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Cationic palladium(II) complexes of the sterically hindered bis(4-methylthiazolyl)isoindoline (4-Mebti) with neutral group XVI donor ligands

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Dedicated to Prof. Dr. Wolfgang Kaim on the occasion of his 60th birthday.

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ABSTRACT

A series of cationic palladium complexes $[(4\text{-Mebti})PdL]^+$ with 4-Mebti = anion of bis(4-methylthiazolylimino)isoindoline and L = neutral ligand with group 16 donor atom has been prepared from the chlorido derivative [(4-Mebti)PdCl] and $NaBAr^F$ (BAr^F = tetrakis(3,5-bis(trifluoromethyl)phenyl)boranate) in the presence of the respective donor ligand. Crystallographic and spectroscopic analyses were achieved for species with L = SMe_2, $SeMe_2$, dmf, acetamide, diphenylurea, and formiate. The latter two complexes represent products from hydrolyses of phenyl isocyanate and dmf, respectively, which occur during the ligand exchange reactions. Several other O-donor ligands like thf, acetone, Me_2O, water, and others are not bound to the palladium ion, and the dinuclear μ-chlorido derivative $[\{(4\text{-Mebti})Pd\}_2Cl]^+$ is isolated in these cases instead. The crystallographic analyses prove the expected presence of distorted, pseudo-planar palladium chelates, and the degree of distortion correlates well with the chemical shifts observed for the proton nuclei of the terminal methyl groups in the ^1H NMR experiment.

1. Introduction

Ligand exchange processes of square-planar palladium(II) compounds and other *low spin* d^8 complexes have always shown associative reaction mechanisms in the cases studied so far [1]. A general possibility to move this mechanism towards a dissociative process and to observe a rare three-coordinate, T-shaped palladium(II) compound would lie in the kinetic destabilization of the square-planar ligand sphere. Such a scenario can be realized by applying a suitably substituted meridional tridentate ligand to a palladium ion. α,ω-Dimethyltripyrrins provide for such a ligand class and have been studied by us in the past towards this goal [2–8]. In these ligands backbones, the terminal methyl groups are oriented in a way that the fourth coordination site of a central palladium atom may not be occupied in the N_3 plane of the cationic (trpy)Pd fragment without significant distortion of either the organic ligand or the coordination geometry. As illustrated in Fig. 1, either of two forms is usually observed, the pseudo-planar form and the helical form, depending on the shape and sterical requirement of the employed additional ligand. In some cases an equilibrium exists, and both forms are observed crystallographically [4,5].

In a foregoing study, we have used group 14 and 15 donor ligands (C, N, P) with a stepwise increase in steric hindrance in order to push a (trpy)PdL compound towards dissociation into the three-coordinate T-shaped 14 VE cation. This approach failed as the system accepts quite large distortions with these strongly binding ligands, and escapes in the case of PMe_3 towards a square–pyramidal five-coordinate 18 VE complex. Applying weaker ligands resulted in the decomposition of the sensitive tripyrrin scaffold [8]. We have now turned to the more robust and structurally related bis(4-methylthiazolylimino)isoindoline (4-Mebti) framework [9,10], and report here a series of cationic palladium complexes with group 16 donor ligands (O, S, Se).

2. Experimental

2.1. General remarks

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. [(4-Mebti)PdCl] **1** [11], sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)boranate ($NaBAr^F$ [12]), and dimethylselenium [13] were prepared according to the literature methods. NMR spectra were recorded on 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 (^1H NMR: 5.32 ppm, ^{13}C NMR: 53.5 ppm). Nomenclature and

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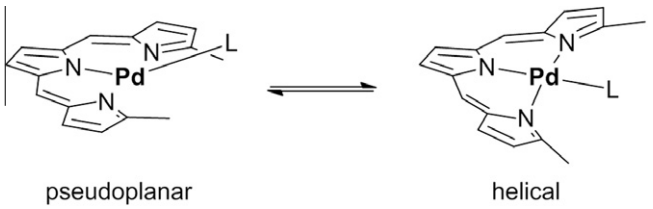

Fig. 1. Conformational dynamics observed for palladium complexes with sterically hindered tripyrrin ligands.

numbering scheme for the assignment of the resonance signals is given in Chart 1. In the case of ^{19}F NMR spectra, $CFCl_3$ was used as external reference. Elemental analyses were carried out on an Elementar Vario EL instrument. Melting points were determined on a Büchi SMP-20 in open capillaries and are not corrected.

2.2. Single crystal X-ray structural determinations

Experimental details relating to the crystallographic characterization are summarized in Table 1. Diffraction data were collected using graphite monochromated Mo Kα radiation on a Stoe IPDS-I instrument at 193(2) K using Φ-scans, or on a Stoe IPDS-II at 173(2) K using ω-scans. The structures were solved by direct methods and refined against F^2 by least-squares utilizing the software packages SHELXL-97 [14], SIR-92 [15], PLATON [16], and WINGX [17]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined using a riding model. Selected bond lengths, distances and angles for **2**–**7** are given in Table 2.

2.3. Syntheses of complexes

2.3.1. General procedure

[(4-Mebti)PdCl] **1** (10.0 mg, 21 μmol) was dissolved in dry toluene or dichloromethane (2 mL), and $NaBAr^F$ (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 vacuum and the solid extracted with dry dichloromethane. After filtration on celite the solvent was removed again, the residue washed with pentane, and dried in vacuum. 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.

2.3.2. [(4-Mebti)Pd(OC(NH$_2$)Me)]$^+$ BAr^{F-} (**2**)

Purified acetamide (5.9 mg, 100 μmol) and dichloromethane were used for the preparation. Single crystals of **2** were obtained after double recrystallization from toluene/*n*-pentane and dichloromethane/*n*-pentane, respectively. (14.6 mg, 51%), mp 168–170 °C ($C_{50}H_{29}BF_{24}N_6OPdS_2 \times CH_2Cl_2$ requires: C, 42.18; H, 2.15; N, 5.79. Found: C, 42.13; H, 2.57; N, 6.02%). ^1H NMR (CD_2Cl_2, 295 K): δ 2.02 (br s, 3H, acetamide), 2.57 (s, 6H, 4-Me_{Th}), 6.40–6.71 (br s, 2H, NH_2), 6.98 (s, 2H, 5-CH_{Th}), 7.56 (s, 4H, *p*-CH_{BAr^F}), 7.71–7.74 (m, 10H, β-CH + *o*-CH_{BAr^F}), 8.02–8.04 ppm (m, 2H, α-CH). ^{13}C NMR (CD_2Cl_2, 295 K): δ 19.3, 115.9, 117.9 (m, *p*-CH_{BAr^F}), 123.4, 125.0 (q, $^1J_{C-F}$ = 271 Hz, CF_3), 129.1 (m, *m*-C_{BAr^F}), 133.1, 135.2, 136.6, 150.2, 154.1, 162.0 (m, BC_{BAr^F}), 167.6 ppm; the remaining signal for the acetamide could not be detected. ^{19}F NMR (CD_2Cl_2, 295 K): δ −65.5 ppm.

2.3.3. [(4-Mebti)Pd(dmf)]$^+$ BAr^{F-} (**3**) and [(4-Mebti)Pd(OCHO)] (**4**)

A mixture of toluene and DMF (60:1) was used for the preparation. Single crystals of **3** were obtained by diffusion of *n*-pentane into a dichloromethane solution at −20 °C. (15.7 mg, 54%), mp 132 °C (decomp.) ($C_{51}H_{31}BF_{24}N_6OPdS_2$ requires: C, 44.36; H, 2.26; N, 6.08. Found: C, 43.92; H, 2.41; N, 5.99%). ^1H NMR (CD_2Cl_2, 295 K): δ 2.60 (s, 6H, 4-Me_{Th}), 2.98 (s, 3H, dmf), 3.01 (s, 3H, dmf), 6.91 (s, 2H, 5-CH_{Th}), 7.56 (s, 4H, *p*-CH_{BAr^F}), 7.66–7.69 (m, 2H, β-CH), 7.73 (br s, 8H, *o*-CH_{BAr^F}), 7.89–7.92 ppm (m, 2H, α-CH), 8.01 (s, 1H, dmf). ^{13}C NMR (CD_2Cl_2, 295 K): δ 19.7, 33.5, 38.2, 115.2, 117.4 (m, *p*-CH_{BAr^F}), 123.0, 124.7 (q, $^1J_{C-F}$ = 273 Hz, CF_3), 128.9 (m, *m*-C_{BAr^F}), 132.6, 134.7, 136.3, 149.5, 153.7, 161.9 (m, BC_{BAr^F}), 166.3, 166.8 ppm. ^{19}F NMR (CD_2Cl_2, 295 K): δ −62.9 ppm. If wet THF is added to the crystallization mixture, a small deposit of crystals of the formiate complex **4** forms over several days.

2.3.4. [(4-Mebti)Pd(OC(NHPh)$_2$)]$^+$ BAr^{F-} (**5**)

Wet toluene and phenylisocyanate (0.1 mL, 92 μmol) were used for the preparation. Single crystals of **5** were obtained by diffusion of *n*-pentane into a dichloromethane solution at −20 °C. (10.2 mg, 58%), mp 172 °C (decomp.) ($C_{61}H_{36}BF_{24}N_7OPdS_2$ requires: C, 48.19; H, 2.39; N, 6.45. Found: C, 47.47; H, 2.95; N, 7.27%). ^1H NMR (CD_2Cl_2, 295 K): δ 2.61 (s, 6H, 4-Me_{Th}), 6.84 (s, 2H, 5-CH_{Th}), 7.10–7.28 (m, 10H, CH_{Ph}), 7.56 (s, 4H, *p*-CH_{BAr^F}), 7.64 (s, 2H, β-CH), 7.73 (m, 10H, α-CH + *o*-CH_{BAr^F}); the NH signal was not detected. ^{13}C NMR (CD_2Cl_2, 295 K): δ 19.8, 115.0, 117.5 (m, *p*-CH_{BAr^F}), 122.9, 123.0, 124.7 (q, $^1J_{C-F}$ = 270 Hz, CF_3), 126.5, 129.0 (m, *m*-C_{BAr^F}), 129.8, 132.6, 134.9, 135.9, 136.2, 149.8, 153.4, 162.0 (m, BC_{BAr^F}), 166.2; the carbonyl carbon atom was not detected. ^{19}F NMR (CD_2Cl_2, 295 K): δ −65.4 ppm.

2.3.5. [(4-Mebti)Pd(SMe$_2$)]$^+$ BAr^{F-} (**6**)

A mixture of toluene and dimethylsulfide (25:1) was used for the preparation. Single crystals of **6** were obtained by diffusion of *n*-pentane into a dichloromethane solution at −20 °C. (18.7 mg, 65%), mp 163–166 °C ($C_{50}H_{30}BF_{24}N_5PdS_3 \times 1.86\ CH_2Cl_2$ (from the crystallographic analysis) requires: C, 40.59; H, 2.23; N, 4.57. Found: C, 40.62; H, 2.42; N, 4.44%). ^1H NMR (CD_2Cl_2, 295 K): δ 2.14 (s, 6H, Me_2S), 2.77 (s, 6H, 4-Me_{Th}), 7.13 (s, 2H, 5-CH_{Th}), 7.56 (br s, 4H, *p*-CH_{BAr^F}), 7.73 (br s, 8H, *o*-CH_{BAr^F}), 7.76 (m, 2H, β-CH),

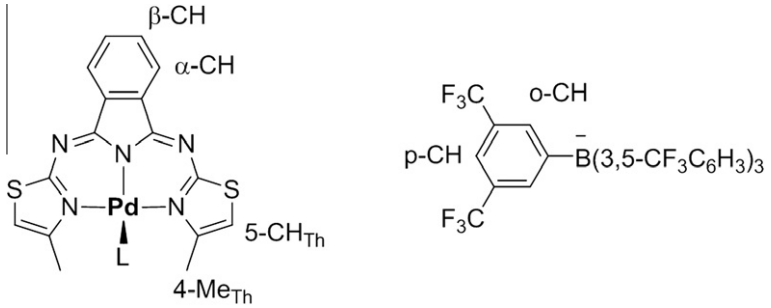

Chart 1. Nomenclature and numbering systems for the spectroscopic assignments.