crystallized from toluene, right side: crystallized from dichloromethane) and of the isomeric $[Pd(4\text{-Mebti})(MeNC)]^+$ cation of **8** (bottom).

From an electronic point of view, the axes N3–Pd–N6–C17–C18 for **7**, **7'** and N3–Pd–C17–N6–C18 for **8** should be linear, or almost linear. In fact, the intramolecular strain imposed by the presence of the terminal methyl groups of the 4-Mebti ligand leads to deviations from this idealized linearity which can be analyzed as tilting and bending distortions, i.e. deviation of the N3–Pd–N6/C17 and of the Pd–N6/C17–C17/N6 angles

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from 180°. The analyses show an almost identical tilting of 21.9°, 20.8° and 20.7°, but a variation of the bending of 17.3°, 14.3° and 11.8°, respectively, for **7**, **7'** and **8**. In addition, the shape of the MeCN and the MeNC ligands is not perfectly linear but deviates from 180° by 1.6° (**7**), 3.0° (**7'**) and 3.1° (**8**). A comparison can be made with an analogous complex $[Pd(trpy)(MeNC)]^+$ for which a tilting of 20.9°, a bending of 13.3°, and a deviation from methylisocyanide linearity of 3.1° has been reported.[7b]

Whereas a differentiation between the MeCN and MeNC ligands by the bond angles discussed above is not successful, a bond lengths analysis provides clear evidence. The stronger *C* donor atom of the MeNC ligand binds more tightly to the palladium atom of the $[Pd(4\text{-Mebti})]^+$ fragment then the nitrogen atom of the acetonitrile ligand. In addition, the Pd–N3 bond *trans* to this interaction is elongated by the stronger *trans* influence of the isocyanide (Table 3). A similar trend has been observed before within a series of tetracoordinate $[(trpy)CoL]^+$ chelates.[11]

Conclusions

We described the interaction of the cationic $[Pd(4\text{-Mebti})]^+$ complex fragment with several group XIV and group XV donor ligands. Formation and successful isolation of the product complexes $[Pd(4\text{-Mebti})L][B(Ar^F)_4]$ was achieved for several medium size and small *N* donor ligands as well as for the small strong field ligands PMe_3 and MeNC. Larger *N* donor ligands, larger group XV homologues and different carbene type ligands on the other hand did not result in isolable products. Seven new complexes were crystallographically characterized and emphasized the known preference of the $[Pd(4\text{-Mebti})]^+$ complex fragment to reside in a pseudoplanar conformation. In the cases of pyridine and 2,6-lutidine co-ligands the first 4-Mebti complexes of palladium with helical conformation were observed. This conformation is present in the solid state as well as in solution and could be detected by optical and NMR spectroscopy.

Experimental Section

Materials and Methods: Reagents were purchased from commercial sources and used without further purification. Solvents were dried by conventional methods and stored under argon. The preparation of the cationic complexes was performed using standard Schlenk techniques. [Pd(4-Mebti)Cl] **1**,[9] sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate ($NaB(Ar^F)_4$[12]), trimethylphosphane and triethylphosphane (PMe_3 and PEt_3[13]), trimethylstibane ($SbMe_3$[14,15]), methylisocyanide (MeNC[16]), diazomethane (CH_2N_2[17]), and bis(4-methylphenyl)diazomethane ($(4\text{-}MeC_6H_4)_2CN_2$[18]) were prepared according to literature methods. NMR spectra were recorded with a Bruker Avance 300 or DRX 400 spectrometer, respectively. Chemical shifts (δ) are given in ppm, using the resonance of the residual solvent CD_2Cl_2 as internal reference (^{1}H NMR: 5.32 ppm, ^{13}C NMR: 53.5 ppm). Nomenclature and numbering scheme for the assignment of the resonance signals is given in Figure 6. In the case of ^{19}F and ^{31}P NMR spectra, $CFCl_3$ and phosphoric acid were used as external references, respectively. Elemental analyses were carried out with an Elementar Vario EL instrument. Melting points were determined with a Büchi SMP-20 in open capillaries and are not corrected.

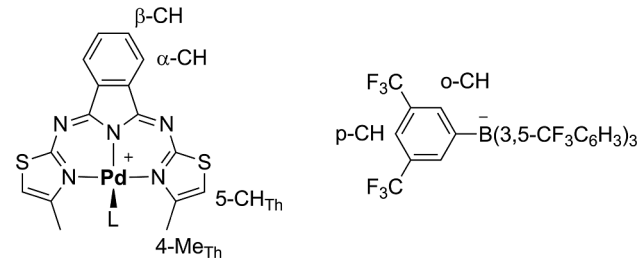

Figure 6. Nomenclature and numbering systems for the spectroscopic assignments.

Preparation of Cationic Complexes – General Procedure: [Pd(4-Mebti)Cl] (**1**) (10.0 mg, 21 μmol) was dissolved in dry toluene or dichloromethane (2 mL), and $NaB(Ar^F)_4$ (18.7 mg, 21 μmol) was added in one portion. The mixture was stirred for 5 min before the neutral ligand was added, and stirring continued for 16 h. If a red solid has precipitated, the solvent was removed in vacuo and the solid extracted with dry dichloromethane. After filtration through celite the solvent was removed again, the residue washed with pentane, and dried in vacuo. If the product remained in solution, the reaction mixture was directly filtered and treated as described. Purification was achieved by crystallization as detailed below for each case.

$[Pd(4\text{-Mebti})(PMe_3)][B(Ar^F)_4]$ (2): PMe_3 (13 mg, 168 μmol) and dichloromethane were used for the preparation. Single crystals of **2** were obtained after crystallization from dichloromethane/*n*-pentane at –20 °C. Yield: 18.4 mg (13 μmol, 63 %). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ = 8.10–8.05 (m, 2 H, α-CH), 7.76–7.72 (m, 10 H, β-CH, *o*-$CH_{B(ArF)4}$), 7.56 (s, 4 H, *p*-$CH_{B(ArF)4}$), 7.11 (s, 2 H, 5-CH_{Th}), 2.77 (s, 6 H, 4-Me_{Th}), 1.37 (d, $^2J_{PH}$ = 11.5 Hz, 9 H, $P(CH_3)_3$). **^{13}C NMR** (100.6 MHz, CD_2Cl_2): δ = 168.7, 161.8 (m, $BC_{B(ArF)4}$), 156.6, 148.5, 137.3, 134.9, 132.9, 129.5–128.4 (m, *m*-$C_{B(ArF)4}$), 124.9 (q, $^1J_{CF}$ = 270.9 Hz, CF_3), 123.2 (*o*$C_{B(ArF)4}$), 117.6 (*p*$C_{B(ArF)4}$), 114.9, 21.0, 17.1 (d, $^1J_{PC}$ = 29.2 Hz, $P(CH_3)_3$). **^{19}F NMR** (188 MHz, CD_2Cl_2): δ = –61.34. **^{31}P NMR** (81 MHz, CD_2Cl_2): δ = –18.13. **UV/Vis** (CH_2Cl_2): λ_{max} = 230, 250, 302, 368, 451 nm. **HRMS** (ESI, MeOH): *m*/*z* 520.0011; calcd. for $[C_{19}H_{21}N_5PPdS_2]^+$: 520.0005.

$[Pd(4\text{-Mebti})(tBuNH_2)][B(Ar^F)_4]$ (3): *tert*-Butylamin (3.4 μL, 32 μmol) and toluene were used for the preparation. Single crystals of **3** were obtained after crystallization from dichloromethane/*n*-pentane at –20 °C. Yield: 17.7 mg (13 μmol, 61 %). calcd. (%) for $C_{52}H_{35}N_6S_2PdBF_{24}$: C 45.22, H 2.55, N 6.08; found: C 44.95, H 2.56, N 6.03. **^{1}H NMR** (300 MHz, CD_2Cl_2): δ = 8.07–8.05 (m, 2 H, α-CH), 7.73 (br.s, 10 H, β-CH, *o*-$CH_{B(ArF)4}$), 7.56 (br.s, 4 H, *p*-$CH_{B(ArF)4}$), 7.14 (s, 2 H, 5-CH_{Th}), 3.05 (br.s, 2 H, NH_2), 2.75 (s, 6 H, 4-Me_{Th}), 1.21 (s, 9 H, $C(CH_3)_3$). **^{13}C NMR** (75 MHz, CD_2Cl_2): δ = 168.0, 162.2 (m, $BC_{B(ArF)4}$), 155.3, 146.8, 136.7, 134.9, 133.0, 129.6–128.3 (m, *m*-$C_{B(ArF)4}$), 124.4 (q, $^1J_{CF}$ = 272.2 Hz, CF_3), 122.9 (*o*$C_{B(ArF)4}$), 117.5 (*p*$C_{B(ArF)4}$), 117.1, 57.7, 30.7, 20.0. **^{19}F NMR** (188 MHz, CD_2Cl_2): δ = –65.33. **UV/Vis** (CH_2Cl_2): λ_{max} = 230, 244, 298, 366, 388, 450 nm.

$[Pd(4\text{-Mebti})(PhNH_2)][B(Ar^F)_4]$ (4): Aniline (2.0 μL, 22 μmol) and toluene were used for the preparation. Single crystals of **4** were obtained after crystallization from dichloromethane/*n*-pentane at –20 °C. Yield: 18.8 mg (13 μmol, 64 %). calcd. (%) for $C_{54}H_{31}N_6S_2PdBF_{24}$: C 46.29, H 2.23, N 6.00; found: C 46.19, H 2.30, N 6.47. **^{1}H NMR**

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(400 MHz, CD_2Cl_2): δ = 8.00 (br.s, 2 H, α-CH), 7.73 (br.s, 10 H, β-CH, *o*$CH_{B(ArF)4}$), 7.57 (br.s, 4 H, *p*-$CH_{B(ArF)4}$), 7.24–7.03 (m, 7 H, CH_{Ph}, 5-CH_{Th}), 4.84 (br.s, 2 H, NH_2), 2.84 (s, 6 H, 4-Me_{Th}). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ = 167.6, 162.1 (m, $BC_{B(ArF)4}$), 154.7, 148.8, 136.5, 134.9, 132.9, 130.5, 129.5–128.5 (m, *m*-$C_{B(ArF)4}$), 124.7 (q, $^1J_{CF}$ = 272.5 Hz, CF_3), 123.2 (*o*$C_{B(ArF)4}$), 120.6, 117.6 (*p*-$C_{B(ArF)4}$), 116.9, 116.7, 19.5; no signal was detected for the quarternary *ipso*-C_{Ph}. **^{19}F NMR** (188 MHz, CD_2Cl_2): δ = –65.37. **UV/Vis** (CH_2Cl_2): λ_{max} = 216, 242, 298, 366, 450 nm.

[Pd(4-Mebti)(py)][B(Ar^F)$_4$] (5): Pyridine (2.5 µL, 32 µmol) and toluene were used for the preparation. Single crystals of **5** were obtained after crystallization from dichloromethane/*n*-pentane at –20 °C. Yield: 23.8 mg (17 µmol, 81 %). calcd. (%) for $C_{53}H_{29}N_6S_2F_{24}BPd$: C 45.89, H 2.11, N 6.06; found: C 45.63, H 2.55, N 5.95. **^{1}H NMR** (300 MHz, CD_2Cl_2): δ = 8.69–8.67 (m, 2 H, *o*-CH_{Py}) 8.02 (t, *J* = 6.8 Hz, 1 H, *p*-CH_{Py}), 7.93–7.89 (m, 2 H, α-CH), 7.72 (br.s, 10 H, β-CH, *o*-$CH_{B(ArF)4}$), 7.65–7.63 (m, 2 H, *m*-CH_{Py}), 7.52 (s, 4 H, *p*-$CH_{B(ArF)4}$), 6.82 (s, 2 H, 5-CH_{Th}), 1.02 (s, 6 H, 4-Me_{Th}). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ = 170.1, 162.2 (m, $BC_{B(ArF)4}$), 153.6, 149.0, 141.6, 136.4, 134.9, 132.7, 129.7–128.4 (m, *m*-$C_{B(ArF)4}$), 128.1, 124.9 (q, $^1J_{CF}$ = 273.1 Hz, CF_3), 123.5 (*o*$C_{B(ArF)4}$), 122.9, 117.6 (*p*-$C_{B(ArF)4}$), 116.1, 17.5. **^{19}F NMR** (282 MHz, CD_2Cl_2): δ = –62.83. **UV/Vis** (CH_2Cl_2): λ_{max} = 229, 301, 387, 487 nm.

[Pd(4-Mebti)(2,6-Me$_2$py)] [B(Ar^F)$_4$] (6): 2,6-Lutidine (14.8 mg, 139 µmol) and toluene were used for the preparation. Single crystals of **6** grew upon crystallization from toluene/*n*-pentane at –20 °C. Yield: 12.1 mg (9 µmol, 41 %). calcd. (%) for $C_{55}H_{33}N_6S_2F_{24}BPd$: C 46.68, H 2.35, N 5.94; found: C 46.26, H 2.57, N 5.81. **^{1}H NMR** (400 MHz, CD_2Cl_2): δ = 8.00–7.99 (m, 2 H, α-CH_{Th}), 7.85 (t, *J* = 8.0 Hz, 1 H, *p*-CH_{Py}), 7.72 (br.s, 10 H, β-CH, *o*-$CH_{B(ArF)4}$), 7.55 (s, 4 H, *p*-$CH_{B(ArF)4}$), 7.37 (d, *J* = 8.0 Hz, 2 H, *m*-CH_{Py}), 6.83 (s, 2 H, 5-CH_{Th}), 3.04 (s, 6 H, *o*-Me_{Py}), 1.08 (s, 6 H, 4-Me_{Th}). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ = 170.2, 162.1 (m, $BC_{B(ArF)4}$), 161.8, 153.9, 149.1, 141.8, 136.3, 134.9, 132.8, 129.6–128.5 (m, *m*-$C_{B(ArF)4}$), 125.7, 124.7 (q, $^1J_{CF}$ = 273.2 Hz, CF_3), 123.5 (*o*$C_{B(ArF)4}$), 117.5 (*p*-$C_{B(ArF)4}$), 116.3, 26.6, 16.9. **^{19}F NMR** (188 MHz, CD_2Cl_2): δ = –62.84. **UV/Vis** (CH_2Cl_2): λ_{max} = 230, 241, 299, 393, 501 nm.

[Pd(4-Mebti)(MeCN)][B(Ar^F)$_4$] (7): A toluene/acetonitrile mixture (2:1) was used for the preparation. Single crystals of **7** were obtained after crystallization from toluene/*n*-pentane (**7**), or from dichloromethane/acetonitrile/*n*-pentane (**7'**), at –20 °C. Yield: 19.1 mg (13 µmol, 64 %). **^{1}H NMR** (400 MHz, C_6D_6): δ = 8.34 (br.s, 8 H, *o*-$CH_{B(ArF)4}$), 7.81–7.78 (m, 2 H, α-CH), 7.66 (br.s, 4 H, *p*-$CH_{B(ArF)4}$), 7.03–7.00 (m, 2 H, β-CH), 5.94 (s, 2 H, 5-CH_{Th}), 1.90 (s, 6 H, 4-Me_{Th}), 0.62 (s, 3 H, MeCN). **^{13}C NMR** (100 MHz, C_6D_6): δ = 166.7, 162.7 (m, $BC_{B(ArF)4}$), 153.3, 148.2, 136.2, 135.4, 133.0, 130.5–129.5 (m, *m*-$C_{B(ArF)4}$), 124.7 (q, $^1J_{CF}$ = 270.9 Hz, CF_3), 123.3 (*o*$C_{B(ArF)4}$), 118.1 (*p*-$C_{B(ArF)4}$), 117.0 (Me-*C*N), 115.4, 19.9, –0.12 (H_3C-CN). **^{19}F NMR** (282 MHz, C_6D_6): δ = –62.02. **UV/Vis** (CH_2Cl_2): λ_{max} = 231, 271, 299, 368, 390, 448 nm. **HRMS** (APCI, MeCN): *m*/*z* 484.9828; calcd. for $[C_{18}H_{15}N_6PdS_2]^+$: 484.9829.

[Pd(4-Mebti)(MeNC)][B(Ar^F)$_4$] (8): Methylisocyanide (1.5 µL, 37 µmol) and dichloromethane were used for the preparation. Single crystals of **8** were obtained after crystallization from dichloromethane/*n*-pentane at –20 °C. Yield: 20.1 mg (15 µmol, 71 %). **^{1}H NMR** (300 MHz, C_6D_6): δ = 8.08–8.03 (m, 2 H, α-CH), 7.76–7.72 (m, 10 H, β-CH, *o*-$CH_{B(ArF)4}$), 7.57 (s, 4 H, *p*-$CH_{B(ArF)4}$), 7.11 (s, 2 H, 5-CH_{Th}), 3.58 (s, 3 H, CN-Me), 2.68 (s, 6 H, 4-Me_{Th}). **^{13}C NMR** (75 MHz, C_6D_6): δ = 168.0, 161.9 (m, $BC_{B(ArF)4}$), 154.2, 149.1, 136.6, 134.9, 133.1, 129.6–128.4 (m, *m*-$C_{B(ArF)4}$), 124.7 (q, $^1J_{CF}$ = 271.5 Hz, CF_3), 123.4 (*o*$C_{B(ArF)4}$), 119.0 (*C*N-CH_3), 117.6 (*p*-$C_{B(ArF)4}$), 115.4, 30.8 (CN-*C*H_3), 22.0 (4-Me_{Th}). **^{19}F NMR** (282 MHz, C_6D_6): δ = –62.82. **UV/Vis** (CH_2Cl_2): λ_{max} = 243, 281, 295, 368, 390, 421, 447 nm. **HRMS** (ESI, MeOH): *m*/*z* 484.9832; calcd. for $[C_{18}H_{15}N_6PdS_2]^+$: 484.9829.

Collection and Reduction of X-ray Data: Intensity data were collected at 130(2) K (**5** and **6**) or at 193(2) K, using a Stoe IPDS-1 X-ray diffractometer (Stoe IPDS-2 for **5**). Graphite monochromated Mo-K_α radiation (0.71073 Å) was used. The structures were solved by direct methods with SIR-92[19] or with SHELXS-97 (**6**).[20] Refinements were carried out by full-matrix least-squares techniques against F^2 using SHELXL-97.[20] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions if not stated otherwise. Selected crystal data are given in Table 1 and Table 2. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-818999, -819000, -819001, -819002, -819003, -819004, -819005, -819006. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk].

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