Syntheses of New Sulfur−Nitrogen Palladacycles − Crystal Structures of $[(AMTTO)PdBr_2]_2 \cdot 3.5THF$, $[(AMTTO)PdI_2]_2 \cdot 3MeOH$, $[(AMTTO)Pd(PPh_3)Br]Br \cdot MeOH$, and $[(AMTTO)Pd(PPh_3)I] \cdot 2MeOH$ (AMTTO = 4-Amino-6-methyl-1,2,4-triazine-3-thione-5-one)

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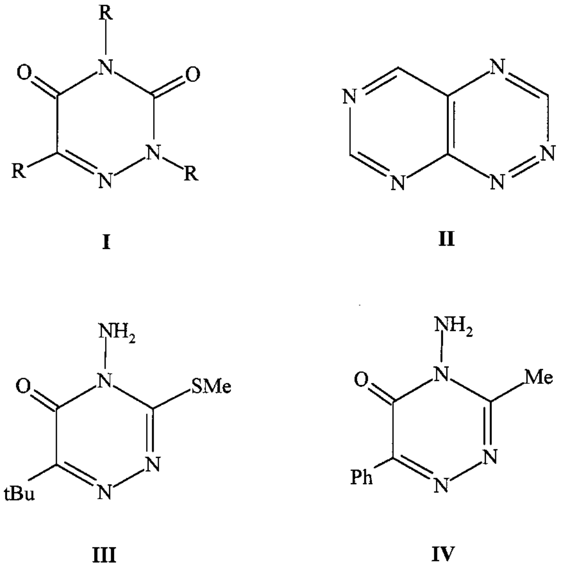
Reactions of $[(AMTTO)PdCl_2] \cdot MeOH$ (**1**) with sodium bromide and sodium iodide led to the palladacycles $[(AMTTO)PdBr_2]_2 \cdot 3.5THF$ (**2**) and $[(AMTTO)PdI_2]_2 \cdot 3MeOH$ (**3**) in excellent yields. Treatment of **2** and **3** with triphenylphosphane gave the complexes $[(AMTTO)Pd(PPh_3)Br]Br \cdot MeOH$ (**4**) and $[(AMTTO)Pd(PPh_3)I] \cdot 2MeOH$ (**5**), respectively. All the complexes have been characterized by IR spectroscopy, elemental analysis, as well as by X-ray diffraction studies. In addition, **4** and **5** have been characterized by ^{31}P NMR spectroscopy. Crystal data for **2** at −80 °C: triclinic, space group $P\bar{1}$, $a = 1150.8(1)$, $b = 1234.1(1)$, $c = 1398.1(1)$ pm, $\alpha = 84.01(1)°$, $\beta = 86.84(1)°$, $\gamma = 66.40(1)°$, $Z = 2$, $R_1 = 0.0366$; for **3** at −50 °C: orthorhombic, space group $Pbcn$, $a = 1476.2(1)$, $b = 1333.1(1)$, $c = 1440.1(1)$ pm, $Z = 4$, $R_1 = 0.0302$; for **4** at −80 °C: monoclinic, space group $P2_1/c$, $a = 993.0(1)$, $b = 993.6(1)$, $c = 2735.5(2)$ pm, $\beta = 97.64(1)°$, $Z = 4$, $R_1 = 0.0464$; for **5** at −70 °C: monoclinic, space group $P2_1/c$, $a = 865.7(2)$, $b = 3760.5(3)$, $c = 861.1(1)$ pm, $\beta = 97.56(1)°$, $Z = 4$, $R_1 = 0.0613$.

Introduction

1,2,4-Triazines are well-known compounds and a variety of synthetic methods for the preparation of substituted derivatives are available. Compounds containing the 1,2,4-triazine moiety are found in natural materials and some of these exhibit biological activity. A large number of synthetic 1,2,4-triazines also show biological activity and have been used for various purposes. For example, 1,2,4-triazine-3,5-diones (**I**) represent aza analogues of pyrimidine nucleic acid bases. A number of neutral antibiotics are derivatives of pyrimido[5,4-*e*]-1,2,4-triazine (**II**). 4-Amino-6-*tert*-butyl-3-methylthio-1,2,4-triazine-5-one (**III**) and 4-amino-3-methyl-6-phenyl-1,2,4-triazine-5-one (**IV**) are used as herbicides (Scheme 1).[1a] Metal complexes of ligands such as S,N-heterocycles, amino acids, and proteins often exhibit enhanced biological activities compared to the uncomplexed ligand.[1b][1c]



Scheme 1. Four important classes of N-containing heterocycles

In our investigations, we have shown that AMTTO − a representative of 4-amino-6-alkyl-1,2,4-triazine-5-one − acts as a chelating ligand in a 1+1 fashion towards $AgNO_3$ in methanol {one strong Ag−S bond and a weak Ag−N contact leading to a distortion of a ideal linear $[AMTTO\text{-}Ag\text{-}AMTTO]^+$ ion} and as a bidentate chelating ligand towards $PdCl_2$ in methanol/acetonitrile to give the air-stable complexes $[(AMTTO)_2Ag]NO_3$ [2] and $[(AMTTO)PdCl_2] \cdot MeOH$ (**1**),[3] respectively. To the best of our knowledge, the latter constitutes the first palladacycle of AMTTO.

We have already studied the reactions of **1** with triphenylphosphane and sodium thiocyanate, which led to the air-stable complexes $[(AMTTO)Pd(PPh_3)Cl]Cl \cdot MeOH$ and $[(AMTTO)Pd(SCN)_2] \cdot MeOH$, respectively.[4]

In this paper, we wish to report the halide exchange reactions of **1** using sodium bromide and sodium iodide, as well

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as the reactions of the bromine and iodine palladacycles with triphenylphosphane.

Results and Discussion

Syntheses and Characterization of 2, 3, 4, and 5

Treatment of **1** with sodium bromide in THF at 20 °C gave **2**; similar treatment with sodium iodide in methanol/acetonitrile gave **3** [Equation (1) and (2)].

$$2\,[\text{(AMTTO)PdCl}_2] + 4\,\text{NaBr} \xrightarrow{\text{THF; 20°C}} \underset{\mathbf{2}}{[\text{(AMTTO)PdBr}_2]_2\cdot 3.5\text{THF}} + 4\,\text{NaCl} \quad (1)$$

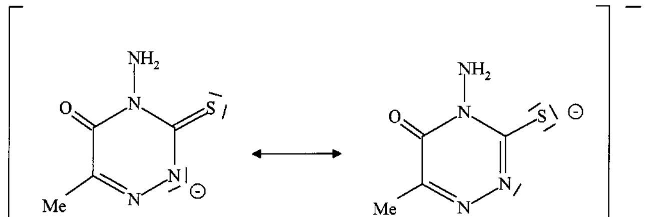
$$2\,[\text{(AMTTO)PdCl}_2] + 4\,\text{NaI} \xrightarrow{\text{MeOH/MeCN; 20°C}} \underset{\mathbf{3}}{[\text{(AMTTO)PdI}_2]_2\cdot 3\text{MeOH}} + 4\,\text{NaCl} \quad (2)$$

Further treatment of **2** and **3** with PPh_3 in methanol at 20 °C led to **4** and **5**, respectively, according to Equation (3) and (4).

$$[\text{(AMTTO)PdBr}_2] + \text{PPh}_3 \xrightarrow{\text{MeOH; 20°C}} \underset{\mathbf{4}}{[\text{(AMTTO)Pd(PPh}_3\text{)Br]Br}\cdot\text{MeOH}} \quad (3)$$

$$[\text{(AMTTO)PdI}_2] + \text{PPh}_3 \xrightarrow{\text{MeOH; 20°C}} \underset{\mathbf{5}}{[\text{(AMTTO)Pd(PPh}_3\text{)I]}\cdot 2\text{MeOH}} + \text{HI} \quad (4)$$

In contrast to Equation (3), reaction according to Equation (4) gives the complex **5** incorporating the anionic ligand $[AMTTO]^-$ (**V**). This results from an abstraction of HI owing to the relatively high acidity of this particular NH group. The coordination of the sulfur atom leads to additional acidification of the amine function (see Scheme 2).



V

Scheme 2. Mesomeric forms of the anionic AMTTO ligand

Compounds **2–5** were found to be air-stable crystalline solids. The ^{13}C NMR spectrum of the ligand AMTTO has been published for the Ag complex $[Ag(AMTTO)_2]NO_3$ [2] and the data are almost unchanged in the spectra of **2–5**. The ^{31}P NMR spectra of **4** and **5** feature only one sharp singlet at $\delta = 30.3$ and $\delta = 26.2$, respectively, in accordance with the geometries of these compounds. In the IR spectra of **2–5**, three absorptions are seen at 452, 369, and 268 cm^{-1} for **2**, at 445, 373, and 173 cm^{-1} for **3**, at 450, 382, and 259 cm^{-1} for **4**, and at 449, 374, and 198 cm^{-1} for **5**, which can be assigned to ν(PdN), ν(PdS), and ν(PdX) absorptions.[5] C=O and C=N vibrations give rise to two bands at 1703 and 1604 cm^{-1} for **2**, at 1718 and 1612 cm^{-1} for **3**, at 1719 and 1595 cm^{-1} for **4**, and at 1725 and 1625 cm^{-1} for **5**. P–C vibrations of the PPh_3 moiety are seen in the range 749–711 cm^{-1} for **4** and in the range 745–691 cm^{-1} for **5**. The N–H valence vibrations give rise to broad bands at 3254 (**2**), 3230 (**3**), 3205 (**4**), and 3250 cm^{-1} (**5**). Broad O–H absorptions, attributable to hydrogen bonding, give rise to the bands at 3620, 3554, and 3472 cm^{-1} (**3**) and at 3446 cm^{-1} (**5**). The corresponding band for **4** could not localized accurately because of the measured line width.

Crystal Structures of 2–5

The structural data of the palladacycles show that **2** (Figure 1), **3** (Figure 2), and **5** (Figure 4) are neutral molecules incorporating [(AMTTO)Pd] complex fragments. **4** is a salt consisting of $[(AMTTO)Pd(PPh_3)Br]^+$ and Br^- ions, while **5** incorporates the anionic ligand $[AMTTO]^-$. The coordination geometry about the palladium center in each of these complexes is essentially square planar. In all the complexes, the bidentate AMTTO ligand is coordinated to palladium(II) forming a five-membered chelate ring. The coordination sphere of **2** is completed by two bromide anions, while that of **3** is completed by two iodide ions. The coordination sites in **4** and **5** are occupied by one halide ion (Br^- in **4**; I^- in **5**, Figure 3 and 4) and a triphenylphosphane ligand. The Pd–S bond lengths of 225.2(2)/225.9(2) and 227.4(2) pm found in **2** and **3**, respectively, do not differ significantly from the Pd–S distances of 227.5(2) and 226.6(2) pm in **4** and **5**. On comparing the data with the lowest literature values for thioether-palladium complexes, i.e. 228–229 pm, these distances are seen to be rather short.[6,7] The Pd–N atom distances are within the range observed for related compounds.[7] The Pd–N bond lengths [211.0(5) pm in **4**; 209.2(7) pm in **5**] are longer than those in **2** and **3** [204.2(6) and 207.9(5) pm, respectively]. This lengthening reflects the *trans* influence of the phosphane ligand. The Pd–X bonds *trans* to the sulfur atom [Pd1–Br1 and Pd2–Br4, 244.7(1) and 244.1(9) pm in **2**; Pd1–I2 259.73(6) pm in **3**] are somewhat longer than the Pd–X distances *cis* to S1 [Pd1–Br2 240.75(6) pm and Pd2–Br3 242.5(1) pm in **2**; Pd1–I1 257.50(6) pm in **3**], reflecting the greater *trans* influence of the sulfur atom as compared to the nitrogen atom. The presence of an $[AMTTO]^-$ ligand in **5** leads only to marginal differences in the bonding parameters due to the delocalization of the charge in **V** (Scheme 2).

The halide atoms in **4** and **5** are oriented *cis* to the nitrogen ligands of the heterocycle, indicating the strong influence of the π-acids C=S and PPh_3. The Pd–Br and Pd–I bond lengths (Pd–Br, mean 243 pm; Pd–I, mean 259.5 pm) are shorter than the sum of the single bond radii for palladium and the halides (Pd: 131 pm, Br: 114 pm, I: 133

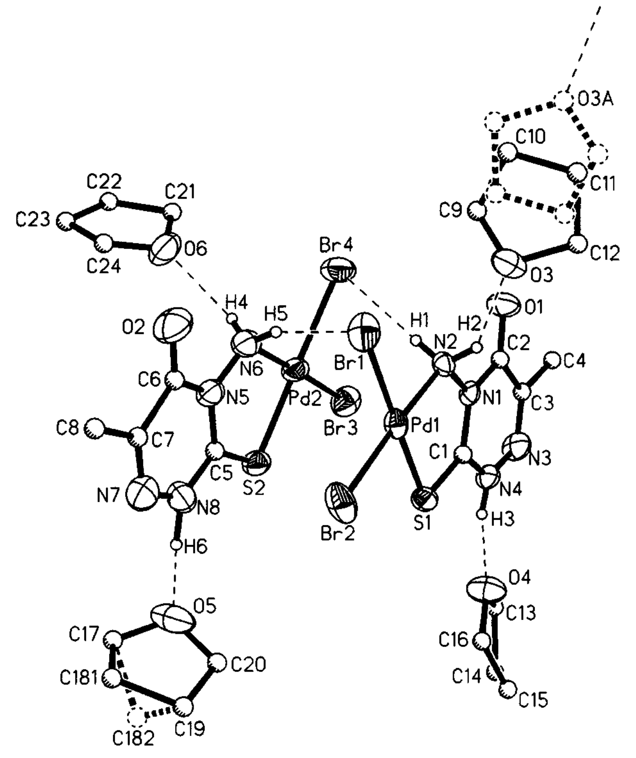


Figure 1. Molecular structure of **2** with showing disorder of the THF molecules (the C atoms are shown as spheres; most of the H atoms are omitted for the sake of clarity; 50% probability level)

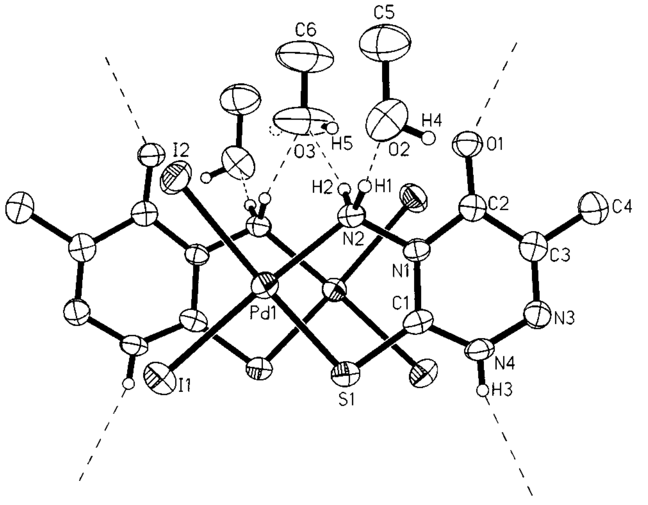


Figure 2. Molecular structure of **3** with showing disorder of the central methanol molecule (most of the H atoms are omitted for the sake of clarity)

pm),[8] but fall within the range observed for similar compounds.[9]

The Pd−P atom distances (average 225 pm) are shorter than the sum of the single bond radii for palladium and phosphorus, i.e. 241 pm,[10] are remarkably shorter than the Pd^{II}−PPh$_3$ bond reference value (230.2 pm) encountered in 248 entries,[11] and fall at the short end of a wide range (221−246 pm). The X−Pd−P angles, which measure 92.04(4)° in **4** and 92.64(7)° in **5**, are similar to values reported in the literature.[12]

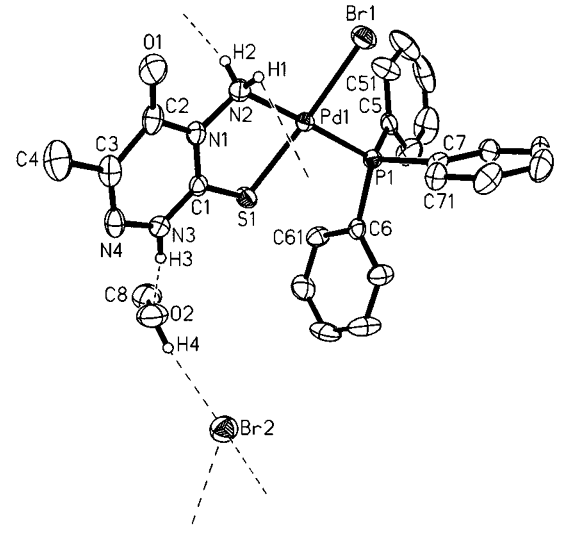


Figure 3. Molecular structure of **4** (most of the H atoms are omitted for the sake of clarity)

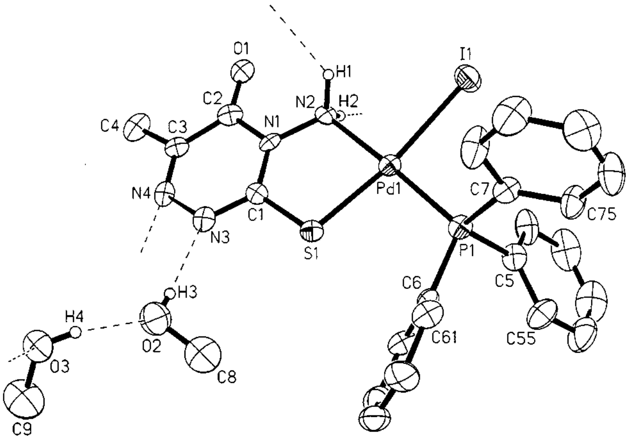


Figure 4. Molecular structure of **5** (most of the H atoms are omitted for the sake of clarity)

There are several medium to strong hydrogen bonds in the complexes. The two independent palladacycle units in **2** are held together by H···Br contacts [N2···Br4: 346.5(7); N6···Br1: 334.2(6) pm]. This leads to an angle of 7° between the "best" planes of the two complexes. THF molecules are hydrogen-bonded to H2 [N2···O3: 286.9(9) pm], H3 [N4···O4: 270.2(7) pm], H4 [N6···O6: 277.1(8) pm], and H6 [N8···O5: 265.3(9) pm]. The THF molecule O3→C12 is disordered about a center of symmetry (see Figure 1).

In **3**, two palladacycles are connected through a methanol molecule, which lies on a twofold axis. This means a disorder of the OH moiety O3−H5 over two positions [N2···O3: 287.9(8)°]. An additional methanol molecule is hydrogen-bonded to each NH$_2$ group [N2···O2: 282.6(7)° pm]. Each [(AMTTO)PdI$_2$]$_2$·3MeOH building block is part of a chain built up by N2−H1···O2 hydrogen bonds [N2···O2: 282.6(7)°; Figure 5] that extends along [010]. The palladacycles in **3** are slightly bent. The dihedral angle between the plane Pd1/I1/I2/N2/S2 and the ligand AMTTO amounts to 7°. In **4**, isotypical to the corresponding complex [(AMTTO)PdCl(PPh$_3$)]Cl·MeOH,[4] N3 (NH function)

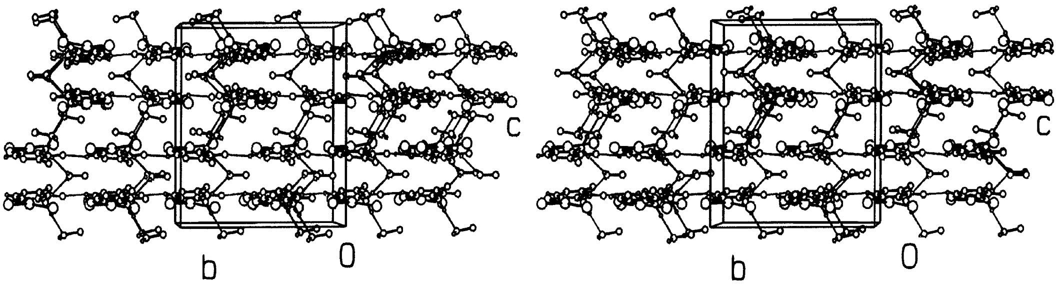


Figure 5. Stereoscopic view of the unit cell of **3**; the chains extending along [010] as a result of hydrogen bonding are also shown

is connected through the methanol molecule [N3···O2: 265.4(7) pm] to Br2 [counterion; O2···Br2: 322.3(5) pm] and then to two nitrogen atoms [N2a, N2b; NH_2 function; N2···Br2a: 338.1(5); N2···Br2b: 320.8(5) pm; Figure 3]. The packing of **4** has already been demonstrated for $[(AMTTO)PdCl(PPh_3)]Cl\cdot MeOH$.[4] In **5**, medium to strong hydrogen bonds link the methanol molecules to N3 and to NH_2 groups of the adjacent AMTTO ligands, respectively (Figure 4). The contacts O3···O2 [266.7(9) pm], O2···N3 [286.9(9) pm], O3···N2a [278.7(9) pm], and N4···N2b [294.8(9) pm] give rise to a 2D-network of complex and solvate molecules that extends parallel to (010) (Figure 6).

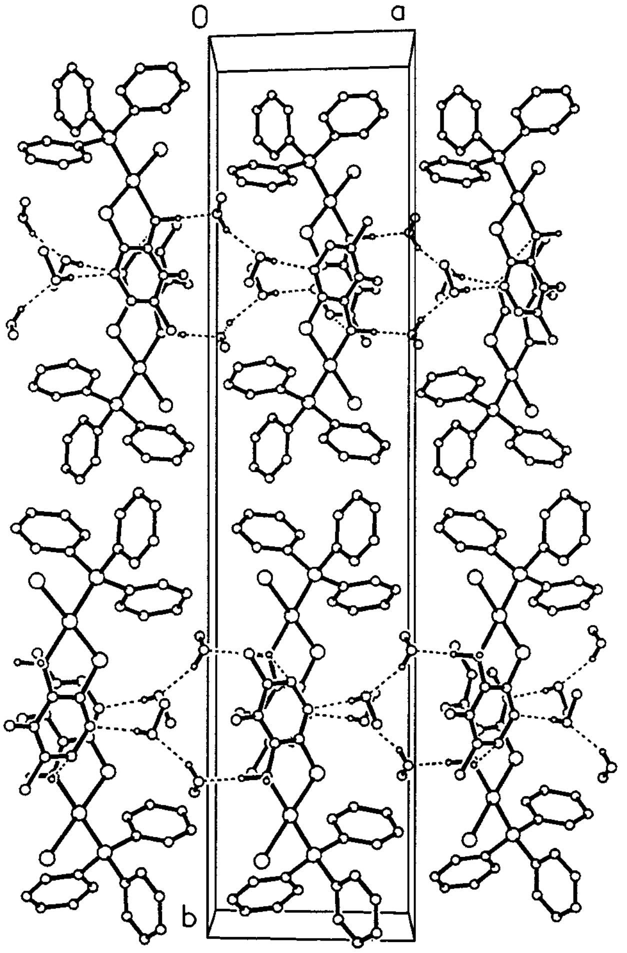


Figure 6. View of the unit cell of **5**; **5** forms layers built-up by hydrogen bonds parallel to (010)

Experimental Section

General Remarks: AMTTO[13] and **1**[3] were prepared according to literature procedures. – IR spectra were recorded on a Perkin–Elmer spectrometer 883 (KBr pellets, Nujol mulls, 4000–250 cm^{-1}) or on a Bruker IFS 88 instrument (CsBr discs, 4000–400 cm^{-1}; polyethylene discs, 500–100 cm^{-1}; Nujol mulls). – ^{31}P NMR spectra were recorded on a Bruker AC-200 spectrometer using 85% aqueous H_3PO_4 as an external standard. – Elemental analyses were performed by the following methods: C, H, N analyses: combustion method; halogen analyses: combustion and titration with $AgNO_3$; sulfur analyses: combustion and titration with $Ba(ClO_4)_2$; phosphorus: decomposition with $HClO_4$ and photometric analysis of the molybdophosphate; palladium analyses: decomposition with $HClO_4$ and analysis by atomic absorption spectroscopy. – The following chemicals were purchased from Merck and used without further purification: sodium bromide, sodium iodide, triphenylphosphane, methanol, and acetonitrile.

Synthesis of $[(AMTTO)PdBr_2]_2\cdot 3.5THF$ (2): A solution of **1** (0.36 g, 0.98 mmol) in THF (20 mL) was treated with NaBr (0.20 g, 1.9 mmol) and the resulting mixture was stirred for 3 h at 20 °C. The white precipitate formed was filtered off and the filtrate was concentrated to a small volume (ca. 5 mL) until an orange solid separated. The crude product was filtered off and the clear solution was kept at 4 °C to give a second crop of orange crystals of **2**. – Yield: 0.96 g (95%). – $C_{22}H_{40}Br_4N_8O_{5.5}Pd_2S_2$ (1011.19): calcd. C 13.16, H 2.21, N 12.27, Br 35.01, Pd 23.31, S 7.02; found C 13.01, H 2.14, N 12.17, Br 34.90, Pd 23.35, S 6.97. – IR (Nujol): $\tilde{\nu}$ = 3254 [w, br, ν(NH)], 1703 [s, ν(C=O)], 1604 [m, ν(N=C)], 1588 (m), 1520 (m), 1321 (m), 1304 (s), 1233 (m), 1166 (m), 1036 (m), 974 (w), 930 (w), 875 (w), 802 (w), 749 (s), 675 (m), 646 (w), 606 (m), 528 (w), 506 (m), 452 [m, ν(PdN)], 409 (w), 369 [w, ν(PdS)], 310 (m), 268 [w, $\nu(PdBr_2)$], 246 (w), 198 (w), 165 (w).

Synthesis of $[(AMTTO)PdI_2]_2\cdot 3MeOH$ (3): To a stirred solution of **1** (0.36 g, 0.98 mmol) in methanol/acetonitrile (1:1 *v*/*v*, 30 mL) at 20 °C was added NaI (0.29 g, 1.9 mmol). The reaction mixture was stirred for a further 5 h. The white solid formed was filtered off and the filtrate was concentrated to a volume of 10 mL and filtered once more. The filtrate was stored at 4 °C overnight to give orange crystals of **3**, which were collected by filtration and washed with cold methanol. – Yield: 1.05 g (93%). – $C_{11}H_{24}I_4N_8O_5Pd_2S_2$ (1133.0): calcd. C 11.66, H 2.14, N 9.89, I 44.81, Pd 18.79, S 5.66; found C 11.55, H 2.10, N 9.56, I 44.92, Pd 18.56, S 5.34. – IR (Nujol): $\tilde{\nu}$ = 3620 [vw, br, ν(OH)], 3554 [w, br, ν(OH)], 3472 [w, br, ν(OH)], 3230 [w, br, ν(NH)], 1719 [s, ν(C=O)], 1595 [m, ν(C=C)], 1538 (w), 1516 (w), 1492 (w), 1335 (m), 1301 (s), 1218 (w), 1150 (w), 1112 (w), 1048 (w), 973 (w), 926 (w), 602 (w), 512 (m), 445 [m, ν(PdN)], 409 (w), 373 [w, ν(PdS)], 325 (vw), 305 (w), 280 (vw), 253 (w), 228 (w), 201 (vw), 173 [w, $\nu(PdI_2)$], 128 (vw) 112 (vw).

Reactions with PPh_3. − General Procedure: A solution of **2** (or **3**) (1.00 mmol) in methanol (30 mL) was treated with PPh_3 (0.26 g, 0.99 mmol) and the resulting mixture was stirred for 3 h at 20 °C. The solution was then concentrated to a small volume (ca. 10 mL) until a yellow solid separated. The crude product was filtered off and the clear filtrate was kept at 4 °C to give yellow crystals of **4** (or **5**).

Synthesis of [(AMTTO)Pd(PPh_3)Br]Br·MeOH (4): Yield: 0.64 g (90%). − $C_{23}H_{25}Br_2N_4O_2PPdS$ (718.73): calcd. C 38.44, H 3.51, N 7.80, Br 22.23, P 4.31, Pd 14.81, S 4.46; found C 38.26, H 3.46, N 7.72, Br 21.98, P 4.15, Pd 14.68, S 4.31. − IR (Nujol): $\tilde{\nu}$ = 3205 [w, br, ν(NH)], 1719 [vs, ν(C=O)], 1612 [m, ν(C=C)], 1573 (m), 1537 (m), 1435 (s), 1348 (m), 1301 (m), 1185 (w), 1146 (w), 1097 (s), 1045 (w), 1024 (w), 1000 (m), 966 (m), 936 (w), 750 (s), 712 (m), 692 (s), 655 (w), 619 (w), 601 (w), 536 (s), 507 (s), 450 [m, ν(NH)], 412 (w), 382 [m, ν(PdS)], 310 (vw), 259 [w, ν(PdBr)], 195 (m), 132 (vw). − ^{31}P NMR (CD_3OD): δ = 30.3 (s).

Synthesis of [(AMTTO)Pd(PPh_3)I]·2MeOH (5): Yield: 0.65 g (91%). − $C_{24}H_{28}IN_4O_3PPdS$ (716.87): calcd. C 40.21, H 3.94, N 7.82, I 17.78, P 4.32, Pd 14.85, S 4.47; found C 39.89, H 3.87, N 7.71, I 17.65, P 4.26, Pd 13.99, S 4.36. − IR (Nujol): $\tilde{\nu}$ = 3446 [vw, br, ν(OH)], 3250 [vw, br, ν(NH)], 1728 [vs, ν(C=O)], 1625 (m, C=

Table 1. Crystallographic data for **2−5**

Compound		**2**	**3**	**4**	**5**
Empirical formula		$C_{22}H_{40}Br_4N_8O_{5.5}Pd_2S_2$	$C_{11}H_{24}I_4N_8O_5Pd_2S_2$	$C_{23}H_{25}Br_2N_4O_2PPdS$	$C_{24}H_{28}IN_4O_3PPdS$
Formula mass		1101.19	1133.0	718.73	716.87
Crystal size (mm)		0.25 × 0.17 × 0.05	0.51 × 0.2 × 0.09	0.38 × 0.13 × 0.09	0.39 × 0.1 × 0.1
Crystal system		triclinic	orthorhombic	monoclinic	monoclinic
Space group		$P\bar{1}$ (no.2)[20]	*Pbcn* (no.60)	$P2_1/n$ (no.14)	$P2_1/c$ (no.14)
a [pm]		1150.8(1)	1476.2(1)	993.0(1)	865.7(2)
b [pm]		1234.1(1)	1333.1(1)	993.6(1)	3760.5(3)
c [pm]		1398.1(1)	1440.1(1)	2735.5(2)	861.1(1)
α [°]		84.01(1)	−	−	−
β [°]		86.84(1)	−	97.64(1)	97.56(1)
γ [°]		66.40(1)	−	−	−
Volume [$pm^3 \cdot 10^6$]		1809.4(3)	2834.0(3)	2675.0(4)	2778.9(8)
Z		2	4	4	4
$D_{calcd.}$ [$g \cdot cm^{-3}$]		2.021	2.655	1.785	1.713
Absorption correction		numerical	empirical	numerical	empirical
$\mu_{Mo\text{-}K\alpha}$ [cm^{-1}]		55.7	58.1	38.5	19.4
Temperature [K]		193	223	193	183
2θ range		4.0−52.06	2.0−50.0	4.22−51.9	5.76−50.0
Index range	*h*	−14→14	−1→17	−12→12	−10→10
	l	−15→15	−2→15	−12→12	−44→0
	k	−17→17	−1→17	−33→33	0→10
Reflections collected		14079	3896	20729	5346
Unique reflections (R_{int})		6530 (0.069)	2498 (0.0244)	5214 (0.0628)	4898 (0.0698)
Reflections with $F_o > 4\,\sigma(F_o)$		3262	1996	3502	3129
Parameters		443	170	407	331
R_1		0.0366	0.0302	0.0464	0.0611
wR_2 (all data)		0.0579[a]	0.0735[b]	0.106[c]	0.1352[d]
largest diff. peak and hole [$(e \cdot pm^{-3}) \cdot 10^{-6}$]		−0.72/0.59	−0.58/0.71	−0.82/0.8	−1.33/0.73

[a] $w = 1/[\sigma^2(F_o)^2]$. − [b] $w = 1/[\sigma^2(F_o) + (0.0375 \cdot P)^2]$; $P = [\max(F_o^2,0) + 2F_c^2]/3$. − [c] $w = 1/[\sigma^2(F_o) + (0.0555 \cdot P)^2]$. − [d] $w = 1/[\sigma^2(F_o) + (0.0375 \cdot P)^2 + 3.91 \cdot P]$.

Table 2. Selected bond lengths [pm] and bond angles [°] in **2−5**

2				**3**		**4**		**5**	
Pd1−Br1	244.7(1)	Pd2−Br3	242.5(1)	Pd1−I1	257.50(6)	Pd1−Br1	242.75(8)	Pd1−I1	261.58(9)
Pd1−Br2	240.75(9)	Pd2−Br4	244.10(9)	Pd1−I2	259.73(6)	Pd1−P1	225.0(1)	Pd1−P1	225.0(3)
Pd1−S1	225.2(2)	Pd2−S2	225.9(2)	Pd1−S1	227.4(2)	Pd1−S1	227.5(2)	Pd1−S1	226.6(2)
Pd1−N2	204.2(6)	Pd2−N6	205.3(8)	Pd1−N2	207.9(5)	Pd1−N2	211.0(5)	Pd1−N2	209.5(7)
S1−C1	169.4(7)	S2−C5	168.5(8)	S1−C1	169.2(6)	S1−C1	171.1(5)	S1−C1	173.1(9)
N1−N2	144.7(8)	N5−N6	144.3(8)	N1−N2	144.3(6)	N1−N2	141.3(7)	N1−N2	143(1)
C1−N1	136.8(7)	N5−C5	137.3(8)	N1−C1	135.3(7)	N1−C1	135.0(7)	N1−C1	137(1)
O1−C2	124.7(8)	O2−C6	121.2(8)	O1−C2	121.2(7)	O1−C2	119.8(8)	O1−C2	122(1)
N4−C1	131.3(8)	N8−C5	133.2(9)	N1−C2	138.7(7)	N1−C2	140.7(7)	N1−C1	140(1)
N3−N4	136.5(8)	N7−N8	137(1)	N3−N4	136.2(7)	N3−N4	137.4(6)	N3−N4	138(1)
Br1−Pd1−Br2	93.46(4)	Br3−Pd2−Br4	92.80(4)	I1−Pd1−I2	91.78(2)	Br1−Pd1−S1	172.90(4)	I1−Pd1−S1	171.38(7)
Br1−Pd1−S1	176.43(6)	Br3−Pd2−S2	91.21(6)	I1−Pd1−S1	91.04(4)	Br1−Pd1−P1	92.09(4)	I1−Pd1−P1	92.64(7)
Br2−Pd1−S1	89.82(6)	Br4−Pd2−S2	174.48(6)	I2−Pd1−S1	177.19(5)	S1−Pd1−P1	93.97(5)	S1−Pd1−P1	92.73(9)
Br1−Pd1−N2	89.5(2)	Br3−Pd2−N6	177.9(2)	I1−Pd1−N2	176.8(1)	Br1−Pd1−N3	88.8(1)	I1−Pd1−N2	89.6(2)
Br2−Pd1−N2	176.6(2)	Br4−Pd2−N6	89.2(2)	I2−Pd1−N2	91.2(1)	S1−Pd1−N2	84.8(1)	S1−Pd1−N2	85.3(2)
S1−Pd1−N2	87.3(2)	S2−Pd2−N6	86.9(2)	S1−Pd1−N2	86.0(1)	P1−Pd1−N2	174.5(1)	P1−Pd1−N2	176.7(2)
Pd1−N2−N1	114.3(4)	Pd2−N6−N5	114.3(5)	Pd1−N2−N1	114.1(3)	Pd1−S1−C1	97.3(2)	Pd1−S1−C1	99.7(3)
Pd1−S1−C1	97.6(3)	Pd2−S2−C5	97.9(3)	Pd1−S1−C1	97.9(2)	Pd1−N2−N1	114.0(3)	Pd1−N2−N1	114.8(5)

C), 1552 (m), 1500 (m), 1437 (m), 1322 (m), 1301 (m), 1228 (m), 1160 (vw), 1097 (m), 1008 (m), 968 (m), 928 (w), 847 (w), 746 (m), 691 (m), 639 (w), 602 (w), 534 (m), 506 (m), 449 [m, ν(PdN)], 409 (w), 374 [w, ν(PdS)], 308 (w), 285 (w), 227 (w), 198 [w, ν(PdI)], 139 (vw), 124 (vw). – ^{31}P NMR (CD$_3$OD): $\delta = 26.2$ (s).

Crystal Structure Analyses of 2, 3, 4, and 5 (Table 1 and 2): The selected crystals of **2–5** were covered with a perfluorinated oil and mounted on the tip of a glass capillary under a flow of cold gaseous nitrogen. The orientation matrix and preliminary unit cell dimensions were determined from 2000 (**2**, Stoe IPDS), 2000 (**3**, Stoe IPDS), 15 (**4**, Siemens P4), and 15 (**5**, Enraf-Nonius CAD4) reflections (graphite-monochromated Mo-K_α radiation in all cases; $\lambda = 71.073$ pm). The final cell parameters were determined from 5000 reflections for **2** and **5**, and from 25 high-angle reflections for **3** and **4**. The intensities were corrected for Lorentz and polarization effects. In addition, absorption corrections were applied for **2** (numerical), **3** (empirical, 10 psi-scans), **4** (numerical), and **5** (empirical, 10 psi-scans). The structures were solved by the Patterson method for **2** and by direct methods for **3–5** (SHELXTL-Plus[14]) and refined against F^2 by full-matrix least-squares using the program SHELXL-97.[15] The hydrogen atoms (C–H) in **2** and **5** were calculated in ideal positions (refinement with a common displacement parameter). The hydrogen atoms of the NH groups were fixed at 85 pm (**2**) or freely refined (**5**). The positions of the H atoms in **3** were freely refined, except for the N2–H2, N3–H3, and O2–H4 distances, which were fixed at 85 pm. The hydrogen atoms in **4** were freely refined. Programs used were SHELXTL-Plus, SHELXL-97, SHELXTL,[16] ORTEP,[17] and PLATON.[18] Splitting models were applied to the following atoms: C181, C182 (and adjacent H atoms, occupancy factors: 0.7, 0.3; **2**); O3, C9, C10, C11, C12 (occupancy factor: 0.5; **2**), H5, H61, H62, H63 (occupancy factor: 0.5; **3**).[19]

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