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FULL PAPER

One compound, two structures: synthesis, structures and reactivity of a novel (tripyrrinato)palladium(II) trifluoracetate complex TrpyPdOAc$_f$

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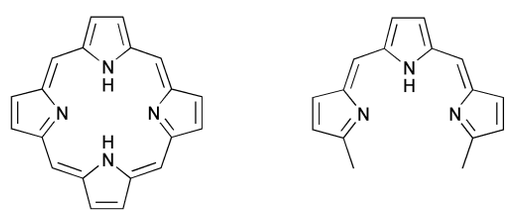
The novel (2,15-dimethyl-3,4,13,14-tetraethyltripyrrinato)palladium(II) trifluoroacetate (TrpyPdOAc$_f$) **7** was found to exhibit two different geometries in the solid state. While in one crystal the tripyrrin ligand is helically distorted to ensure a square-planar coordination of the central palladium(II) ion, the bonding geometry of the metal centre of the other geometrical isomer found in a different crystal showed a pronounced tetrahedral deviation from planarity, accompanied with an almost planar tripyrrolic ligand. In solution, non-planar structures of **7** can not be detected, as judged by the results of variable temperature proton NMR spectroscopy. The energy stored in the strained complexes **6** and **7**, however, becomes "visible" in fast ligand exchange processes, which enable us to prepare a number of new TrpyPdX complexes with X = Cl, Br, I, N_3, NCO, SCN and OAc, of which the latter two decompose in solution. As the X-ray crystallographic analysis of TrpyPdBr **9** demonstrates, complexes with a tilted fourth ligand are predominant in the solid state with donor atoms larger than oxygen.

Introduction

The coordination of the rigid and planar porphyrin ligand to d^8-ions like Ni^{II}, Pd^{II}, Pt^{II} or Au^{III} always results in square-planar and low-spin complexes with little reactivity.[1] Conceptually, removing one of the pyrrole moieties from the porphyrin[2,3] should free one of the metal coordination sites in the plane and thus result in novel reactivity schemes related to the chemistry of other meridional tridentate *N*,*N*,*N* ligand complexes[4–7] (Scheme 1).



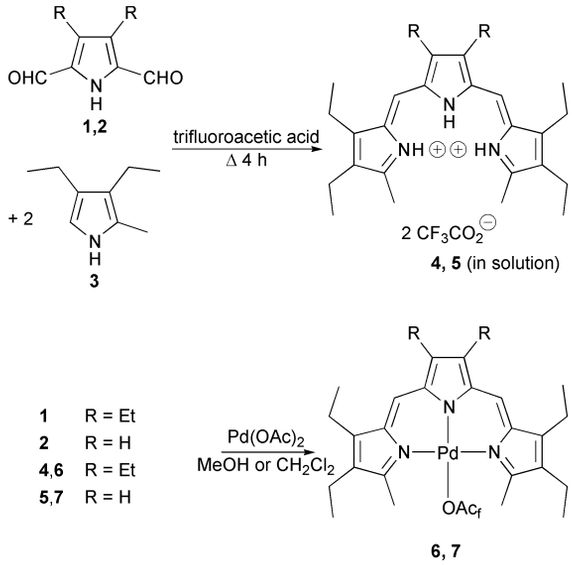
Scheme 1

In a recent communication we reported the synthesis and first palladium(II) complex **6** of such a tripyrrin ligand **4**.[8] As the structural analysis revealed, the coordination environment of the Pd^{II} centre in TrpyPdOAc$_f$ **6** is sterically too encumbered for a planar arrangement due to the interaction of the terminal methyl groups of the tripyrrin ligand with the oxygen donor. Instead, the tripyrrin ligand was found to be helically distorted, thereby arranging the terminal methyl groups far enough away from each other to allow the trifluoroacetato ligand to bind to a square-planar coordinated palladium(II) centre. It was of interest for us to study this *out-of-plane* distortion in more detail, since the strained nature of this bonding mode could be expected to serve as an energy storage device, which eases ligand exchange reactions. In this paper we present the first structural data and reactivity studies for TrpyPdOAc$_f$ complexes **6** and **7** of two differently substituted tripyrrin ligands **4** and **5**.

Results and discussion

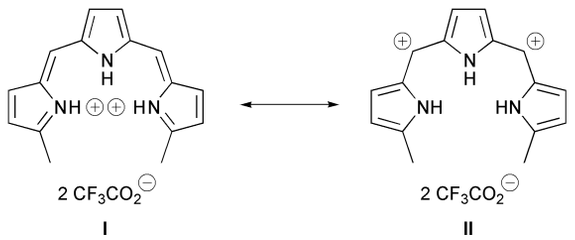
Syntheses of TrpyPdOAc$_f$ 6 and 7

The attempted syntheses of tripyrrins **4** and **5** using standard protocols for the condensation of pyrrole aldehydes with pyrroles (HBr in hot methanol *etc.*)[9] were unsuccessful. An initial colour change indicated the formation of the desired, diprotonated tripyrrin, but the species decayed under these conditions before it could be isolated. However, if trifluoroacetic acid was used as both reagent and solvent stable solutions of diprotonated tripyrrins **4** and **5** were obtained (Scheme 2).



Scheme 2 Syntheses of tripyrrins **4** and **5** and palladium complexes TrpyPdOAc$_f$ **6** and **7**.

Characterization of the diprotonated tripyrrins was attempted by performing the reactions in an NMR tube and using deuterated trifluoroacetic acid as the reaction medium. By NMR spectroscopy, **4** could be proven to be the almost exclusive product.[8] The condensation yielding the less substituted **5**, however, is not selective, and the NMR spectra show a number of by-products. If resonance structures **I** and **II** of the diprotonated tripyrrin are taken into account, the *meso* positions appear particularly polarized and therefore prone



Scheme 3 Assumed resonance structures of diprotonated tripyrrins.

to nucleophilic attack with concomitant decay (Scheme 3). We believe that the reduced steric shielding of the *meso* positions caused by the smaller number of peripheral ethyl groups in **5** is responsible for the lower selectivity in this case.

Treatment of the dark green residues obtained after evaporation of all volatiles from the above ligand preparations with a slurry of palladium(II) acetate in methanol (for **4**) or dichloromethane (for **5**) results in the formation of TrpyPdOAc$_f$ complexes **6** and **7**, which are easily purified by radial chromatography. **6** and **7** are air-stable, crystalline compounds with comparable spectroscopic properties. Although excess acetate is available at the stage of preparation, the TrpyPd complexes are exclusively formed as the trifluoroacetates, if the reaction time is sufficiently long.

Polymorphism of 7

The structure of **6** was already reported in an earlier communication.[8] Suitable crystals of the new complex **7** could be obtained by slow concentration of dichloromethane–*n*-hexane solutions. **7** was found to build up two different solid state structures under the same experimental conditions. A first sample **7-I** crystallized in the monoclinic system, space group $P2_1/c$, with four molecules in the unit cell. The CF_3 group shows rotational disorder with an occupancy of 45 : 55. A second sample **7-II** crystallized in the triclinic system, space group $P\bar{1}$, with two molecules per unit cell. Again, the CF_3 group shows rotational disorder with an occupancy of 70 : 30. The results from the X-ray crystallographic molecular structure determination of **7-I** and **7-II** are shown in Fig. 1. Bond lengths and angles are listed in Table 1.

7-I displays a molecular structure similar to that reported for **6**. The palladium(II) centre is bound in an almost square-planar fashion [mean deviation of the PdN_3O fragment from planarity: 0.040 Å; bond angles N(2)–Pd–O(1): 177.19(7)°, N(1)–Pd–N(3): 176.44(7)°], with two long [Pd–N(1): 2.044(2) Å; Pd–N(3): 2.0212(19) Å] and one short Pd–N bond [Pd–N(2): 1.9735(18) Å]. The alternating C–C bond lengths of the ligand perimeter [C(2) – C(15)] indicate an unequal charge distribution, in that the negative charge of the deprotonated Trpy ligand is mainly located at the central C_4N unit. This explains the above mentioned finding of a short Pd–N(2) bond. In order to create a sufficiently large binding pocket for the oxygen centre of the trifluoroacetato ligand within a square-planar coordination geometry, the terminal methyl groups C(1) and C(16) of **7-I** have to occupy positions above and below the PdN_3O plane. This is achieved by a pronounced helical twist and non-planar structure of the Trpy ligand [mean deviation of the $C_{14}N_3$ perimeter from planarity: 0.390 Å], similar to the ruffled conformation shown by a number of metalloporphyrins.[10] The bound oxygen of the trifluoroacetato ligand is thereby located almost ideally amid the terminal methyl groups [C(1) ··· C(16): 5.820 Å; C(1) ··· O(1): 2.928 Å; C(16) ··· O(1): 2.916 Å]. Due to the helicity of the Trpy ligand in **7-I**, the complex is chiral in the solid state, and both enantiomers are found in the unit cell in a 1 : 1 ratio.

An entirely different scenario is found for **7-II**. The Trpy ligand of **7-II** has an almost planar conformation [mean deviation of the $C_{14}N_3$ perimeter from planarity: 0.109 Å], but the coordination environment of the palladium centre deviates from planarity towards a tetrahedron, mainly due to the distal binding of the oxygen donor [mean deviation of the PdN_3O fragment from planarity: 0.216 Å; bond angles N(2)–Pd–O(1): 163.52(7)°, N(1)–Pd–N(3): 169.15(7)°]. The influence of the differing conformations of the Trpy ligand in **7-I** and **7-II** on the C–C bond lengths is almost negligible. Interestingly, however, the C–C$_{meso}$–C bond angles at the *meso* positions C(6) and C(11) in **7-II** are 0.8° and 1.5° wider than those in **7-I**. These enlargements increase the distance between the terminal methyl groups of the tripyrrin ligand in **7-II** to 4.744 Å, resulting in sufficiently large C_{term} ··· O(1) distances of 2.815 Å and 2.914 Å.

The conformations of **7-I** and **7-II** are both strained and it appears likely that two different, though energetically similar, ways to escape the dilemma of steric congestion could be investigated in the solid state. This is, however, not the case in solution. Using VT NMR techniques, no diastereotopic splitting of the ethyl-CH_2 protons was observed in CD_2Cl_2 solution down to 183 K, at which temperature the rotation of these substituents starts to freeze. Since the structural results implicate non-planar minimum structures for TrpyPdOAc$_f$ complexes, a fast exchange between different non-planar forms must be concluded. The alternative scenario, that TrpyPdOAc$_f$ complexes build separated ion pairs in solution, was, as expected, excluded by the results of conductivity measurements. Whether a dissociative mechanism or inversion processes at the metal and/or the tripyrrin ligand are responsible for the fast exchange remains to be answered.

Table 1 Selected bond lengths, distances (Å) and angles (°) for **7-I**, **7-II** and **9**

	7-I [X = O(1)]	**7-II** [X = O(1)]	**9** [X = Br]
Pd–N(1)	2.044(2)	2.0510(18)	2.032(3)
Pd–N(2)	1.9735(18)	1.9982(18)	2.029(3)
Pd–N(3)	2.0212(19)	2.0269(19)	2.038(4)
Pd–X	2.0411(15)	2.0565(16)	2.4673(7)
N(1)–C(2)	1.337(3)	1.332(3)	1.336(5)
N(1)–C(5)	1.413(3)	1.414(3)	1.405(5)
N(2)–C(7)	1.357(3)	1.374(3)	1.372(5)
N(2)–C(10)	1.363(3)	1.374(3)	1.362(6)
N(3)–C(12)	1.421(3)	1.405(3)	1.408(6)
N(3)–C(15)	1.327(3)	1.334(3)	1.320(6)
C(2)–C(3)	1.443(4)	1.449(3)	1.443(6)
C(3)–C(4)	1.353(4)	1.368(3)	1.365(6)
C(4)–C(5)	1.448(4)	1.447(3)	1.446(6)
C(5)–C(6)	1.350(3)	1.360(3)	1.354(6)
C(6)–C(7)	1.407(4)	1.415(3)	1.416(6)
C(7)–C(8)	1.413(3)	1.416(3)	1.422(6)
C(8)–C(9)	1.366(4)	1.369(4)	1.381(7)
C(9)–C(10)	1.400(3)	1.417(3)	1.424(8)
C(10)–C(11)	1.422(4)	1.421(3)	1.416(7)
C(11)–C(12)	1.350(3)	1.361(3)	1.339(7)
C(12)–C(13)	1.434(4)	1.446(3)	1.462(6)
C(13)–C(14)	1.361(3)	1.367(4)	1.340(7)
C(14)–C(15)	1.446(3)	1.452(3)	1.451(6)
C(1) ··· C(16)	5.820	4.744	4.685
C(1) ··· X	2.928	2.815	3.285
C(16) ··· X	2.916	2.914	3.289
N(1)–Pd–N(2)	89.28(8)	92.05(7)	90.58(14)
N(1)–Pd–N(3)	176.44(7)	169.15(7)	169.23(15)
N(1)–Pd–X	92.67(7)	91.51(7)	91.61(10)
N(2)–Pd–N(3)	88.90(8)	90.08(8)	91.22(15)
N(2)–Pd–X	177.19(7)	163.52(7)	147.98(10)
N(3)–Pd–X	89.27(7)	89.44(7)	92.49(11)
C(5)–C(6)–C(7)	126.5(2)	128.3(2)	127.7(4)
C(10)–C(11)–C(12)	126.2(2)	126.8(2)	129.3(4)

Ligand exchange studies on 6

The strain induced by the steric shielding of the fourth coordination site by the tripyrrin terminal methyl groups of TrpyPdOAc$_f$ complexes **6** and **7** should help the exchange of the

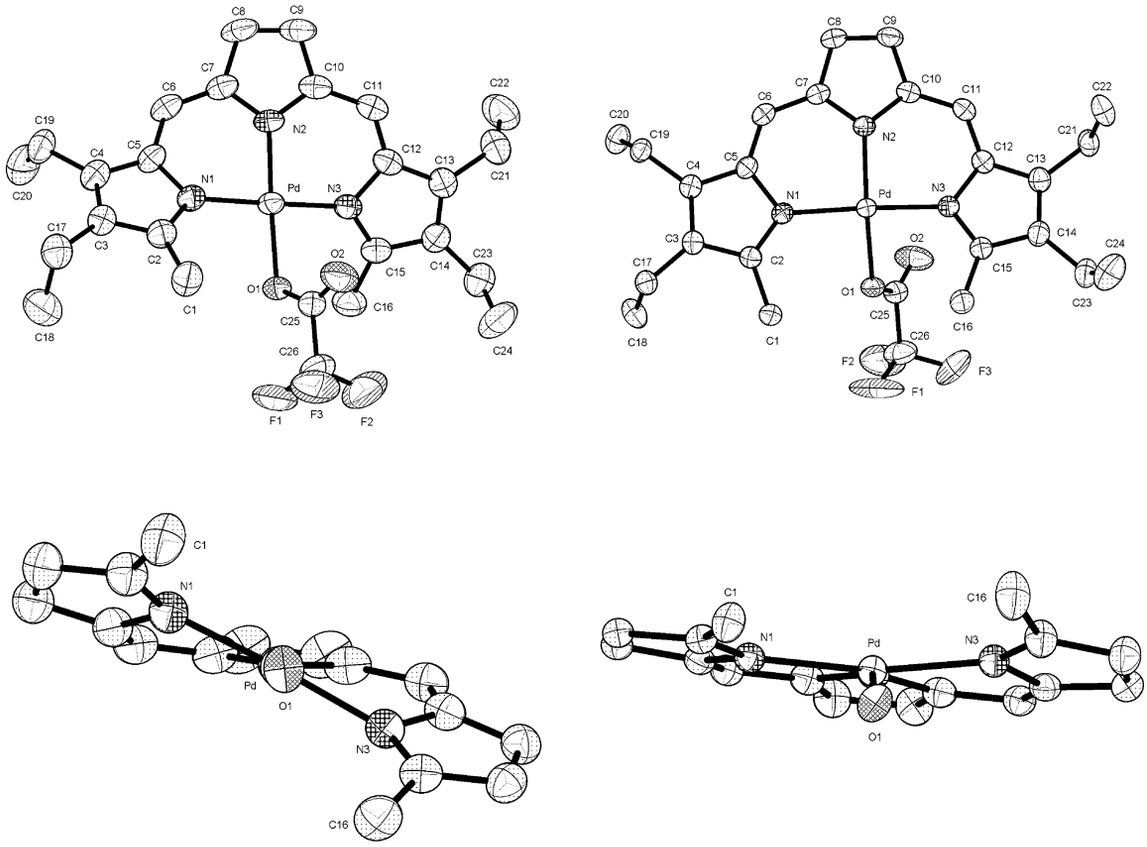
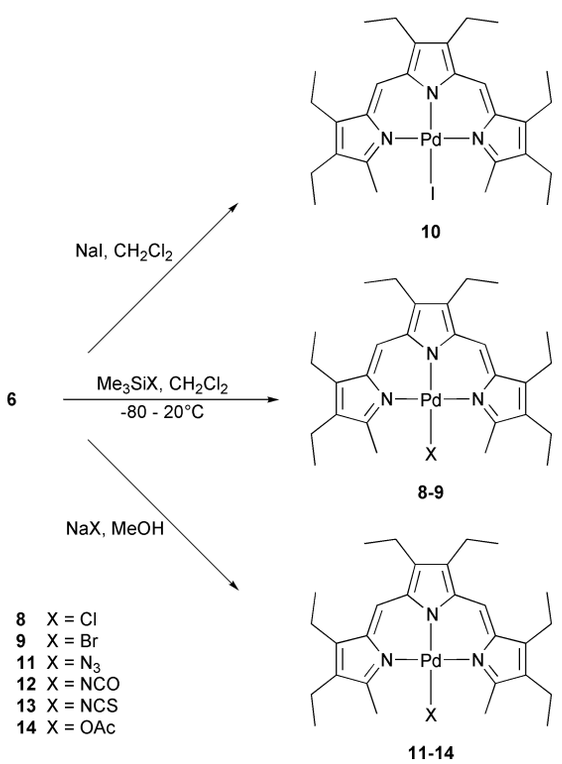


Fig. 1 ORTEP[15] plots (50% probability) of the molecular structures of **7-I** (left) and **7-II** (right). Top row: top views with numbering schemes; Bottom row: front views; ethyl- and trifluoroacyl groups omitted for clarity.

trifluoroacetato ligand compared to other donors. In search of suitable reaction conditions we first considered the treatment of dichloromethane solutions of **6** with simple sodium salts like NaCl, NaN_3 or NaI. In all cases except for NaI no reaction occurred, probably due to the insolubility of these salts in the reaction medium. Sodium iodide, however, produced TrpyPdI **10** in a quick and clean fashion. Working in cold, homogeneous solutions using trimethylsilyl-chloride, -bromide and -azide as reagents produces the desired TrpyPdCl **8** and TrpyPdBr **9**, but not the azide derivative **11**, even at 60 °C. Obviously, the reaction is driven by the high bonding energy of the Si–O moiety formed, while the stability of the Si–N_3 bond is too high to favour the exchange. As a third opportunity, ligand exchange was performed in biphasic mixtures of **6** and NaX (X = N_3, NCO, SCN, OAc, OPh) in ether–water. After several hours the formation of new TrpyPdX complexes **11**–**14** by this method is complete, while NaOPh leads to decomposed material only. With X = SCN and OAc the transformations do not proceed in a clean fashion. From proton NMR spectroscopy it can be concluded that the complexes **13** and **14**, with limited stability, are initially formed in addition to a number of unassigned by-products, but decay in the course of two hours. All attempts to isolate pure **13** or **14** failed. The anticipated reactivity of $TrpyPdOAc_f$ complexes, which was deduced from the structure elucidations, could however be proven by the successful approaches, and five new complexes **8**–**12** were obtained in good to reasonable yields.[11]

From the ligand exchange studies described above it becomes apparent that the decomposition of TrpyPd complexes is always induced by nucleophilic anions. Most probably, the *meso* positions of metallotripyrrins are polarized in the fashion shown in Scheme 4 for the diprotonated ligand. The attack of the anion might therefore occur not at the metal site only, but also at these somewhat fragile methine units. Within this alternative reactivity scenario, the more nucleophilic anions might thus induce the irreversible cleavage of the tripyrrolic



Scheme 4 Summary of ligand exchange reactions of $TrpyPdOAc_f$ **6**.

ligand framework with the result that the desired TrpyPdX complexes will not be detectable by spectroscopic means or only be so for a limited time. Unfortunately, no ligand-attacked intermediate has been detected so far to support this hypothesis.

All new complexes **8**–**12** were fully characterized by proton and carbon NMR and by combustion analyses. Of the labile **13** and **14**, only proton NMR spectra could be obtained. The

bromo derivative **9** grew suitable crystals for an X-ray diffraction study from dichloromethane–*n*-hexane. **9** crystallizes in the monoclinic system, space group *C*2/*c*, with eight molecules per unit cell [*a* = 15.392(3), *b* = 17.056(3), *c* = 21.450(4) Å, *β* = 107.80(3)°]. The molecular structure of **9** is shown in Fig. 2. Selected bond lengths and angles are given in Table 1.

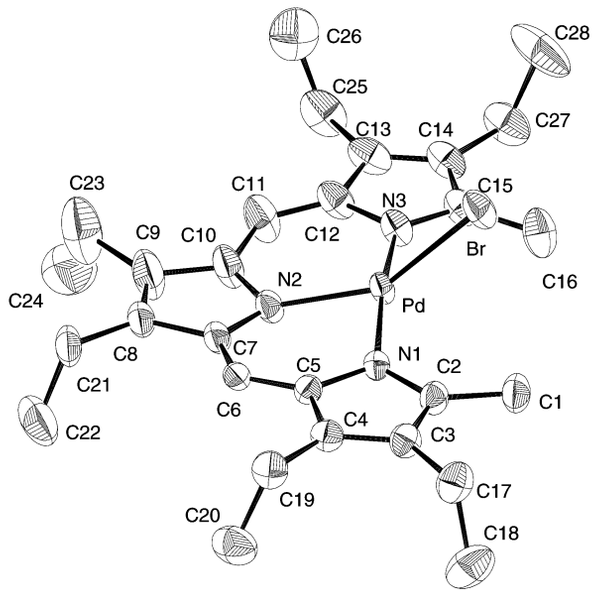


Fig. 2 ORTEP plot (50% probability) of the molecular structure of **9**.

The general structure of **9** is of the same type as that of **7-II**. The increased covalent radius of the bromo ligand with respect to the oxygen donor of **7-II** results in a remarkably strong tilt of the N_3Br coordination arrangement around the central Pd^{II} ion, leaving a N(2)–Pd–Br angle of only 147.98(10)°. The molecular parameters of the tripyrrin ligand of **9**, however, are largely comparable with those of the trifluoroacetate **7-II** with respect to bond lengths and angles, the planarity of the $C_{14}N_3$ moiety (mean deviation from plane = 0.072 Å) and the distance of the methyl termini C(1) ··· C(16) = 4.685 Å. The tilted coordination sphere of the palladium ion is apparently the major geometry for tripyrrin complexes carrying a fourth donor centre larger than oxygen and can be regarded as a characteristic feature of compounds of this type.

Conclusion

Our studies on $TrpyPdOAc_f$ complexes have shown that the formal removal of one of the pyrrole moieties from the porphyrin ring system produces a ligand with entirely new coordination properties. Other than the strictly square-planar and inert (porphyrinato)palladium(II) complexes, our metallotripyrrins constitute chelates with a high degree of structural flexibility and enhanced ligand exchange reactivity. Even within the well-developed group of metal complexes of meridional tridentate ligands this property is new. The use of the simple exchange of one ligand from TrpyMX compounds for the preparation of cationic metallotripyrrin species and for catalytic purposes is currently under investigation.

Experimental

All reagents and solvents were purchased from commercial sources and dried using standard procedures. NMR spectra were obtained on a Bruker AMX 400 spectrometer and measured at room temperature unless stated otherwise. Mass spectra (EI, 70 eV; CI, *i*-butane or FAB, nitrophenyl-*n*-octylether) were recorded on a Finnigan 90 MAT instrument. *m*/*z* values are given for the most abundant isotopes only. IR spectra were measured on a Bruker Vector 22 IR spectrometer. Melting points were determined by DTA on a Thermoanalyzer DuPont 9000. Elemental analyses (C, H, N) were performed at the microanalytical laboratory of the Institut für Anorganische Chemie, Universität Würzburg. Starting pyrroles **1**,[12] **2**,[13] and **3**[14] were prepared as previously described.

Syntheses

2,15-Dimethyl-3,4,13,14-tetraethyltripyrrin·2CF_3CO_2H 5. 2,5-Diformylpyrrole **2** (24.6 mg, 0.2 mmol) and 3,4-diethyl-2-methylpyrrole **3** (54.8 mg, 0.4 mmol) were dissolved in trifluoroacetic acid-*d* (0.8 ml) in a sealed NMR tube and heated to 70 °C for 10 h. After cooling to room temperature NMR spectra were taken of the sample.

Spectroscopic data for ***5****.* ^{1}H NMR (200 MHz; trifluoroacetic acid-*d*): *δ* 7.40 (s, 2H), 7.28 (s, 2H), 2.66 (q, *J* = 7.6 Hz, 4H), 2.56 (s, 6H), 2.46 (q, *J* = 7.6 Hz, 4H), 1.14 (t, *J* = 7.6 Hz, 6H), 1.06 (t, *J* = 7.6 Hz, 6H). ^{13}C NMR (50.3 MHz; trifluoroacetic acid-*d*): *δ* 176.6, 158.7, 141.1, 139.5, 137.0, 126.6, 124.6, 20.1, 19.0, 17.1, 15.4, 14.7.

Trifluoracetato(2,15-dimethyl-3,4,13,14-tetraethyltripyrrinato)palladium(II) 7. 2,5-Diformylpyrrole **2** (175 mg, 1.4 mmol) and 3,4-diethyl-2-methylpyrrole **3** (384 mg, 2.8 mmol) were dissolved in trifluoroacetic acid (10 ml) and heated to reflux for 10 h. After cooling to room temperature all volatiles were removed *in vacuo*, and the resulting dark residue was treated with a slurry of palladium(II) acetate (317 mg, 1.4 mmol) and sodium acetate (347 mg, 4.23 mmol) in dichloromethane (50 ml). After stirring at room temperature for 16 h, the mixture was again taken to dryness, then redissolved in dichloromethane and filtered. From the filtrate, the title compound can be isolated by radial chromatography on silica with dichloromethane (dark green fraction) and subsequent recrystallization from dichloromethane–*n*-hexane. **7** yields violet, air-stable crystals.

Spectroscopic data for ***7****.* (150 mg, 19%), mp 218 °C (Found: C, 53.79; H, 5.31; N, 6.95. $C_{26}H_{30}F_3N_3O_2Pd$ requires: C, 53.85; H, 5.21; N, 7.25%). ^{1}H NMR (CD_2Cl_2): *δ* 6.78 (s, 2H), 6.63 (s, 2H), 2.54 (q, *J* = 7.6 Hz, 4H), 2.34 (s, 6H), 2.32 (q, *J* = 7.6 Hz, 4H), 1.18 (t, *J* = 7.6 Hz, 6H), 1.04 (t, *J* = 7.6 Hz, 6H). ^{13}C NMR (CD_2Cl_2): *δ* 175.1, 161.9 (q, *J* = 35.3 Hz, CF_3CO_2), 148.8, 140.3, 139.2, 138.4, 123.8, 122.2, 115.5 (q, *J* = 291.9 Hz, CF_3CO_2), 31.0, 18.2, 17.0, 16.6, 14.5. MS (EI): *m*/*z* 466.2 $[M–OAc_f]^+$.

Crystal data for ***7-I****.* $C_{26}H_{30}F_3N_3O_2Pd$, *M* = 579.96, monoclinic, *a* = 12.6243(14), *b* = 18.028(2), *c* = 11.4931(13) Å, *β* = 104.859(2)°, *U* = 2528.2(5) Å^3, *T* = 293 K, space group $P2_1/c$, *Z* = 4, *μ*(Mo-K*α*) = 0.784 mm^{-1}, 4450 reflections measured, 4450 unique (R_{int} = 0.000), which were used in all calculations. The final $wR(F^2)$ was 0.0731 (all data).

CCDC reference number 172680.

Crystal data for ***7-II****.* $C_{26}H_{30}F_3N_3O_2Pd$, *M* = 579.96, triclinic, *a* = 8.8220(7), *b* = 11.3413(9), *c* = 13.9761(11) Å, *α* = 113.2790(10), *β* = 100.8980(10), *γ* = 93.0320(10)°, *U* = 1248.66(17) Å^3, *T* = 173 K, space group $P\bar{1}$, *Z* = 2, *μ*(Mo-K*α*) = 0.794 mm^{-1}, 24080 reflections measured, 4404 unique (R_{int} = 0.0265), which were used in all calculations. The final $wR(F^2)$ was 0.0639 (all data).

CCDC reference number 172681.

Chloro(2,15-dimethyl-3,4,8,9,13,14-hexaethyltripyrrinato)palladium(II) 8 and bromo(2,15-dimethyl-3,4,8,9,13,14-hexaethyltripyrrinato)palladium(II) 9 — general procedure. A solution of **6** (211.9 mg; 0.33 mmol) in dry toluene (30 ml) was treated dropwise, at −78 °C, with a precooled solution of the respective trimethylsilylhalide (0.33 mmol) in the same solvent (40 ml). The mixture, which changed from green to blue during the addition, was allowed to warm to room temperature, whereupon the solvent was removed *in vacuo*. The residue was taken up in dichloromethane (10 ml), filtered, and purified by radial chromatography on silica with dichloromethane as the

eluent. The green, major band was collected and recrystallized from dichloromethane–*n*-hexane to yield violet microcrystalline solids.

Spectroscopic data for ***8***. (173 mg, 94%), mp 204 °C (decomp.) (Found: C, 60.03; H, 6.79; N, 6.91. $C_{28}H_{38}ClN_3Pd$ requires: C, 60.22; H, 6.86; N, 7.52%). ^{1}H NMR (CD_2Cl_2): δ 6.71 (s, 2H), 2.65 (s, 6H), 2.58–2.49 (m, 8H), 2.34 (q, J = 7.6 Hz, 4H), 1.20 (t, J = 7.6 Hz, 6H), 1.12 (t, J = 7.6 Hz, 6H), 1.05 (t, J = 7.6 Hz, 6H). ^{13}C NMR (CD_2Cl_2): δ 175.9, 148.5, 140.0, 137.0, 136.5, 119.7, 20.4, 18.4, 18.3, 17.9, 17.3, 16.8, 14.6. MS (EI): *m*/*z* 522 $[M - Cl]^+$.

Spectroscopic data for ***9***. (160.0 mg, 81%), mp 147 °C (decomp.) (Found: C, 56.21; H, 6.14; N, 6.51. $C_{28}H_{38}BrN_3Pd$ requires: C, 55.78; H, 6.35; N, 6.97%). ^{1}H NMR (CD_2Cl_2): δ 6.72 (s, 2 H), 2.76 (s, 6H), 2.55 (q, J = 7.6 Hz, 4 H), 2.54 (q, J = 7.6 Hz, 4 H), 2.35 (q, J = 7.6 Hz, 4 H), 1.19 (t, J = 7.6 Hz, 6 H), 1.15 (t, J = 7.6 Hz, 6 H), 1.07 (t, J = 7.6 Hz, 6 H). ^{13}C NMR (CD_2Cl_2): δ 175.2, 148.3, 139.5, 138.1, 137.4, 136.7, 119.2, 22.4, 18.5, 18.3, 18.0, 17.3, 16.8, 14.6. MS (CI): *m*/*z* 522 $[M - Br]^+$.

Crystal data for ***9***. $C_{28}H_{38}BrN_3Pd$, M = 602.95, monoclinic, a = 15.392(3), b = 17.056(3), c = 21.450(4) Å, β = 107.80(3)°, U = 5361.8(19) Å^3, T = 173 K, space group $C2/c$, Z = 8, μ(Mo-Kα) = 2.203 mm^{-1}, 21727 reflections measured, 4732 unique (R_{int} = 0.0722), which were used in all calculations. The final $wR(F^2)$ was 0.1077 (all data).

CCDC reference number 172679.

See http://www.rsc.org/suppdata/dt/b1/b109510m/ for crystallographic data in CIF or other electronic format.

Iodo(2,15-dimethyl-3,4,8,9,13,14-hexaethyltripyrrinato)-palladium(II) 10. Trifluoracetate **6** (73.0 mg, 0.15 mmol) and excess sodium iodide were stirred in dichloromethane (20 ml) at room temperature for 2 h. The resulting mixture was filtered over Celite, and the filtrate concentrated and subjected to radial chromatography (silica, dichloromethane). The material from the green major fraction was recrystallized from dichloromethane–*n*-hexane to yield a violet solid.

Spectroscopic data for ***10***. (73.1 mg, 98%), mp 143 °C (decomp.) (Found: C, 51.81; H, 5.87; N, 6.49. $C_{28}H_{38}IN_3Pd$ requires: C, 51.74; H, 5.89; N, 6.47%). ^{1}H NMR (C_6D_6): δ 6.67 (s, 2 H), 2.92 (s, 6 H), 2.41 (q, J = 7.6 Hz, 4 H), 2.16 (q, J = 7.6 Hz, 4 H), 1.95 (q, J = 7.6 Hz, 4 H), 1.08 (t, J = 7.6 Hz, 6 H), 0.88 (t, J = 7.6 Hz, 6 H), 0.81 (t, J = 7.6 Hz, 6 H). ^{13}C NMR (C_6D_6): δ 173.7, 147.5, 139.3, 137.4, 137.0, 136.7, 118.8, 26.2, 18.1, 18.0, 17.3, 16.7, 16.5, 14.4. MS (EI): *m*/*z* 522 $[M - I]^+$.

TrpyPdX complexes 11 (X = N_3), 12 (X = NCO), 13 (X = SCN) and 14 (X = OAc) — general procedure. Trifluoroacetate **6** (40.0 mg, 62.9 μmol) and excess NaX were stirred in a biphasic mixture of diethyl ether (15 ml) and degassed water (15 ml) for 16 h. The organic layer was separated and taken to dryness *in vacuo*, before the residue was redissolved in dry dichloromethane and filtered over Celite. Evaporation of the solvent yielded a violet solid.

Spectroscopic data for ***11***. (28.1 mg, 79%), mp 138 °C (decomp.) (Found: C, 59.17; H, 6.88; N, 13.76. $C_{28}H_{38}N_6Pd$ requires: C, 59.52; H, 6.78; N, 14.87%). ^{1}H NMR (CD_2Cl_2): δ 6.72 (s, 2H), 2.65 (s, 6H), 2.55 (q, J = 7.6 Hz, 4H), 2.53 (q, J = 7.6 Hz, 4H), 2.37 (q, J = 7.6 Hz, 4H), 1.20 (t, J = 7.6 Hz, 6H), 1.11 (t, J = 7.6 Hz, 6H), 1.08 (t, J = 7.6 Hz, 6H). ^{13}C NMR (CD_2Cl_2): δ 174.5, 148.8, 139.7, 137.9, 137.8, 137.5, 119.7, 18.4, 18.3, 17.9, 17.3, 17.2, 16.8, 14.6. MS(EI): *m*/*z* 521 $[M - N_3]^+$. IR (Nujol): ν = 2028 cm^{-1} (ν_{NNN}).

Spectroscopic data for ***12***. (21.3 mg, 60%), mp 185 °C (decomp.) (Found: C, 61.75; H, 6.78; N, 9.85. $C_{29}H_{38}N_4OPd$ requires: C, 61.64; H, 6.78; N, 9.92%). ^{1}H NMR (CD_2Cl_2): δ 6.74 (s, 2H), 2.56 (s, 6H), 2.56 (q, J = 7.6 Hz, 4H), 2.51 (q, J = 7.6 Hz, 4H), 2.36 (q, J = 7.6 Hz, 4H), 1.20 (t, J = 7.6 Hz, 6H), 1.11 (t, J = 7.6 Hz, 6H), 1.07 (t, J = 7.6 Hz, 6H). ^{13}C NMR (CD_2Cl_2): δ 175.0, 148.7, 139.7, 137.7, 137.4, 136.7, 119.9, 18.9, 18.4, 18.3, 17.9, 17.3, 16.8, 14.6. MS(EI): *m*/*z* 522 $[M–NCO]^+$. IR (Nujol): ν = 2250 cm^{-1} (ν_{NCO}).

Spectroscopic data for ***13***. ^{1}H NMR (200 MHz; CD_2Cl_2): δ 6.75 (s, 2H), 2.57 (q, J = 7.6 Hz, 4H), 2.56 (s, 6H), 2.55 (q, J = 7.6 Hz, 4H), 2.37 (q, J = 7.6 Hz, 4H), 1.20 (t, J = 7.6 Hz, 6H), 1.11 (t, J = 7.6 Hz, 6H), 1.09 (t, J = 7.6 Hz, 6H). IR (Nujol): ν = 2132 cm^{-1} (ν_{CN}).

Spectroscopic data for ***14***. ^{1}H NMR (200 MHz; CD_2Cl_2): δ 6.72 (s, 2H), 2.55 (q, J = 7.6 Hz, 4H), 2.53 (q, J = 7.6 Hz, 4H), 2.37 (q, J = 7.6 Hz, 4H), 2.36 (s, 6H), 1.86 (s, 3H), 1.23 (t, J = 7.6 Hz, 6H), 1.15 (t, J = 7.6 Hz, 6H), 1.05 (t, J = 7.6 Hz, 6H).

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