Cyclopalladated *N,N*-dimethylthiophene-2- and -3-carboselenoamide derivatives

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Abstract

N,N-Dimethylthiophene-2- and -3-carboselenoamides, abbreviated as Hats and Hbts, respectively, were easily obtained by the reaction of the corresponding carboxamide with phenyldichlorophosphine selenide. Hats and Hbts reacted with lithium tetrachloropalladate in methanol to give $[PdCl(ats)]_2$ and $[PdCl(bts)]_2$, respectively. Several derivatives of the two were prepared with ligands (L) such as pyridine (py) or tri-n-butylphosphine (PBu_3). The new compounds were characterized spectroscopically and the structures of $[PdCl(bts)(PBu_3)]$ and [PdCl(ats)(tbp)] (tbp = 4-tert-butylpyridine) were determined by X-ray analysis. The former was shown to be a *trans*-(C, Cl) isomer, while the latter a *cis*-(C, Cl) one, where C represents the palladated carbon atom. Hats was palladated at position 3 of the thiophene ring and Hbts exclusively at position 2 of the ring. The selenoamide group was coordinated through the selenium atom to form a five-membered palladaselenaheterocycle. The *trans* influence of a *trans* donor was reflected in the Pd–Se bonds: 2.4147(8) Å (*trans* to PBu_3) in $[PdCl(bts)(PBu_3)]$ and 2.359(1) Å (*trans* to Cl) in [PdCl(ats)(tbp)].

Introduction

Studies of the coordination chemistry of thiophene and its methyl derivatives became active recently with the intention of obtaining insight into thiophene hydrodesulfurization in petrochemistry [1]. Thiophenes have been found to adopt several modes of coordination under the influence of the coordinating metal ions and the experimental conditions: η^5-, η^4-, η^2-, η^1-S-, or η^1-C-coordination, a C,S-bidentate chelate with ring opening, and some bridging modes. In most complexes thiophenes are involved in π-coordination modes (η^5, η^4 or η^2). Complexes of η^1-S- and η^1-C-coordinated thiophenes are very rare [2–4] and need to be investigated. Complexes of η^1-S- and η^1-C-thiophenes can be formed when a thiophene ring has additional donor groups: thiaporphyrin is an example of the former [5] and an example of the latter is 2-pyridylthiophene which forms a metal–carbon σ-bond by cyclometallation [6]. We have been interested in complexes of η^1-C-coordinated thiophenes obtained by cyclopalladation [7].

In our previous papers [7, 8], an *N,N*-dimethylthiocarbamoyl group is shown to be a good auxiliary group which promotes cyclopalladation of furan and thiophene rings. The selenium analogue, the *N,N*-dimethylselenocarbomoyl group, is attractive being a similar auxiliary group and the investigation is now extended to *N,N*-dimethylthiophene-2- and -3-carboselenoamides, abbreviated as Hats and Hbts, respectively. The selenoamides have been found to be cyclopalladated at the thiophene ring similarly to the corresponding *N,N*-dimethylthiophene-2- and -3-carbothioamide (Hatt and Hbtt), and the cyclopalladated structures with η^1-C-coordinated thiophenes, have been confirmed by X-ray analysis. To the best of our knowledge, there has been no previous X-ray structural characterization of a cyclopalladated selenoamide.

Results and discussion

N,N-Dimethylthiophene-2- and -3-carboselenoamides (Hats and Hbts) were prepared by the reaction of the corresponding carboxamide with phenyldichlorophosphine selenide in hot xylene [9], and obtained as low melting red and orange solids, respectively (Table 1). The IR and NMR spectra are given in Tables 2

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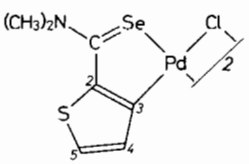
TABLE 1. Yields, melting points and analytical results of the selenoamides and complexes[a]

Compound	Yield (%)	Melting point[b] (°C)	Analysis: found (calc.) (%)		
			C	H	N
Hats	87	27–29	38.54 (38.54)	4.09 (4.16)	6.40 (6.42)
Hbts	96	39–41	38.44 (38.54)	4.15 (4.16)	6.43 (6.42)
$[PdCl(ats)]_2$	95	204 (dec.)	23.38 (23.42)	2.29 (2.25)	3.84 (3.90)
$[PdCl(ats)(PBu_3)]$	81	134–137	40.35 (40.65)	6.08 (6.28)	2.53 (2.50)
$[PdI(ats)(PBu_3)]$	84	161–164	34.67 (34.96)	5.16 (5.40)	2.20 (2.15)
[PdCl(ats)(py)]	90	218 (dec.)	32.54 (32.90)	2.59 (2.99)	6.13 (6.39)
[PdCl(ats)(tbp)]	81	169 (dec.)	38.53 (38.88)	4.08 (4.28)	5.79 (5.67)
$[Pd(ats)(py)_2]BF_4$	55	142 (dec.)	35.79 (35.91)	3.06 (3.19)	7.38 (7.39)
$[Pd(ats)(bpy)]BF_4$	81	167 (dec.)	35.60 (36.04)	2.68 (2.87)	7.56 (7.42)
$[PdCl(bts)]_2$	97	180 (dec.)	23.35 (23.42)	2.25 (2.25)	3.87 (3.90)
$[PdCl(bts)(PBu_3)]$	97	118–120	40.51 (40.65)	6.29 (6.28)	2.53 (2.50)
[PdCl(bts)(py)]	62	197 (dec.)	32.84 (32.90)	2.73 (2.99)	6.13 (6.39)
[PdCl(bts)(tbp)]	88	199 (dec.)	38.52 (38.88)	4.09 (4.28)	5.80 (5.67)

[a]Abbreviations: Hats = *N*,*N*-dimethylthiophene-2-carboselenoamide; Hbts = *N*,*N*-dimethylthiophene-3-carboselenoamide; PBu_3 = tri-n-butylphosphine; py = pyridine; tbp = 4-tert-butylpyridine; bpy = 2,2′-bipyridine. [b]dec. = decomposition.

and 3. $[PdCl(ats)]_2$ and $[PdCl(bts)]_2$ in dimethyl sulfoxide (dmso) may actually be dmso complexes, [PdCl(ats)(dmso)] and [PdCl(bts)(dmso)], similar to those of the corresponding thioamides (*N*,*N*-dimethylthiophene-2- and -3-carbothioamide; abbreviated as Hatt and Hbtt, respectively) [7]. The characteristic $^{13}C\{^1H\}$ NMR signal of the selenoamide group (C=Se) is at $\delta = 192.9$ ppm ($^1J(^{13}C-^{77}Se) = 205.9$ Hz) for Hats and 198.1 ppm (207.8 Hz) for Hbts. The following differences in the ^1H NMR spectra (in $CDCl_3$ at ambient temperature and 90 MHz) between the seleno- and thioamides should be noted. The ^1H signals of the selenoamide methyl groups of Hbts appeared as two sharp singlets, while those of Hats as two broad singlets. The methyl signals of Hbtt were observed as two broad singlets, while those of Hatt as one broad singlet. These spectral patterns indicate qualitatively that the rotational barrier of an amide C–N bond with partially double bond character is higher for the selenoamides than for the thioamides, and that the barrier is higher for the 3-isomers than for the 2-isomers. The same trend is also true for the two corresponding carboxamide isomers [10]. For further discussion a quantitative study is required but this is beyond the scope of the present.

Hats and Hbts reacted with lithium tetrachloropalladate in methanol at room temperature to afford $[PdCl(ats)]_2$ and $[PdCl(bts)]_2$, respectively (Table 1). The spectral data are given in Tables 2 and 3. Se-coordination of the selenoamide group is revealed by a higher frequency shift of the ν(C–N) band in the IR spectra [11] of the complexes, and the presence of ν(Pd–Cl) shows coordination of Cl. The ^1H NMR spectra show that one ring proton is missing. The $^{13}C\{^1H\}$ NMR spectrum of $[PdCl(ats)]_2$ is not available because of its low solubility. The ^{13}C spectrum of $[PdCl(bts)]_2$ in dmso-d_6 shows a significantly lower field shift of the 2-C signal and palladation at the 2-C atom of the thiophene ring is suggested (structures **I** and **II**).



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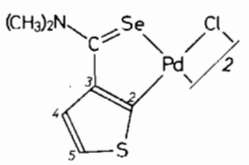


II

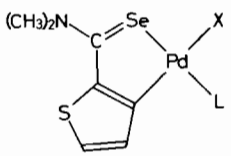
The ^1H and $^{13}C\{^1H\}$ NMR spectra of $[PdX(ats)(PBu_3)]$ (X = Cl, Br; PBu_3 = tri-n-butylphosphine) in $CDCl_3$ are complicated, but can be satisfactorily explained by

TABLE 2. ^1H and $^{31}P\{^1H\}$ NMR spectra (δ ppm relative to tetramethylsilane and 85% H_3PO_4, respectively, and figures in parentheses are J(H–H) in Hz)[a] and IR spectra (nujol mull, cm^{-1}) of the selenoamides and complexes

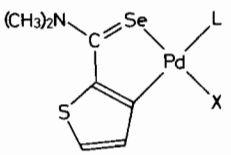
Compound	^1H NMR			^{31}P NMR	IR spectra	
	4-H	5-H	$N(CH_3)_2$		ν(C–N)	ν(Pd–Cl)
Hats[b]	6.95dd	7.43dd	3.61		1520	
	(5.1, 3.7)	(5.1, 1.3)	3.34			
Hbts[c]	7.12dd	7.25dd	3.64		1525	
	(5.1, 3.1)	(5.1, 1.3)	3.19			
$[PdCl(ats)]_2$[d]	7.85d	8.02d	3.72		1562	292
	(5.1)	(5.1)	3.68			220
$[PdCl(ats)(PBu_3)]$					1555	294
trans-(C, Cl)	7.05dd	7.67dd	3.70	13.1		
	(5.1)	(5.1)	3.69	[126][f]		
	[2.0][e]	[1.5][e]				
cis-(C, Cl)	8.16dd	7.77dd	3.74	3.1		
	(4.8)	(4.8)	3.72			
	[2.2][e]	[3.5][e]				
$[PdI(ats)(PBu_3)]$					1552	
trans-(C, I)	7.12dd	7.77dd	3.68	12.0		
	(5.1)	(5.1)				
	[1.5][e]	[1.5][e]				
cis-(C, I)	8.62dd	7.64dd	3.72	−1.0		
	(5.1)	(5.1)				
	[2.0][e]	[3.5][e]				
$[PdCl(ats)(py)]$[g]	8.23d	7.72d	3.73		1552	301
	(5.1)	(5.1)	3.71			
$[PdCl(ats)(tbp)]$[g]	8.18d	7.66d	3.72		1552	300
	(5.1)	(5.1)				
$[Pd(ats)(py)_2]BF_4$[d]	6.19d	8.15d	3.84		1570	
	(5.1)	(5.1)	3.80			
$[Pd(ats)(bpy)]BF_4$[d]	8.36d	7.48d	3.81		1585	
	(5.1)	(5.1)	3.77			
$[PdCl(bts)]_2$[d]	7.32s	7.32s	3.69		1569	295
			3.64			224
$[PdCl(bts)(PBu_3)]$[h]	7.14m	7.14m	3.71	4.4	1548	313
			3.69	13.4		
			3.63	[128][f]		
$[PdCl(bts)(py)]$	7.15s	7.15s	3.69		1553	317
			3.66			
$[PdCl(bts)(tbp)]$	7.12s	7.12s	3.67		1547	307
			3.63			

[a] $CDCl_3$ is used as a solvent unless otherwise noted. This Table contains only the ^1H signals due to the selenoamides. The $N(CH_3)_2$ signals are all singlet. s = singlet, d = doublet, m = multiplet. [b] 3-H: 7.09dd (3.7, 1.3). $\delta(^{77}Se) = 774$ ppm. [c] 2-H: 7.36dd (3.1, 1.3). $\delta(^{77}Se) = 711$ ppm. [d] Solvent is dmso-d_6. [e] $J(^{31}P–^1H)$. [f] $J(^{77}Se–^{31}P)$. [g] Very weak signal is observed at *c.* 6.4 ppm. [h] A mixture of *trans*-(C, Cl) and *cis*-(C, Cl).

assuming the presence of two geometrical isomers (**III** (*trans*-(C, X)) and **IV** (*cis*-(C, X)) where C represents



III, *trans*-(C, X)



IV, *cis*-(C, X)

a palladated carbon atom). Spectral assignments are given in Tables 2 and 3. In the *cis*-(C, X) isomers, where 4-H is situated close to X, the chemical shifts of 4-H are significantly affected by the kind of X: a similar deshielding upon replacing Cl with I is observed for analogous complexes [7, 8]. In the ^{13}C NMR spectra, the J(P–C) values of 3-C of the *cis*-(C, X) isomers are those expected for a *trans* P–Pd–C geometry [7, 8]. The $^{31}P\{^1H\}$ NMR spectra support the assignment: the ^{31}P chemical shifts of the *cis*-(C, X) isomers are at a higher field than those of the *trans*-(C, X) isomers, as the P donor in the former is coordinated *trans* to a carbon donor with a stronger *trans* influence [12]. The coupling constant $J(^{31}P–^{77}Se)$ observed for the *trans*-(C, Cl) isomer is in the range expected for a *trans* P–Pd–Se arrangement [13].

The *cis*/*trans* isomer distributions of $[PdX(ats)(PBu_3)]$ (X = Cl, I) are estimated from the ^1H signal intensities:

TABLE 3. $^{13}C\{^1H\}$ NMR spectra of some of the complexes (δ ppm relative to tetramethylsilane and figures in parentheses are $J(^{31}P-^{13}C)$ in Hz)[a]

Compound	2-C	3-C	4-C	5-C	C=Se	$N(CH_3)_2$
Hats	148.1	124.6	126.2	129.0	192.9 [206][b]	48.3br, 45.0br
$[PdCl(ats)(PBu_3)]$						
cis-(C, Cl)	137.6 (4.5)	179.3 (139)	134.4 (12.4)	132.6 (5.5)	190.0 (16.2)	49.3, 45.5 (4,2)
trans-(C, Cl)	140.4 (2.1)	163.6	137.0 (13.1)	137.1 (1.0)	190.8	48.8, 45.9
$[PdI(ats)(PBu_3)]$						
cis-(C, I)	145.9 (4.1)	176.6 (140)	135.5 (12.1)	133.1 (5.2)	190.4 (15.2)	49.0, 45.8
trans-(C, I)	[c]	169.2	136.3 (12.4)	138.5 (1.0)	[c]	49.2, 45.5 (4.5)
[PdCl(ats)(tbp)]	138.8	162.8	132.8	121.9	187.1	48.6, 45.7
$[Pd(ats)(py)_2]BF_4$[d]	137.0	160.1	134.1	136.2	181.9	48.8, 45.9
Hbts	122.4	145.8	126.2	124.9	198.1 [208][b]	47.3, 44.7
$[PdCl(bts)]_2$[d]	166.6	146.5	127.9	127.6	188.2	49.9, 47.9
$[PdCl(bts)(PBu_3)]$						
cis-(C, Cl)	185.5 (153)	149.0	127.4 (6.2)	125.3	193.6 (3.5)	48.6br, 46.5[e]
trans-(C, Cl)	165.0	143.8	125.5	125.1	191.7 (14.5)	46.2
[PdCl(bts)(tbp)]	168.3	144.9	126.9	125.5	188.8	48.7, 46.6

[a] $CDCl_3$ is used as a solvent unless otherwise noted. This Table contains only the signals due to the selenoamides. [b] $J(^{13}C-^{77}Se)$. [c] Not detected. [d] $(CD_3)_2SO$ is used as a solvent. [e] Not assigned for isomers. Low solubilities of the other complexes prevented us from taking ^{13}C NMR measurements.

cis-(C, Cl)/*trans*-(C, Cl) = 65/35 and *cis*-(C, I)/*trans*-(C, I) = 85/15. The ratios of isomers should be those of equilibrium mixtures since, as shown below by X-ray analysis, the crystals of $[PdCl(bts)(PBu_3)]$ consist of only the *trans*-(C, Cl) isomer and dissolution in $CDCl_3$ results in a mixture of isomers. A comparison of these values with those of the corresponding thioamide complexes [7], $[PdX(att)(PBu_3)]$ (X = Cl, I): *cis*-(C, Cl)/*trans*-(C, Cl) = 15/85 and *cis*-(C, I)/*trans*-(C, I) = 55/45, indicates that the selenoamide complexes prefer a *cis* geometry. A factor determining the *cis*/*trans* ratios seems, at a glance, to be a difference in strength of *trans* influence between the selenium and sulfur donor atoms. Further discussion requires a deeper investigation of the electronic structures of the complexes.

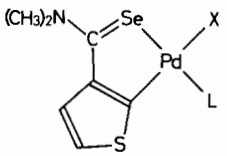
Nitrogen donor ligands reacted with PdCl(ats) to give [PdCl(ats)L] (L = pyridine (py) and 4-tert-butylpyridine (tbp)), $[Pd(ats)(py)_2]BF_4$ and [Pd(ats)-(bpy)]BF_4 (bpy = 2,2′-bipyridine). The spectral data are given in Tables 2 and 3. The ^1H NMR spectra of [PdCl(ats)L] show a very weak signal at *c.* 6.4 ppm, in addition to the main signals, and its intensity is less than 5% of a unit intensity of the main signals. The main ^1H spectra of [PdCl(ats)L] (L = py, tbp) are essentially similar to those of *cis*-(C, X)-$[PdX(ats)(PBu_3)]$, suggesting a *cis*-(C, Cl) isomer (structure **IV**). The *cis*-(C, Cl) structure of [PdCl(ats)(tbp)] has been confirmed by X-ray analysis (see below). A significant difference appears in the 4-H chemical shifts between the two cationic complexes $[Pd(ats)(py)_2]BF_4$ and [Pd(ats)-(bpy)]BF_4 (Table 2): 4-H of the former is considerably shielded by the anisotropic effect of the adjacent pyridine ring nearly perpendicular to the coordination plane (py in the site X of structure **IV**), while for the latter there is no such shielding, the bpy ligand being in the coordination plane (X, L = bpy). On this basis, the weak signals found at *c.* 6.4 ppm in the spectra of [PdCl(ats)L] should be assigned to 4-H of the *trans*-(C, Cl) isomers (structure **III**), where 4-H is shielded by the adjacent pyridine ring. For [PdCl(ats)L] in $CDCl_3$ the ratio *cis*-(C, Cl)/*trans*-(C, Cl) $\geq$ 95/5 is obtained. Compared with the above PBu_3 complexes, the pyridine donors definitely prefer a *cis*-(C, Cl) geometry.

In the ^1H NMR spectra of [PdCl(bts)L] (L = PBu_3, py and tbp) (Table 2), the chemical shifts of 4-H and 5-H happen to be identical, affording no useful structural information. The ^{31}P and ^{13}C spectra of $[PdCl(bts)(PBu_3)]$ in $CDCl_3$ (Tables 2 and 3) are interpreted similarly to the above $[PdX(ats)(PBu_3)]$ and reveal the ratio *cis*-(C, Cl)/*trans*-(C, Cl) = 55/45 (struc-

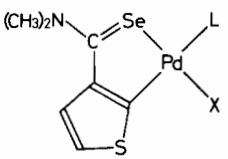
TABLE 4. Positional parameters ($\times 10^4$) and equivalent temperature factors (Å^2) of [PdCl(bts)(PBu_3)]

	x	y	z	B_{eq}
Pd	8636.2(3)	3609.0(2)	1258.8(4)	3.5
Se	10293.1(4)	4179.4(3)	1660.9(7)	4.9
Cl	9160(1)	2908(1)	−313(2)	5.2
S	7255(1)	4426(1)	2955(2)	5.1
P	7082(1)	3031(1)	878(1)	3.8
N	10579(4)	5436(3)	2694(5)	5.3
C1	8353(4)	4342(2)	2403(6)	4.1
C2	8996(4)	4885(3)	2884(6)	4.2
C3	8590(6)	5328(3)	3728(7)	5.1
C4	7664(6)	5150(3)	3833(7)	5.3
C5	9970(4)	4918(3)	2497(6)	4.3
C6	10330(7)	6075(3)	3183(10)	6.7
C7	11561(6)	5420(4)	2407(8)	6.5
C8	7047(5)	2248(3)	−2(6)	4.7
C9	7807(5)	1743(3)	944(7)	4.8
C10	7876(7)	1158(4)	20(9)	6.5
C11	8600(9)	632(4)	869(11)	8.0
C12	6719(5)	2846(3)	2521(7)	5.1
C13	7623(7)	2703(3)	3953(8)	6.1
C14	7302(11)	2667(4)	5345(9)	8.6
C15	6566(16)	2113(7)	5296(13)	12.8
C16	5894(4)	3440(3)	−413(7)	4.8
C17	5953(6)	3590(5)	−1939(8)	6.9
C18	4966(8)	3936(6)	−3000(10)	8.3
C19	4983(16)	4029(8)	−4547(15)	12.9

tures **V** and **VI**). The site of cyclopalladation of the



V, *trans*-(C, X)



VI, *cis*-(C, X)

thiophene ring of Hbts has been confirmed by X-ray analysis of [PdCl(bts)(PBu_3)].

The structures of [PdCl(bts)(PBu_3)] (**1**) and [PdCl(ats)(tbp)] (**2**) have been determined by X-ray analysis. The atomic positional parameters are given in Tables 4 and 5 and the selected bond lengths and angles in Tables 6 and 7. The two complexes are square planar (Fig. 1): **1** has a *trans*-(C, Cl) geometry, but **2** a *cis*-(C, Cl) one. The significant difference in the Pd–Se bond lengths (2.4147(8) Å for **1** and 2.359(1) Å for **2**) reflects the *trans* influence of the different donors *trans* to the bond (PBu_3 for **1** and Cl for **2**). The other bond lengths and angles are of those normally observed for similar cyclopalladated complexes. A detailed discussion on the structure of the selenoamide moiety requires the accumulation of further data, there being little data available on free selenoamides, and their complexes need to be characterized structurally.

The pyridine ring plane of tbp in [PdCl(ats)(tbp)] has a dihedral angle of 67.8(2)° with the coordination

TABLE 5. Positional parameters ($\times 10^4$) and equivalent temperature factors (Å^2) of [PdCl(ats)(tbp)]

	x	y	z	B_{eq}
Pd	2141.8(5)	337.5(2)	8280.2(4)	2.8
Se	2372.4(10)	−297.2(4)	6505.1(6)	4.9
Cl	1995(2)	1003(1)	10052(1)	4.2
S	987(3)	1899(1)	5058(2)	5.3
N1	1915(11)	327(5)	4158(6)	5.9
N2	2745(6)	−566(3)	9479(4)	3.5
C1	1873(8)	442(4)	5327(5)	4.0
C2	1488(7)	1092(4)	5830(5)	3.7
C3	1556(7)	1145(3)	7097(5)	3.1
C4	1187(9)	1840(4)	7406(7)	4.4
C5	866(11)	2289(4)	6405(8)	5.4
C6	1523(17)	877(8)	3155(8)	7.8
C7	2321(20)	−364(9)	3753(10)	9.0
C8	4080(7)	−843(3)	9793(5)	3.2
C9	4486(6)	−1396(3)	10642(5)	2.8
C10	3475(7)	−1686(3)	11221(5)	3.4
C11	2077(8)	−1409(4)	10864(6)	3.7
C12	1736(7)	−854(3)	9979(6)	3.7
C13	3925(7)	−2285(3)	12180(5)	3.6
C14	5020(11)	−1986(5)	13332(7)	5.7
C15	4628(17)	−2889(5)	11677(10)	6.9
C16	2623(10)	−2567(6)	12607(10)	6.3

TABLE 6. Bond distances (l (Å)) and angles (ϕ (°)) of [PdCl(bts)(PBu_3)]

Pd–Se	2.4147(8)	Pd–Cl	2.359(2)
Pd–P	2.311(1)	Pd–C(1)	1.979(6)
Se–C(5)	1.845(6)	S–C(1)	1.731(7)
S–C(4)	1.710(7)	P–C(8)	1.820(7)
P–C(12)	1.827(2)	P–C(16)	1.830(5)
N–C(5)	1.321(8)	N–C(6)	1.482(10)
N–C(7)	1.430(11)	C(1)–C(2)	1.392(7)
C(2)–C(3)	1.445(10)	C(2)–C(5)	1.472(9)
C(3)–C(4)	1.327(11)	C(8)–C(9)	1.511(8)
C(9)–C(10)	1.519(10)	C(10)–C(11)	1.490(11)
C(12)–C(13)	1.489(9)	C(13)–C(14)	1.525(15)
C(14)–C(15)	1.503(22)	C(16)–C(17)	1.507(11)
C(17)–C(18)	1.523(12)	C(18)–C(19)	1.485(19)
Se–Pd–Cl	86.68(5)	Se–Pd–P	177.98(4)
Se–Pd–C(1)	83.1(2)	Cl–Pd–P	91.76(6)
Cl–Pd–C(1)	167.6(2)	P–Pd–C(1)	98.6(2)
Pd–Se–C(5)	97.7(2)	C(1)–S–C(4)	94.5(3)
Pd–P–C(8)	114.3(2)	Pd–P–C(12)	118.2(2)
Pd–P–C(16)	112.2(2)	C(8)–P–C(12)	103.3(3)
C(8)–P–C(16)	103.6(2)	C(12)–P–C(16)	103.7(3)
C(5)–N–C(6)	125.4(7)	C(5)–N–C(7)	120.9(6)
C(6)–N–C(7)	113.7(6)	Pd–C(1)–S	126.2(3)
Pd–C(1)–(2)	125.9(5)	S–C(1)–C(2)	107.9(4)
C(1)–C(2)–C(3)	112.9(6)	C(1)–C(2)–C(5)	116.8(5)
C(3)–C(2)–C(5)	130.3(5)	C(2)–C(3)–C(4)	113.9(6)
S–C(4)–C(3)	110.7(6)	Se–C(5)–N	120.8(5)
Se–C(5)–C(2)	115.5(4)	N–C(5)–C(2)	123.7(6)
P–C(8)–C(9)	116.5(4)	C(8)–C(9)–C(10)	112.3(5)
C(9)–C(10)–C(11)	115.9(6)	P–C(12)–C(13)	116.2(6)
C(12)–C(13)–C(14)	114.2(8)	C(13)–C(14)–C(15)	113.1(8)
P–C(16)–C(17)	114.0(5)	C(16)–C(17)–C(18)	113.7(8)

TABLE 7. Bond distances (l (Å)) and angles (ϕ (°)) of [PdCl(ats)(tbp)]

Pd–Se	2.359(1)	Pd–Cl	2.362(2)
Pd–N(2)	2.138(6)	Pd–C(3)	1.986(6)
Se–C(1)	1.879(8)	S–C(2)	1.745(7)
S–C(5)	1.693(11)	N(1)–C(1)	1.323(13)
N(1)–C(6)	1.491(19)	N(1)–C(7)	1.459(22)
N(2)–C(8)	1.330(9)	N(2)–C(12)	1.342(9)
C(1)–C(2)	1.430(10)	C(2)–C(3)	1.391(9)
C(3)–C(4)	1.418(11)	C(4)–C(5)	1.363(14)
C(8)–C(9)	1.386(9)	C(9)–C(10)	1.399(9)
C(10)–C(11)	1.383(10)	C(10)–C(13)	1.530(10)
C(11)–C(12)	1.409(18)	C(13)–C(14)	1.526(13)
C(13)–C(15)	1.497(18)	C(13)–C(16)	1.532(13)
Se–Pd–Cl	177.58(6)	Se–Pd–N(2)	97.7(2)
Se–Pd–C(3)	84.7(2)	Cl–Pd–N(2)	88.3(2)
Cl–Pd–C(3)	94.4(2)	N(2)–Pd–C(3)	177.2(2)
Pd–Se–C(1)	98.3(2)	C(2)–S–C(5)	91.0(4)
C(1)–N(1)–C(6)	123.3(10)	C(1)–N(1)–C(7)	121.7(11)
C(6)–N(1)–C(7)	115.0(12)	Pd–N(2)–C(8)	123.3(10)
Pd–N(2)–C(12)	118.2(5)	C(8)–N(2)–C(12)	118.1(6)
Se–C(1)–N(1)	119.4(7)	Se–C(1)–C(2)	113.8(5)
N(1)–C(1)–C(2)	126.8(8)	S–C(2)–C(1)	128.0(6)
S–C(2)–C(3)	111.5(5)	C(1)–C(2)–C(3)	120.4(6)
Pd–C(3)–C(2)	122.8(8)	Pd–C(3)–C(4)	126.0(5)
C(3)–C(4)–C(5)	113.0(8)	S–C(5)–C(4)	113.4(8)
C(8)–C(9)–C(10)	120.1(6)	C(9)–C(10)–C(11)	116.5(6)
C(9)–C(10)–C(13)	120.3(6)	C(11)–C(10)–C(13)	123.2(6)
C(10)–C(11)–C(12)	120.3(7)	N(2)–C(12)–C(11)	121.8(6)
C(10)–C(13)–C(14)	108.3(6)	C(10)–C(13)–C(15)	111.7(8)
C(10)–C(13)–C(16)	111.6(7)	C(14)–C(13)–C(15)	108.5(9)
C(14)–C(13)–C(16)	107.3(7)	C(15)–C(13)–C(16)	109.3(9)

plane to avoid steric repulsions between the 2,6-Hs of tbp and the neighboring ligands. While Hats has no choice of cyclopalladation site in a thiophene ring, Hbts has two sites available for cyclopalladation: position 2 or 4 of the thiophene ring. In [PdCl(bts)(PBu_3)] the thiophene ring is cyclopalladated at position 2 and this fact is in agreement with the general pattern of organic reactions of thiophene derivatives [14].

Experimental

Measurements

NMR spectra were recorded on Hitachi R-90H (^{1}H, 90 MHz; ^{13}C, 22.6 MHz; ^{31}P, 36.4 MHz; ^{77}Se, 17.2 MHz) and Joel PMX-60 (^{1}H, 60 Hz) spectrometers. Chemical shifts (δ, ppm) were relative to internal tetramethylsilane (^{1}H, ^{13}C), to external 85% H_3PO_4 (^{31}P), and to external saturated H_2SeO_3/D_2O (=1292 ppm) (^{77}Se). IR spectra (Nujol mulls) were measured on Jasco IR-A3 and Hitachi EPI-L spectrometers.

Synthesis

Yields, melting points and analytical results are summarized in Table 1.

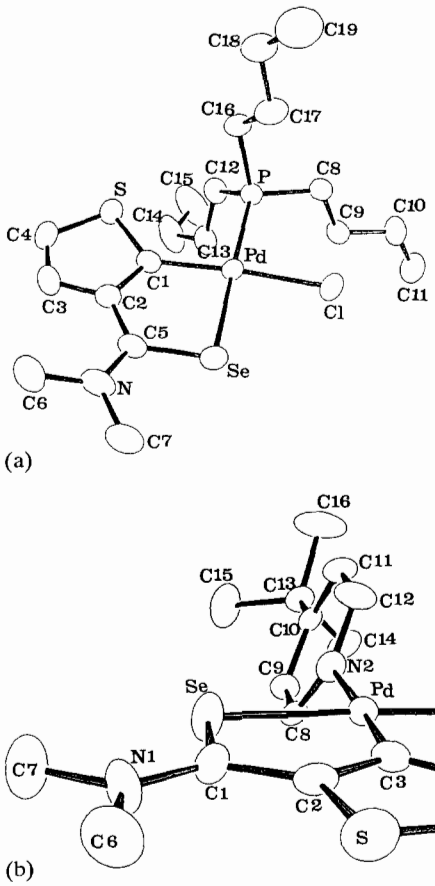


Fig. 1. Perspective view of [PdCl(bts)(PBu_3)] (a) and [PdCl(ats)(tbp)] (b).

N,N-Dimethyl-2- and -3-thiophenecarboselenoamides (Hats and Hbts)

The two selenoamides were prepared following the literature procedure [9]. A mixture of 2.37 g (30 mmol) of selenium powder and 4.47 g (25 mmol) of phenyldichlorophosphine was heated for 40 min at 175 °C and the cooled reaction mixture was dissolved in 12.5 cm^3 of xylene. The unreacted selenium was filtered off and to the filtrate was added 10 mmol of the corresponding carboxamide. The solution was heated for 5 h at 100 °C, cooled, diluted with 100 cm^3 of toluene, and then mixed with 100 g of alumina (activity II–III). The slurry was put onto a column filled with alumina (100 mm×35mm diam.), and the column was washed with hexane and eluted with diethyl ether. The orange eluent was evaporated to give the selenoamides as a red oil, which solidified on freezing.

[PdCl(ats)]$_2$ and [PdCl(bts)]$_2$

One mmol of selenoamide was added to a solution of 1 mmol of lithium tetrachloropalladate in 20 cm^3 of methanol prepared *in situ* from 1 mmol of palladium(II) chloride and 2 mmol of lithium chloride. The mixture was stirred for several hours at room tem-

perature to give a brown precipitate. The precipitate was collected by filtration, washed with methanol, and dried in air.

[PdCl(ats)L], [PdCl(bts)L] (L = PBu_3, py, tbp) and [PdI(ats)(PBu_3)]

To a suspension 0.5 mmol of $[PdCl(ats)]_2$ (or $[PdCl(bts)]_2$) in 30 cm^3 of dichloromethane was added 1 mmol of PBu_3 (or a two-fold excess of py or tbp), and the mixture was stirred until it had become clear (for several minutes). The solution was mixed with 20 cm^3 of hexane, filtered, and concentrated to a small volume to precipitate yellow or orange crystals, which were filtered, washed with hexane, and dried in air.

The iodo complex $[PdI(ats)(PBu_3)]$ was obtained upon metathesis of the corresponding chloro one (0.5 mmol) with a large excess of lithium iodide in acetone.

[Pd(ats)($py)_2$]BF_4 and [Pd(ats)(bpy)]BF_4

A mixture of 0.5 mmol of $[PdCl(ats)]_2$ and 1 mmol of bpy in a mixed solvent of 20 cm^3 of acetone and 20 cm^3 of water was stirred at room temperature until they had dissolved, and then 1 mmol of silver nitrate was added to the solution. After 1.5 h stirring, the precipitated silver chloride was filtered off, 1.1 mmol of sodium tetrafluoroborate dissolved in a small amount of water was added to the filtrate, and the acetone was evaporated off to give a yellow precipitate. The precipitate was washed with acetone, dried in air, and could be recrystallized from hot acetone. The py complex was similarly prepared by use of an excess of pyridine. The complex is more soluble in acetone.

The molar conductance of the py complex in acetonitrile is 126 Ω^{-1} cm^2 mol^{-1} and that of the bpy one 95 Ω^{-1} cm^2 mol^{-1} at 25 °C.

X-ray analyses of [PdCl(bts)(PBu_3)] (1) and [PdCl(ats)(tbp)] (2)

Recrystallization of **1** and **2** from dichloromethane–ether or acetone solutions gave yellow and dark yellow crystals, respectively. Diffraction data of a crystal with approximate dimensions, $0.8 \times 0.4 \times 0.3$ mm for **1** and $0.5 \times 0.5 \times 0.45$ mm for **2** were collected on a Rigaku AFC-5R diffractometer with graphite Mo Kα radiation ($\lambda = 0.71069$ Å). Crystal data for **1**: monoclinic, $P2_1/a$, $a = 13.339(2)$, $b = 20.770(2)$, $c = 9.464(1)$ Å, $\beta = 110.86(1)°$, $V = 2450.2(5)$ Å^3, $Z = 4$, $D_m = 1.51(2)$, $D_x = 1.52$ g cm^{-3}, μ(Mo Kα) = 24.78 cm^{-1}; **2**: monoclinic, $P2_1/c$, $a = 9.508(2)$, $b = 18.786(2)$, $c = 11.077(2)$ Å, $\beta = 105.30(1)°$, $V = 1908.5(6)$ Å^3, $Z = 4$, $D_m = 1.73(2)$, $D_x = 1.72$ g cm^{-3}, μ(Mo Kα) = 30.93 cm^{-1}. Within the range $2\theta < 60°$, 4457 and 1530 independent reflections with $|F_o| > 3\sigma(|F_o|)$ were obtained for **1** and **2**, respectively. Absorption corrections were made by using the DABEX program [15]. All the computations were performed on a HITAC M-680H computer at the Computer Center of the Institute for Molecular Science using the Universal Crystallographic Computation Program System UNICS III [15]. The structures were solved by the usual heavy-atom method. The positions of all the non-hydrogen atoms were identified in subsequent Fourier maps and the hydrogen atoms were identified in subsequent difference-Fourier maps. For **1**, final R was 0.044 for 3259 unique reflections. The atomic parameters of the non-hydrogen atoms are listed in Table 4. For **2**, final R was 0.044 for 1530 reflections. The atomic parameters of the non-hydrogen atoms are listed in Table 5.

Supplementary material

The anisotropic thermal parameters for all the non-hydrogen atoms, hydrogen atomic parameters, and the complete lists of $|F_o|$ and $|F_c|$ values of both complexes are available from the authors on request.

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