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CYCLOPALLADATION OF *N*-(*p*-THIOTOLUOYL)PYRROLIDINE AND -PIPERIDINE

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Abstract—Reaction of *N*-(*p*-thiotoluoyl)pyrrolidine (Hpr) with lithium tetrachloropalladate(II) in methanol at room temperature resulted in an *ortho* C—H activation of the benzene ring and a benzene ring-*ortho*palladated complex PdCl (bpr) was obtained. Another reaction in hexamethylphosphoric triamide at 80°C resulted in an α-CH_2 activation of the pyrrolidine ring to form PdCl (ppr) with an aliphatic α-C—Pd bond. Under the latter reaction conditions *N*-(*p*-thiotoluoyl)piperidine (Hpi) was similarly cyclopalladated at α-CH_2 of the piperidine ring to give PdCl (ppi) but under the former experimental conditions no cyclopalladation occurred. These complexes and some of their derivatives were characterized spectroscopically. The results suggested that the steric bulk of the thioamide-N substituents was of prime importance to cyclopalladation-reactivity of thioamides. To verify the facts, the structures of *N*-(2-thionaphthoyl)pyrrolidine, Pd(acac) (bpr) (acac = acetylacetonate ion), and {1,3-bis(1-pyrrolidinothiocarbonyl)-phenyl-C^2,S,S′} chloropalladium(II) were determined by X-ray analysis. A pyrrolidino group is a sterically more favorable thioamide-substituent than a dimethylamino group to fulfil the requirements of aromatic ring cyclopalladation of tertiary thioamides with palladium(II).

Cyclopalladation permits selective activation of C—H bonds in heterosubstituted organic molecules and a wide variety of donor atoms are known.[1] The majority of examples of cyclopalladated complexes contain nitrogen and phosphorus as auxiliary donor atoms. Such reaction of organosulfur derivatives has, on the other hand, received much less attention and further investigations seem to be required for proper understanding of the reaction. In previous papers, cyclopalladation of *N*,*N*-dimethylthioamide derivatives of benzene, thiophene, and furan with palladium(II) have been reported; *N*,*N*-dimethylthiobenzamide (abbreviated as Hbt) is palladated at one of the *N*-methyl group (structure **I**)[2] while *N*,*N*-dimethylthiophene- (and furan) 2-carbothioamide (Hat) at the five-membered heteroaromatic rings (structure **II**).[3] The sharp contrast (formation of either **I** and **II**) stimulated us to investigate further cyclopalladation of other thioamide derivatives bearing different steric and electronic properties. The inhibited orthopalladation of the benzene ring of Hbt is explained based on the steric hindrance between the *ortho* hydrogen atom of the ring and one of the *N*-methyl groups which hindrance would be produced upon orthopalladation of Hbt.[2] In this paper we have

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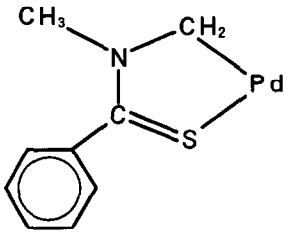
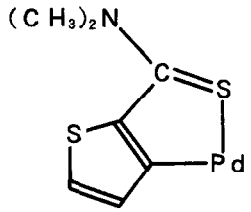


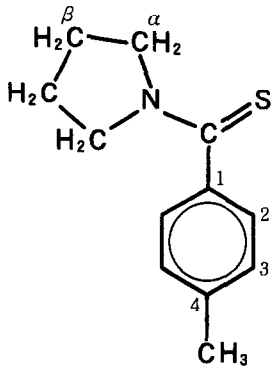
I, Pd(bt)

Structure 1



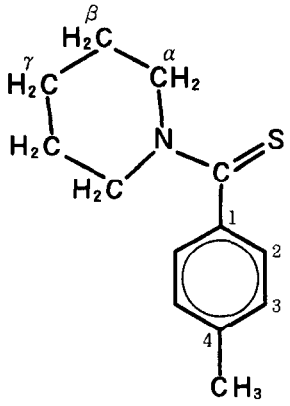
II, Pd(at)

Structure 2



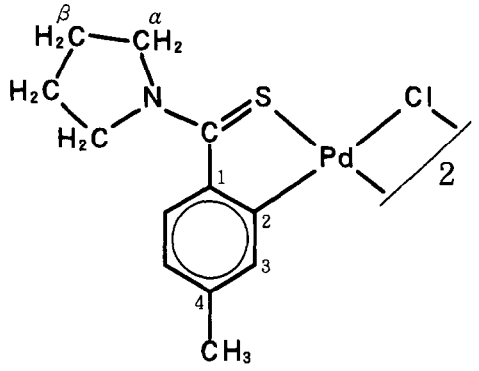
III, H(pr)

Structure 3



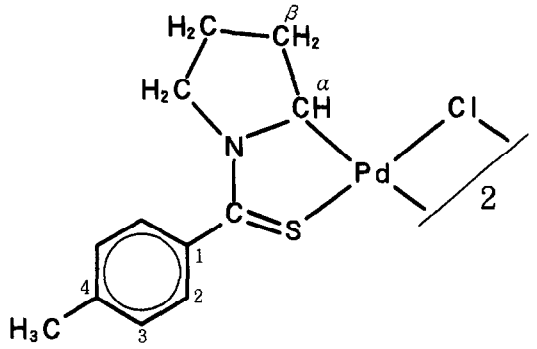
IV, H(pi)

Structure 4



V, PdCl(bpr)

Structure 5



VI, PdCl(ppr)

Structure 6

examined the steric effect of the thioamide group attached to a benzene ring on cyclopalladation. *N*-(*p*-Thiotoluoyl)pyrrolidine (Hpr) and *N*-(*p*-thiotoluoyl)piperidine (Hpi) (structures **III** and **IV**) were subjected to cyclopalladation.

Hpr was cyclometallated with palladium(II) at either the benzene ring or the pyrrolidine ring (structures **V** and **VI**, respectively) depending upon reaction conditions, but Hpi only at the piperidine ring. The results are discussed together with those previously obtained for Hbt. The five-membered pyrrolidino moiety of Hpr is interpreted to be less bulky than the dimethylamino group of Hbt since bridging the two methyl groups with an ethylene chain contracts the bulk around the thioamide-nitrogen atom.

RESULTS AND DISCUSSION

The thioamides were obtained by the modified method reported by Amupitan[4] and characterized spectroscopically (Tables 1, 2, 3, and 4). The aryl rings of the thioamides seem to be nearly per-

Table 1. Melting points, yields, analytical results and infrared spectra of the thioamide and complexes[a]

Compound	M.p. (°C)[b]	Yield (%)	Analysis; Found (Calc.) % C	H	N	IR (cm^{-1})[c] ν(C—N)	ν(Pd—X)
Hpr	71–72	77	70.2 (70.2)	7.4 (7.2)	6.8 (6.8)	1485	
Hpi	98–100	80	71.0 (71.2)	7.7 (7.8)	6.3 (6.4)	1483	
Hnr	127–128	70	74.3 (74.6)	6.1 (6.3)	5.7 (5.8)	1487	
Hmpr	146–148	68	63.0 (63.1)	6.5 (6.6)	9.1 (9.2)	1481	
PdCl (bpr)	222 (dec)	78	41.6 (41.6)	4.0 (4.1)	3.9 (4.0)	1515	282, 252
PdI (bpr)	244 (dec)	96	33.1 (32.9)	3.5 (3.2)	3.0 (3.2)	1513	138
Pd (acac) (bpr)	224–225	82	49.9 (49.8)	5.1 (5.2)	3.3 (3.4)	1527	
PdCl (bpr) (tbp)	256 (dec)	93	52.2 (52.4)	5.6 (5.7)	5.5 (5.8)	1516	292
PdI (bpr) (tbp)	246 (dec)	93	44.3 (44.0)	4.8 (4.8)	4.8 (4.9)	1516	135
PdCl (bpr) (PBu_3)	131–132	91	52.7 (52.6)	7.4 (7.5)	2.5 (2.6)	1520	278
PdI (bpr) (PBu_3)	74–78	93	45.3 (45.0)	6.4 (6.5)	2.0 (2.2)	1519	133
PdCl (ppr)	222 (dec)	81	41.6 (41.6)	3.9 (4.1)	3.9 (4.0)	1555	277
PdI (ppr)	215 (dec)	76	33.6 (32.9)	3.3 (3.2)	3.1 (3.2)	1556	129
Pd (acac) (ppr)	168 (dec)	61	50.1 (49.8)	5.2 (5.2)	3.3 (3.4)	1581	
PdCl (ppr) (tbp)	199 (dec)	45	52.3 (52.4)	5.6 (5.7)	5.8 (5.8)	1557	293
PdI (ppr) (tbp)	180 (dec)	60	43.6 (44.0)	4.7 (4.8)	4.6 (4.9)	1555	131
PdCl (ppr) (PBu_3)	160–162	84	52.8 (52.6)	7.3 (7.5)	2.4 (2.6)	1558	286
PdI (ppr) (PBu_3)	132–136	92	45.4 (45.0)	6.6 (6.5)	2.2 (2.2)	1556	137
PdCl (ppi)	235 (dec)	78	43.5 (43.4)	4.6 (4.5)	3.8 (3.9)	1580	277
PdI (ppi)	212 (dec)	84	35.2 (34.6)	3.8 (3.6)	3.0 (3.1)	1579	126
Pd (acac) (ppi)	174 (dec)	61	51.2 (51.0)	5.4 (5.5)	3.2 (3.3)	1579	
PdCl (ppi) (tbp)	212 (dec)	58	53.2 (53.3)	5.9 (5.9)	5.6 (5.7)	1579	291
PdI (ppi) (tbp)	207 (dec)	82	45.3 (45.0)	5.0 (5.0)	4.7 (4.8)	1573	130
PdCl (ppi) (PBu_3)	161–164	66	53.2 (53.4)	5.5 (5.7)	2.4 (2.5)	1558	286
PdI (ppi) (PBu_3)	140–141	80	46.0 (45.9)	6.6 (6.6)	2.1 (2.1)	1559	133
PdCl (mpr)	295 (dec)	95	43.1 (43.2)	4.4 (4.3)	6.4 (6.3)	1508	294

[a] Abbreviations: Hpr = *N*-(*p*-thiotoluoyl)pyrrolidine, bpr = benzene-ring orthopalladated Hpr, ppr = pyrrolidine-ring α-CH_2 cyclopalladated Hpr, Hpi = *N*-(*p*-thiotoluoyl)piperidine, ppi = piperidine-ring α-CH_2 cyclopalladated Hpi, Hnr = *N*-(2-thionaphthoyl)pyrrolidine, Hmpr = 1,3-bis(1-pyrrolidinothiocarbonyl)benzene, acac = acetylacetonate ion, PBu_3 = tri-*n*-butylphosphine, and tbp = 4-*tert*-butylpyridine.

[b] dec = decomposition.

[c] Measured of Nujol mulls. X = Cl or I.

pendicular to the thioamide plane because, in the ^1H NMR spectra (Tables 2 and 3), one of the α-CH_2 groups of the thioamides is shielded by the ring current compared to that of *N*-thiopyvaloylpyrrolidine (the chemical shifts of α-CH_2 are 3.88 and 3.80 ppm).[5] *N*-(2-Thionaphthoyl)pyrrolidine (Hnr) was prepared for X-ray analysis because the crystals of Hpr were not suited for the analysis. The conformation is confirmed by the X-ray structure of Hnr (see below).

The reaction of Hpr with lithium tetrachloropalladate(II) in methanol at room temperature gave a yellow precipitate PdCl (bpr) (the abbreviation bpr is used for the benzene-ring orthopalladated *N*-(p-thiotoluoyl)pyrrolidine to distinguish it from the pyrrolidine-ring α-CH_2 cyclopalladated one, which is abbreviated as ppr). The complex is only slightly soluble in dimethylsufoxide (dmso) and the ^1H NMR spectrum shows that one aromatic ring proton is lost while the pyrrolidine ring protons retain the original intensity (Table 2). The large shifts of $^{13}C\{^1H\}$ signals in the aromatic region also suggest the participation of the benzene ring in the reaction. The IR spectrum (Nujol mull) (Table 1) shows a higher frequency shift of the ν(C—N) band of a thioamide group upon complex formation indicating S-coordination of the thioamide group.[6] The structure V is proposed for PdCl (bpr). The presence of ν(Pd—Cl) is consistent with this and the assignment of the band is confirmed by the fact that the band is replaced with ν(Pd—I) in the spectrum of PdI (bpr).

The reaction of Hpr with palladium(II) chloride at 80°C in hexamethylphosphoric triamide (HMPA), that is, under more forcing conditions, gave PdCl (ppr) with the same chemical composition as above but different properties (Tables 1, 3, and 4). A unique multiplet (intensity 1 H) is

Table 2. ^{1}H NMR spectra (90 MHz) of Hpr and the benzene-ring orthopalladated complexes (δ ppm from tetramethylsilane)[a]

Compound	H-3	H-5	H-6	CH_3	α-CH_2	β-CH_2
Hpr	7.19 m	7.19 m	7.19 m	2.34 s	3.96 t, 3.48 t (6.7) (6.2)	2.00 m
PdCl (bpr)[b]	7.97 s	6.92 dd (8.1, 1.0)	7.38 d (8.1)	2.27 s	4.17 m, 3.92 m	2.08 m
PdI (bpr)[b]	8.10 s	6.92 dd (8.2, 1.0)	7.40 d (8.2)	2.28 s	4.16 m, 3.93 m	2.08 m
Pd (acac) (bpr)	7.83 d (1.5)	6.78 dd (8.4, 1.5)	7.17 d (8.4)	2.33 s	4.07 m	2.10 m
PdCl (bpr) (tbp)						
cis	8.37 s	6.76 dd (8.3, 1.3)	7.14[c]	2.30 s	4.05 m	2.10 m
trans	6.37 s	[d]	[d]	2.10 s	[d]	[d]
PdI (bpr) (tbp)						
cis	8.80 s	6.76 dd (8.3, 1.3)	7.14[c]	2.29 s	4.09 m	2.10 m
trans	6.11 s	[d]	[d]	2.12 s	[d]	[d]
PdCl (bpr) (PBu_3)						
cis	8.38 dd (7.1, 1.3)	[d]	[d]	2.31 s	[d]	[e]
trans	7.15 d (1.0)	6.72 dd (8.1, 1.0)	7.11 d (8.1)	2.26 s	4.02 m	[e]
PdI (bpr) (PBu_3)						
cis	8.94 dd (7.5, 0.5)	[d]	[d]	2.30 s	[d]	[e]
trans	7.18 d (1.1)	6.68 dd (8.3, 1.1)	7.09 d (8.3)	2.27 s	4.00 m	[e]

[a] $CDCl_3$ was used as a solvent unless otherwise noted. s = singlet, d = doublet, t = triplet, q = quartet, br = broad, and m = multiplet. The labeling of atoms is given in structures **III** and **V**. *Trans* and *cis* isomers are defined as structures **VII** and **VIII**. Signals of acac, tbp, and PBu_3 are excluded from the table.

[b] Dimethylsulfoxide-d_6 (dmso-d_6) was used as a solvent.

[c] Partially overlapped with the signals of tbp.

[d] Could not be assigned because these signals were overlapped with or obscured by the strong signals of the major isomers.

[e] Covered by the strong signals of PBu_3.

observed at 4.70 ppm and the total intensity of the pyrrolidine ring protons was reduced to 7 H while the signals of *p*-tolyl moiety hold the initial intensity of 4 H. The low solubility prevented the detection of the palladated carbon signal (the palladated carbon signal is surely observed in the more soluble derivatives discussed below), but the ^{13}C spectral change in the aromatic region is rather small. The IR spectrum shows S-coordination of the thioamide group and the low energy ν(Pd—Cl) band shows that Cl is coordinated *trans* to a donor with a high *trans* influence. The structure **VI** is suggested for PdCl (ppr).

The piperidine thioamide, Hpi, gave no definite complex upon reaction with lithium tetrachloropalladate(II) in methanol at room temperature (the ^{1}H NMR of the brown precipitate formed gave no indication of *ortho*- or cyclopalladation). Under the forcing conditions employed above, Hpi was cyclopalladated at α-CH_2 to afford the complex PdCl (ppi) with a structure similar to VI (a structure where a piperidine ring is substituted for the pyrrolidine ring of VI) (Tables 1, 3, and 4). No evidence was obtained for the benzene ring orthopalladation of Hpi. Hmpr was easily palladated at C-2 of the benzene ring and a dmso solution of PdCl (mpr) gave crystals suitable for X-ray analysis (see below).

The low solubilities of the above complexes precluded reliable characterization and more soluble

Table 3. ^{1}H NMR spectra (90 MHz) of Hpr and Hpi, and the pyrrolidine and piperidine ring α-CH_2 cyclopalladated complexes (δ ppm from tetramethylsilane)[a]

Compound	H-2	H-3	CH_3	α-CH	α-CH_2	β, γ-CH
Hpr	7.19 m	7.19 m	2.34 s		3.96 t, 3.48 t (6.7) (6.2)	2.00 m
Hpi	7.08 s	7.08 s	2.27 s		4.28 m, 3.46 m	1.61 m
PdCl (ppr)[b]	7.67 d (8.4)	7.38 d (8.4)	2.41 s	4.70 m	3.97 m, 3.35 m	1.85 m
PdI (ppr)[b]	7.66 d (8.2)	7.39 d (8.2)	2.42 s	4.81 m	3.84 m, 3.35 m	1.87 m
Pd (acac) (ppr)	7.53 d (7.7)	7.22 d (7.7)	2.39 s	4.80 m	3.75 m, 3.30 m	1.93 m
PdCl (ppr) (tbp)	7.52 d (7.9)	7.23 d (7.9)	2.39 s	4.95 m	3.68 m, 3.31 m	2.75 m, 1.89 m
PdI (ppr) (tbp)	7.49 d (8.4)	7.23 d (8.4)	2.39 s	5.00 m	3.72 m, 3.29 m	2.92 m, 1.89 m
PdCl (ppr) (PBu_3)	7.45 d (8.2)	7.20 d (8.2)	2.38 s	4.40 m	3.55 m, 3.30 m	[c]
PdI (ppr) (PBu_3)						
cis	7.49 d (8.1)	7.25 d (8.1)	2.40 s	4.67 m	3.67 m, 3.29 m	[c]
trans	7.49 d (8.1)	7.20 d (8.1)	2.37 s	4.67 m	3.67 m, 3.29 m	[c]
PdCl (ppi)[b]	7.39 s	7.39 s	2.41 s	4.69 m	3.62 m, 3.33 m	1.71 m
PdI (ppi)[b]	7.40 s	7.40 s	2.41 s	4.96 m	3.72 m, 3.33 m	1.72 m
Pd (acac) (ppi)	7.23 s	7.23 s	2.38 s	4.70 dd (11.2, 3.1)	3.79 br, d, 3.05 m (12.7)	1.72 m
PdCl (ppi) (tbp)	7.25 s	7.25 s	2.39 s	4.92 dd (11.2, 2.8)	3.78 br, d, 3.00 m (13.0)	1.74 m
PdI (ppi) (tbp)	7.24 s	7.24 s	2.39 s	5.17 dd (11.4, 2.6)	3.77 br, d, 3.14 m (12.3)	1.74 m
PdCl (ppi) (PBu_3)	7.22 s	7.22 s	2.37 s	4.35 dd (13.7, 7.6)	3.82 br, d, 3.11 m (12.6)	[c]
PdI (ppi) (PBu_3)	7.23 s	7.23 s	2.38 s	4.60 dd (13.6, 7.7)	3.89 br, d, 3.16 m (12.3)	[c]

[a,b] See footnotes *a* and *b* of Table 2. The labeling of atoms is given in structures **IV** and **VI**.
[c] Obscured by the strong signals of PBu_3.

derivatives have been prepared (Table 1). Sodium acetylacetonate {Na(acac)} reacted with the above three complexes to give the chloride-free complexes, Pd(acac) (A) (A = bpr, ppr, and ppi). Pd(acac) (bpr) gave the ^{1}H signals due to acac at 5.35, 2.10, and 1.96 ppm, the ^{13}C ones at 187.7, 186.4, 100.0, 28.1 and 27.9 ppm. The IR spectrum gave characteristic bands at 1575 and 441 cm^{-1}. The spectral data indicated a usual O,O-chelating coordination mode[7] and the structure was confirmed by X-ray analysis (see below). Both Pd(acac) (ppr) and Pd (acac) (ppi) had similar NMR and IR properties and should have the usual O,O-chelating acac ligand.

The three complexes, PdCl (A) (A = bpr, ppr, and ppi) were soluble in dichloromethane containing tri-*n*-butylphosphine (PBu_3) and 4-*tert*-butylpyridine (tbp) to form the adducts. The metathesis reaction of the chloro complexes with lithium bromide and iodide gave the corresponding bromo and iodo derivatives, respectively. The bromo derivatives have almost intermediate properties between those of the chloro and iodo derivatives and thus are not included in the report (Table 1). The IR spectra of the adducts show that the thioamide groups retain the S-coordination and the assignment of ν(Pd—Cl) bands were confirmed

Table 4. $^{13}C\{^1H\}$ NMR spectra (22.6 MHz) of the thioamide and some complexes (δ ppm against tetramethylsilane)[a]

Compound	C-1	C-2	C-3	C-4	CH_3	C=S	α-C	β, γ-C
Hpr	141.1	125.6	128.6	138.5	21.2	197.3	53.7, 53.4	26.4, 24.6
Hpi	140.5	125.4	128.7	138.1	21.2	199.5	53.1, 50.6	26.8, 25.4, 24.1
PdCl (bpr)	[b]	155.7	142.7	145.1	23.1	194.0	57.1, 56.8	27.7, 25.0
Pd (bpr) (acac)	141.8	155.1	133.9	143.8	22.0	196.5	55.1, 54.8	26.9, 23.9
PdCl (bpr) (PBu_3)								
cis	141.7	166.9	141.4	[b]	[c]	198.3	55.1, 54.8	[c]
	(5.5)	(141)	(10.4)			(18.3)		
trans	139.8	157.9	138.9	146.6	[c]	195.7	55.1, 54.2	[c]
	(5.5)	(2.4)	(13.5)	(0.7)		(3.1)		
PdI (bpr) (PBu_3)								
cis	143.6	166.4	142.1	146.5	[c]	199.1	55.9, 55.4	[c]
	(3.1)	(143)	(8.3)			(17.3)		
trans	140.5	163.4	139.0	145.9	[c]	199.3	55.5, 54.8	[c]
	(5.5)	(4.8)	(13.5)	(0.7)		(3.1)		
PdCl (ppr)	133.0	130.7	129.6	144.0	21.3	[b]	[b], 53.3	23.0, 22.6
Pd (ppr) (acac)	132.4	129.1	128.0	142.1	21.5	188.2	64.7, 51.7	29.8, 21.9
PdCl (ppr) (tbp)	131.7	128.8	127.7	141.9	21.2	186.5	65.9, 51.6	32.0, 22.0
PdI (ppr) (tbp)	132.0	128.9	127.7	141.9	21.4	186.5	63.7, 51.8	36.1, 23.6
PdCl (ppr) (PBu_3)	133.2	128.9	127.9	141.6	21.4	190.2	67.3, 51.5	32.3, [c]
	(2.4)					(2.4)	(2.8)	(1.4)
PdI (ppr) (PBu_3)								
cis	132.3	129.0	127.7	141.8	23.0	185.5	77.3, 52.7	34.8, [c]
	(1.4)					(16.6)	(131) (4.5)	(1.7)
trans	132.9	128.9	127.9	141.6	21.4	192.2	75.9, 50.9	31.9, [c]
	(2.4)					(2.8)	(1.0)	(1.0)
PdCl (ppi)	132.3	129.3	126.4	140.9	20.9	188.8	[b], 55.2	[b], 26.8, 25.9
Pd (ppi) (acac)	133.3	129.1	126.4	140.6	21.4	190.5	68.6, 54.3	34.0, 27.9, 25.4
PdCl (ppi) (tbp)	132.9	129.2	126.2	140.7	21.3	189.3	70.5, 54.9	36.7, 27.8, 25.9
PdI (ppi) (tbp)	132.5	129.0	126.0	140.4	21.2	188.8	67.3, 55.2	39.1, 27.6, 26.3
PdCl (ppi) (PBu_3)	134.1	129.2	126.2	140.2	21.4	191.7	71.6, 55.7	36.7, [c]
	(2.1)					(2.1)	(1.0)	(1.7)
PdI (ppi) (PBu_3)	133.7	129.0	125.9	140.0	21.2	193.5	79.9, 55.4	36.7, [c]
	(2.1)						(0.9)	(1.0)

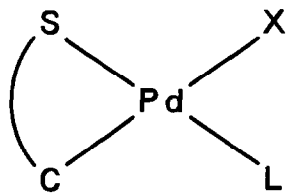
[a] The solvents were the same as those for ^1H NMR spectra (Tables 2 and 3). Figures in parentheses are J(P—C) in Hz.

[b] These signals could not be assigned.

[c] Overlapped with the signals of PBu_3 and could not be identified.

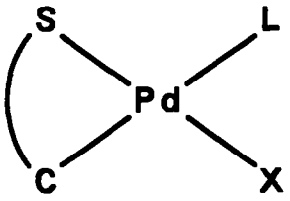
by the replacement of the bands with lower frequency ν(Pd—I) bands. The positions of ν(Pd—Cl) bands are low in frequency and reflect strongly the *trans* influences of the donor atoms coordinating *trans* to the chloro ligands.[8]

The complicated ^1H and $^{13}C\{^1H\}$ NMR spectra of a $CDCl_3$ solution of PdX (bpr) (PBu_3) (X = Cl and I) (Tables 2 and 4) are explained on the basis of the presence of two isomers, *trans*-(C,X) and *cis*-(C,X) (the geometries are defined as structures **VII** and **VIII**, respectively. "C" in the parenthesis means a palladated carbon). The ratio of isomers was estimated from the signal intensities of the ^1H NMR spectra: the ratio of *cis*-(C,Cl); *trans*-(C,Cl) of PdCl (bpr) (PBu_3) was *ca* 1 : 5 and that of PdI (bpr) (PBu_3) was *ca* 1 : 3. The *cis* isomer is characterized by the fact that X affects strongly the chemical shift of H-3,[9] which in this isomer is situated proximal



VII, trans-(C, X)

Structure 7



VIII, cis-(C, X)

Structure 8

to X and the *J* (P—C) of the palladated-carbon (C-2) exceeds 100 Hz,[9] the C-2 being coordinated *trans* to the P donor. Of the *trans* isomer, on the contrary, the chemical shift of H-3 is insensitive to X and the *J* (P—C) of C-2 is much smaller (less than 5 Hz).[8]

Isomers also exist in the $CDCl_3$ solution of PdX (bpr) (tbp) (X = Cl and I) (Table 2). The ratio of *cis*-(C,Cl) : *trans*-(C,Cl) was 3 : 1 and that of *cis*-(C,I) : *trans*-(C,I) was 2 : 1. For the *cis* isomers the H-3 chemical shifts depend on X, the situation being similar to the above *cis*-PdX (bpr) (PBu_3), and for the *trans* isomers the H-3 was markedly shielded, the proton being placed in the anisotropic shielding region of the ring current of tbp nearly perpendicular to the coordination plane. In $CDCl_3$ PdX (bpr) (tbp) is liable to dissociate the tbp ligand and no satisfactory $^{13}C\{^1H\}$ NMR spectra has been obtained so far. It should be noted that the major isomer of the tbp complexes is *cis*-(C,X) while the major of the PBu_3 ones is *trans*-(C,X), probably reflecting the difference in *trans* influences of tbp and PBu_3 ligands.

The ^1H signals due to tbp of *cis*-PdCl (bpr) (tbp) (major isomer) are at 1.29 (^{t}Bu) and 8.66 (H-2,6) while those of the *trans* one are at 1.34 and 8.77 ppm, respectively. The corresponding signals of PdCl (ppr) (tbp) are at 1.29 and 8.68 ppm, respectively, and those of PdCl (ppi) (tbp) at 1.27 and 8.64 ppm. The results suggest that PdCl (A) (tbp) (A = ppr and ppi) has a *cis*-(C,Cl) geometry (structure **VIII**). The *cis*-(C,Cl) geometry has been confirmed by the X-ray analysis of PdCl (ats) (tbp) (ats = thiophene ring C-3 cyclopalladated *N*,*N*-dimethylthiophene-2-carboselenoamide).[3] The NMR similarity of the iodo analogues PdI (A) (tbp) (A = ppr and ppi) indicates also a *cis*-(C,I) geometry for them.

The small *J* (P—C) values of α-C (bound to Pd) of PdX (A) (PBu_3) (X = Cl and I; A = ppr and ppi) [except a *cis*-(C,I) isomer of PdI (ppr) (PBu_3)] (Table 4) suggest a *trans*-(C,X) arrangement (structure **VII**). The X-dependent chemical shifts of the α-C of PdX (A) (PBu_3) show an opposite trend to those of the above mentioned PdX (A) (tbp), for which a *cis*-(C,X) structure is proposed and the X-dependence of the PBu_3 complexes is more intense. The α-C chemical shifts are expected to be more strongly affected by the nature of the *trans* X donor than the *cis* as observed. The large *J* (P—C) (131 Hz) found for the minor isomer of PdI (ppr) (PBu_3) is characteristic of a *trans*-(C,P) arrangement, namely, *cis*-(C,I) geometry (structure **VIII**): the ratio of *cis* (C,I) : *trans*-(C,I) was roughly 1 : 2.

Hbt was cyclopalladated with Pd(II) only at the N—CH_3 group (structure **I**)[1] but Hpr both at the *ortho* position (C-2) of the benzene ring and at the α-CH_2 group (Structures **V** and **VI**, respectively). To obtain insight into the inhibited *ortho*-palladation of the benzene ring of Hbt, the structure of free Hnr was determined by X-ray analysis and compared to that of Hbt reported previously.[10] The structure of the free thioamide, Hnr, is shown in Fig. 1 and bond lengths and angles are given in Table 5. The bond lengths and angles around the thioamide group are in the normal range. The nearly planar thioamide group [S, C(11), N, C(12), and C(15)] make a dihedral angle of 60.94(8)° with the planar naphthalene ring and the angle is comparable to that (63°) of Hbt.[10] The structure shows that one of the α-CH_2 groups [C(15)] is in the shielding region of an anisotropic aromatic ring current and the shielded ^1H NMR signal (3.47 ppm) should be assigned to the CH_2 group.

The C—N—C angle, 113.2(4)°, of the dimethylamino group of Hbt is wider than the corresponding angle, 110.5(3)°, of pyrrolidino group of Hnr revealing that the latter pyrrolidino substituent is less bulky than the former dimethylamino substituent. This fact should show that the pyrrolidinothiocarbonyl group can more easily be situated coplanar to the naphthalene ring than the dimethylthiocarbonyl group: placing the S atom in the same plane as an aromatic ring plane is a condition required for aromatic ring orthopalladation to occur.

To characterize the structural features of the coordinated pyrrolidinothiocarbonyl group, the structures of Pd (acac) (bpr) and PdCl (mpr) have been determined and are shown in Figs 2 and 3, respectively. The bond lengths and angles are given in Tables 6 and 7, respectively, and most of these values are normal. The unit cell of PdCl (mpr) contains two independent molecules with nearly identical structures and one of them is considered here. In both complexes the C=S bonds are longer than that of free Hnr but the C—N bond lengths are not significantly altered upon coordination of the thioamide groups. The Pd—O bond lengths of Pd (acac) (bpr) reflect the *trans* influences of the S and C(1) donor atoms. The Pd—S length of Pd

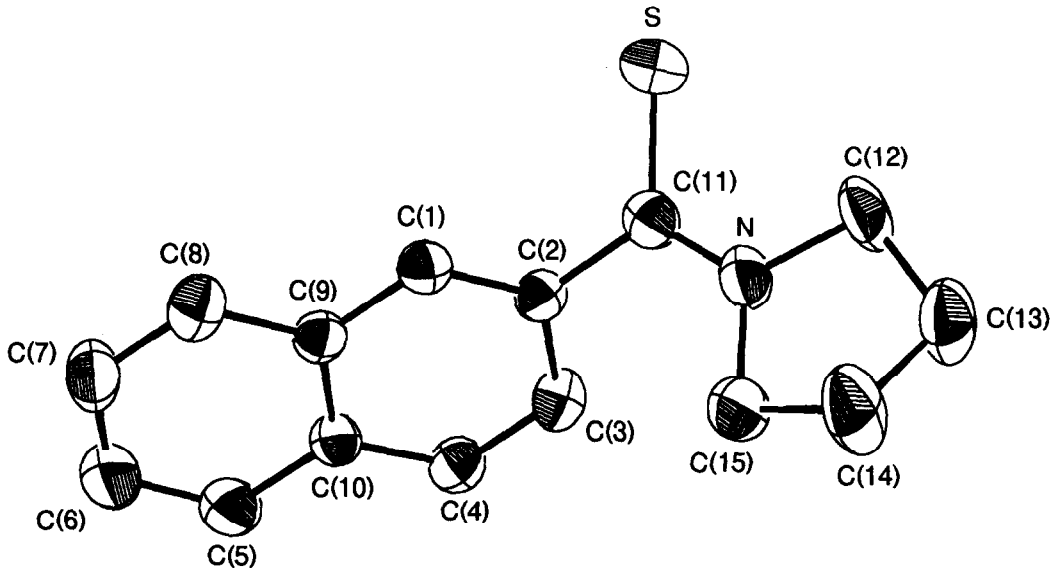


Fig. 1. Perspective view of Hnr with the atomic labeling scheme.

(acac) (bpr) (S is *trans* to O) is shorter than those of PdCl (mpr) (S is *trans* to S) suggesting that the *trans* influence of thioamide-S donor atoms is stronger than that of acac-O atoms.

The pyrrolidine ring of Pd (acac) (bpr) is distorted: the angle at C(12), 99.4(8)°, is unusually small and the C(9)—N—C(12) angle, 113.7(8)°, is widened compared to that of the above free Hnr, 110.5(3)°. The origin of the ring distortion is not clear so far, but a molecular model suggests that there is steric crowding between the two hydrogen atoms, H—C(12) and H—C(5) if the two carbon atoms, C(12) and C(5) are in the same coordination plane. To avoid the extreme approach of the two

Table 5. Intramolecular distances (Å) and angles (°) of *N*-(2-thionaphthoyl)pyrrolidine (Hnr) and esd in parentheses

S—C(11)	1.670(4)	C(5)—C(6)	1.361(6)
N—C(11)	1.325(4)	C(5)—C(10)	1.408(5)
N—C(12)	1.471(5)	C(6)—C(7)	1.402(6)
N—C(15)	1.496(5)	C(7)—C(8)	1.363(6)
C(1)—C(2)	1.361(5)	C(8)—C(9)	1.416(5)
C(1)—C(9)	1.416(5)	C(9)—C(10)	1.422(5)
C(2)—C(3)	1.426(5)	C(12)—C(13)	1.497(7)
C(2)—C(11)	1.486(5)	C(13)—C(14)	1.502(8)
C(3)—C(4)	1.362(5)	C(14)—C(15)	1.511(6)
C(4)—C(10)	1.418(5)		

C(11)—N—C(12)	123.8(3)	C(1)—C(9)—C(8)	122.9(3)
C(11)—N—C(15)	125.3(3)	C(1)—C(9)—C(10)	119.4(3)
C(12)—N—C(15)	110.5(3)	C(8)—C(9)—C(10)	117.7(3)
C(2)—C(1)—C(9)	121.2(3)	C(4)—C(10)—C(5)	122.4(3)
C(1)—C(2)—C(3)	119.7(3)	C(4)—C(10)—C(9)	118.0(3)
C(1)—C(2)—C(11)	121.0(3)	C(5)—C(10)—C(9)	119.6(3)
C(3)—C(2)—C(11)	119.2(3)	S—C(11)—N	122.6(3)
C(2)—C(3)—C(4)	120.0(3)	S—C(11)—C(2)	120.2(2)
C(3)—C(4)—C(10)	121.7(3)	N—C(11)—C(2)	117.2(3)
C(6)—C(5)—C(10)	120.9(4)	N—C(12)—C(13)	103.6(4)
C(5)—C(6)—C(7)	120.0(4)	C(12)—C(13)—C(14)	103.6(4)
C(6)—C(7)—C(8)	120.5(4)	C(13)—C(14)—C(15)	104.1(4)
C(7)—C(8)—C(9)	121.2(4)	N—C(15)—C(14)	102.8(3)

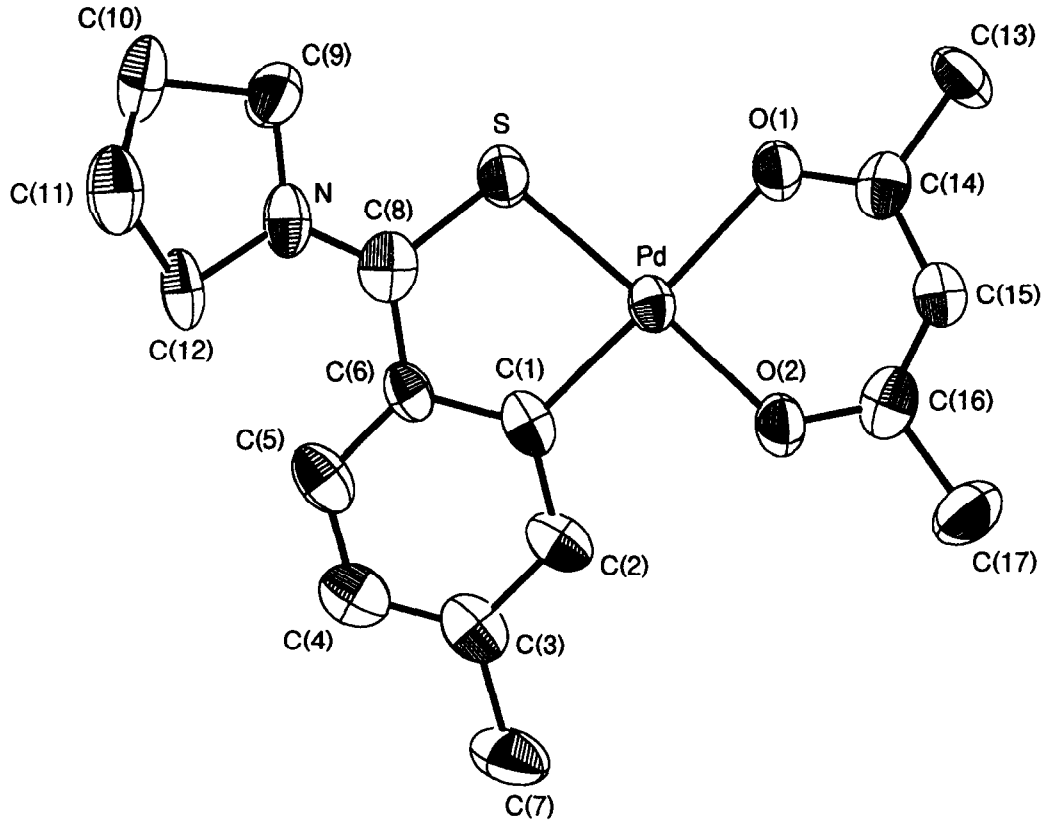


Fig. 2. Perspective view of Pd (acac) (bpr) with the atomic labeling scheme.

hydrogen atoms, C(12) of the thioamide group deviates by 1.17(2) Å from the coordination plane and the result of the deviation separates C(5) and C(12) at a distance of 2.99(1) Å. The deviation is smaller than the corresponding value (1.52(2) Å) found for one of the N—CH_3 groups of a related complex, Pd (edc) (bbt) (edc = *N*,*N*-diethyldithiocarbamate ion and bbt = benzene-ring ortho-palladated *N*,*N*-dimethylthiobenzamide) [obtained by oxidative addition of *N*,*N*-dimethyl-ortho-bromothiobenzamide to Pd(0)] suggesting that the pyrrolidino substituent is favorable for ortho-palladation of thiobenzamide over the dimethylamino one. The dihedral angles between the thioamide plane and aromatic ring (18.4(3)°) and between the pyrrolidino group C(9)—N—C(12) and the S—C(8)—C(6) plane (6.7(8)°) of Pd (bpr) (acac) are smaller than the corresponding angles (22.1(4) and 18.6(8)°, respectively) of Pd (edc) (bbt).[2] These facts should also suggest that Pd (edc) (bbt) is more strained than Pd (bpr) (acac).

In the palladated thioamides the angles around the thioamide-carbon are modified remarkably: the angle S—C(11)—N, 122.6(3)°, of free Hnr is reduced to 118.2(8)° [S—C(8)—N] of Pd (acac) (bpr) and to 117.8(2)° [S(1A)—C(7A)—N(1A)] and 117.2(2)° [S(2A)—C(12A)—N(2A)] of PdCl (mpr), while the angle C(2)—C(11)—N, 117.2(3)° of free Hnr is enlarged to 125.4(9)° [C(6)—C(8)—N] of Pd (acac) (bpr) and to 125.5(3)° [C(2A)—C(7A)—N(1A)] and 126.6(3)° [C(6A)—C(12A)—N(2A)] of PdCl (mpr). The remarkable angle changes should be required for releasing some steric repulsions between H—C(5) and H—C(12) of Pd (acac) (bpr) and between H—C(3A) and H—C(11A), and H—C(5A) and H—C(16A) of PdCl (mpr). The repulsive interaction is also reflected in the enlarged angles of C(11A)—N(1A)—C(7A) and C(16A)—N(2A)—C(12A) and the reduced angles of C(8A)—N(1A)—C(7A) and C(13A)—N-(2A)—C(12A): the distortion further separates C(11A) from C(3A) and C(16A) from C(5A).

The pyrrolidino rings of PdCl (mpr) are rather regular (Table 7) and compared to the dimethylamino group of structurally very similar PdCl (mpt) (mpt = cyclopalladated *N*,*N*,*N*′,*N*′-tetramethyl-dithioisophthalamide).[11] In PdCl (mpt), one of the thioamide N-CH_3 groups showed a large deviation [1.52(1) Å] from the coordination plane while in PdCl (mpr), the most deviated C(11A) atom is situated by 0.693(4) Å out of the coordination plane. This result is similar to that discussed above for Pd (edc) (bbt) and Pd (acac) (bpr),

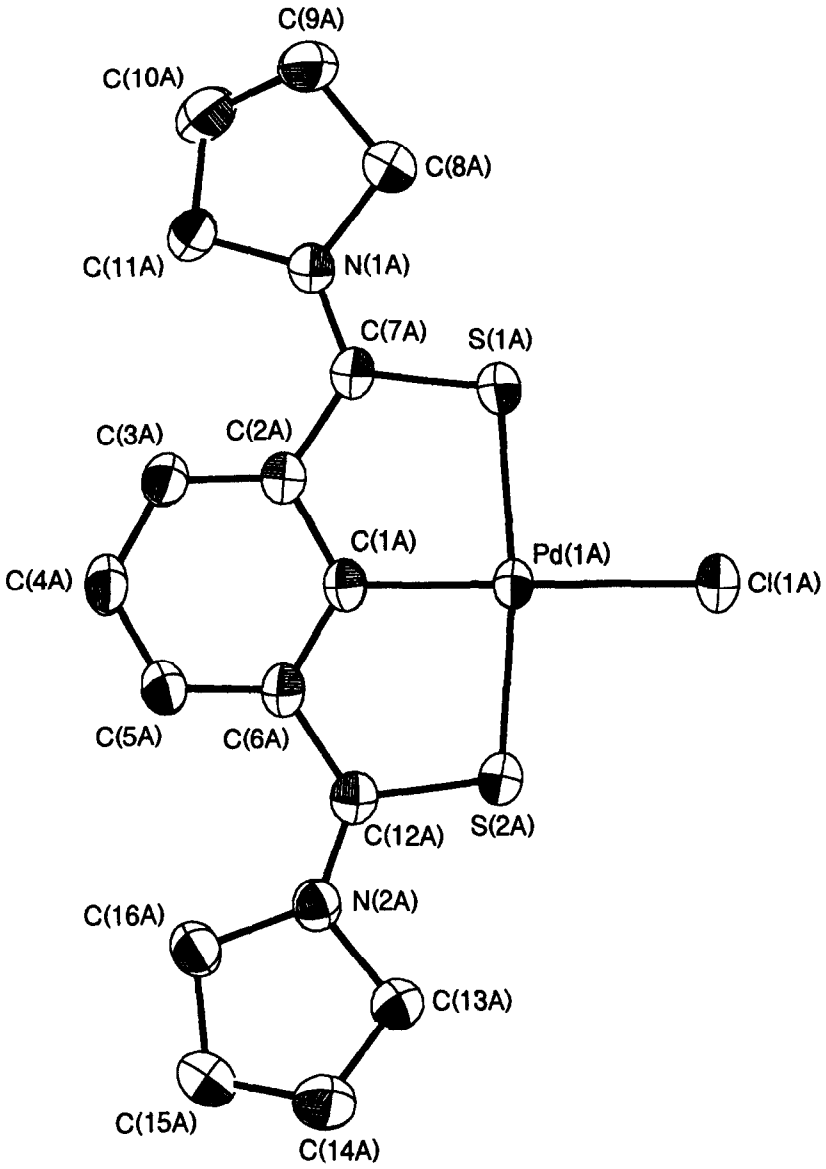


Fig. 3. Perspective view of a molecule A of PdCl (mpr) with the atomic labeling scheme.

and a pyrrolidino group has proved to be a more sterically favorable thioamide-substituent than a dimethylamino group to fulfil the requirements of aromatic ring cyclopalladation of a tertiary thioamide with Pd(II).

EXPERIMENTAL

Measurements

^1H (90 MHz) and $^{13}C\{^1H\}$ (22.6 MHz) NMR spectra were measured on a Hitachi R-90H NMR spectrometer at room temperature and chemical shifts were given in δ ppm relative to internal tetramethylsilane. IR spectra were recorded on a Perkin-Elmer System 2000 FTIR spectrometer. The KBr disk method was applied for the region 5200–450 cm^{-1} and Nujol mulls were used for 700–100 cm^{-1}. Elemental analyses were performed on a Leco CHN 900 analyser.

Synthesis of the thioamides

Yields, melting points, and analytical results are given in Table 1. The four thioamides were obtained similarly by the modified Amupitan's method and as a representative, the preparation of Hpr is described as follows: A mixture of sulfur (4.92 g, 0.154 mol), pyrrolidine (10.27 g, 0.154 mol), *p*-tolualdehyde (12.38 g, 0.103 mol), and acetic acid (9.01 g, 0.155 mol) in 40 cm^3 of *N*,*N*-dimethylformamide (DMF) was heated to 100°C over

Table 6. Intramolecular distances (Å) and angles (°) of Pd(acac) (bpr) with esd in parentheses

Pd—S	2.244(3)	C(3)—C(4)	1.32(2)
Pd—O(1)	2.108(6)	C(3)—C(7)	1.52(2)
Pd—O(2)	2.041(7)	C(4)—C(5)	1.39(2)
Pd—C(1)	1.986(9)	C(5)—C(6)	1.39(1)
S—C(8)	1.72(1)	C(6)—C(8)	1.48(1)
O(1)—C(14)	1.25(1)	C(9)—C(10)	1.54(1)
O(2)—C(16)	1.28(1)	C(10)—C(11)	1.52(2)
N—C(8)	1.33(1)	C(11)—C(12)	1.56(2)
N—C(9)	1.46(1)	C(13)—C(14)	1.52(1)
N—C(12)	1.51(1)	C(14)—C(15)	1.42(1)
C(1)—C(2)	1.39(1)	C(15)—C(16)	1.40(1)
C(1)—C(6)	1.43(1)	C(16)—C(17)	1.53(2)
C(2)—C(3)	1.41(1)		

S—Pd—O(1)	92.8(2)	C(3)—C(4)—C(5)	121(1)
S—Pd—O(2)	176.8(2)	C(4)—C(5)—C(6)	120(1)
S—Pd—C(1)	85.0(3)	C(1)—C(6)—C(5)	119.8(9)
O(1)—Pd—O(2)	90.1(3)	C(1)—C(6)—C(8)	114.1(8)
O(1)—Pd—C(1)	177.7(3)	C(5)—C(6)—C(8)	126.1(9)
O(2)—Pd—C(1)	92.1(3)	S—C(8)—N	118.2(8)
Pd—S—C(8)	101.1(4)	S—C(8)—C(6)	116.4(7)
Pd—O(1)—C(14)	124.9(6)	N—C(8)—C(6)	125.4(9)
Pd—O(2)—C(16)	124.9(6)	N—C(9)—C(10)	103.6(9)
C(8)—N—C(9)	121.2(8)	C(9)—C(10)—C(11)	102(1)
C(8)—N—C(12)	124.6(9)	C(10)—C(11)—C(12)	105(1)
C(9)—N—C(12)	113.7(8)	N—C(12)—C(11)	99.4(8)
Pd—C(1)—C(2)	119.3(7)	O(1)—C(14)—C(13)	117.4(9)
Pd—C(1)—C(6)	120.9(7)	O(1)—C(14)—C(15)	125.8(9)
C(2)—C(1)—C(6)	119.7(9)	C(13)—C(14)—C(15)	116.7(9)
C(1)—C(2)—C(3)	121(1)	C(14)—C(15)—C(16)	126(1)
C(2)—C(3)—C(4)	118(1)	O(2)—C(16)—C(15)	127(1)
C(2)—C(3)—C(7)	122(1)	C(15)—C(16)—C(17)	119.1(9)
C(4)—C(3)—C(7)	122(1)	C(15)—C(16)—C(17)	119.1(9)

1 h with stirring. The mixture was stirred for an additional 3 h at this temperature and cooled to room temperature. The resulting mixture was poured with stirring into 300 cm^3 of water cooled in an ice bath and the stirring was continued until the oily product had solidified. The solids were filtered, washed with water, dried in air, and dissolved in 600 cm^3 of hot methanol. The remaining solids (mainly unreacted sulfur) were removed by filtration and the red solution was treated with charcoal. The filtered solution was evaporated to 30 cm^3 under reduced pressure to give a faint yellow precipitate, which was recrystallized from warm diethyl ether (dissolved in 500 cm^3 and concentrated to 10 cm^3).

For the preparation of light yellow Hpi, piperidine was substituted stoichiometrically for pyrrolidine, while for yellow Hnr and Hmpr the *p*-tolualdehyde was replaced, respectively, with 2-naphthaldehyde and isophthalaldehyde. Crystals of Hnr suitable for X-ray analysis formed upon recrystallization from ethanol. NMR of Hnr, ^1H ($CDCl_3$): 1.97 m (β-CH_2), 3.47 t, 4.00 t (α-CH_2), 7.4–7.9 m (naphthyl) ppm and $^{13}C\{^1H\}$: 24.6, 26.4 (β-C), 53.4, 53.7 (α-C), 123.7, 124.4, 126.4, 126.5, 127.5, 127.9, 128.2, 132.5, 132.9, 141.0 (naphthyl), 196.8 (C=S) ppm. NMR of Hmpr, ^1H ($CDCl_3$): 2.01 q (β-CH_2), 3.50 t, 3.93 t (α-CH_2), 7.34 (phenyl) ppm and $^{13}C\{^1H\}$: 24.5, 26.4 (β-C), 53.4, 53.8 (α-C), 123.1 (C-5), 125.7 (C-4,6), 128.1 (C-2), 143.6 (C-1,3), 195.6 (C=S) ppm.

Preparation of the complexes

Melting points, yields and analytical results of the new complexes are summarized in Table 1.

PdCl (bpr): To a methanol (30 cm^3) solution of lithium tetrachloropalladate, prepared *in situ* from

Table 7. Intramolecular distances (Å) and angles (°) of PdCl (mpr) with esd in parentheses

Pd(1A)—Cl(1A)	2.3858(9)	Pd(1B)—Cl(1B)	2.383(1)
Pd(1A)—S(1A)	2.2700(9)	Pd(1B)—S(1B)	2.2870(8)
Pd(1A)—S(2A)	2.2556(8)	Pd(1B)—S(2B)	2.2552(8)
Pd(1A)—C(1A)	1.963(3)	Pd(1B)—C(1B)	1.956(3)
S(1A)—C(7A)	1.714(3)	S(1B)—C(7B)	1.722(3)
S(2A)—C(12A)	1.722(3)	S(2B)—C(12B)	1.721(3)
N(1A)—C(7A)	1.317(3)	N(1B)—C(7B)	1.314(3)
N(1A)—C(8A)	1.488(5)	N(1B)—C(8B)	1.481(4)
N(1A)—C(11A)	1.479(4)	N(1B)—C(11B)	1.482(4)
N(2A)—C(12A)	1.319(4)	N(2B)—C(12B)	1.314(4)
N(2A)—C(13A)	1.488(3)	N(2B)—C(13B)	1.486(4)
N(2A)—C(16A)	1.485(4)	N(2B)—C(16B)	1.493(5)
C(1A)—C(2A)	1.417(3)	C(1B)—C(2B)	1.416(4)
C(1A)—C(6A)	1.423(4)	C(1B)—C(6B)	1.421(4)
C(2A)—C(3A)	1.395(4)	C(2B)—C(3B)	1.396(5)
C(2A)—C(7A)	1.481(4)	C(2B)—C(7B)	1.485(4)
C(3A)—C(4A)	1.383(5)	C(3B)—C(4B)	1.376(5)
C(4A)—C(5A)	1.384(3)	C(4B)—C(5B)	1.382(4)
C(5A)—C(6A)	1.398(4)	C(5B)—C(6B)	1.395(5)
C(6A)—C(12A)	1.485(3)	C(6B)—C(12B)	1.476(4)
C(8A)—C(9A)	1.512(4)	C(8B)—C(9B)	1.511(4)
C(9A)—C(10A)	1.506(6)	C(9B)—C(10B)	1.500(6)
C(10A)—C(11A)	1.516(4)	C(10B)—C(11B)	1.507(4)
C(13A)—C(14A)	1.510(5)	C(13B)—C(14B)	1.512(5)
C(14A)—C(15A)	1.519(5)	C(14B)—C(15B)	1.503(6)
C(15A)—C(16A)	1.517(4)	C(15B)—C(16B)	1.519(4)

Cl(1A)—Pd(1A)—S(1A)	93.96(3)	Cl(1B)—Pd(1B)—S(1B)	96.52(3)
Cl(1A)—Pd(1A)—S(2A)	93.99(3)	Cl(1B)—Pd(1B)—S(2B)	92.07(3)
Cl(1A)—Pd(1A)—C(1A)	179.1(1)	Cl(1B)—Pd(1B)—C(1B)	177.11(8)
S(1A)—Pd(1A)—S(2A)	172.00(3)	S(1B)—Pd(1B)—S(2B)	171.34(4)
S(1A)—Pd(1A)—C(1A)	86.39(8)	S(1B)—Pd(1B)—C(1B)	86.01(8)
S(2A)—Pd(1A)—C(1A)	85.65(7)	S(2B)—Pd(1B)—C(1B)	85.42(8)
Pd(1A)—S(1A)—C(7A)	100.0(1)	Pd(1B)—S(1B)—C(7B)	99.2(1)
Pd(1A)—S(2A)—C(12A)	101.40(8)	Pd(1B)—S(2B)—C(12B)	100.9(1)
C(7A)—N(1A)—C(8A)	120.8(2)	C(7B)—N(1B)—C(8B)	121.7(3)
C(7A)—N(1A)—C(11A)	128.9(3)	C(7B)—N(1B)—C(11B)	128.3(3)
C(8A)—N(1A)—C(11A)	109.7(2)	C(8B)—N(1B)—C(11B)	109.7(2)
C(12A)—N(2A)—C(13A)	121.3(3)	C(12B)—N(2B)—C(13B)	120.5(3)
C(12A)—N(2A)—C(16A)	129.1(2)	C(12B)—N(2B)—C(16B)	129.8(3)
C(13A)—N(2A)—C(16A)	109.6(2)	C(13B)—N(2B)—C(16B)	109.7(2)
Pd(1A)—C(1A)—C(2A)	119.6(2)	Pd(1B)—C(1B)—C(2B)	120.4(2)
Pd(1A)—C(1A)—C(6A)	120.9(2)	Pd(1B)—C(1B)—C(6B)	120.9(2)
C(2A)—C(1A)—C(6A)	119.4(2)	C(2B)—C(1B)—C(6B)	118.6(3)
C(1A)—C(2A)—C(3A)	119.4(3)	C(1B)—C(2B)—C(3B)	119.9(3)
C(1A)—C(2A)—C(7A)	116.4(2)	C(1B)—C(2B)—C(7B)	115.8(3)
C(3A)—C(2A)—C(7A)	124.1(2)	C(3B)—C(2B)—C(7B)	124.1(3)
C(2A)—C(3A)—C(4A)	120.5(2)	C(2B)—C(3B)—C(4B)	120.7(3)
C(3A)—C(4A)—C(5A)	120.8(3)	C(3B)—C(4B)—C(5B)	120.3(4)
C(4A)—C(5A)—C(6A)	120.6(3)	C(4B)—C(5B)—C(6B)	121.0(3)
C(1A)—C(6A)—C(5A)	119.1(2)	C(1B)—C(6B)—C(5B)	119.4(3)
C(1A)—C(6A)—C(12A)	115.7(2)	C(1B)—C(6B)—C(12B)	115.2(3)
C(5A)—C(6A)—C(12A)	125.0(3)	C(5B)—C(6B)—C(12B)	125.2(3)
S(1A)—C(7A)—N(1A)	117.8(2)	S(1B)—C(7B)—N(1B)	118.5(2)
S(1A)—C(7A)—C(2A)	116.7(2)	S(1B)—C(7B)—C(2B)	116.6(2)
N(1A)—C(7A)—C(2A)	125.5(3)	N(1B)—C(7B)—C(2B)	124.8(3)
N(1A)—C(8A)—C(9A)	103.7(3)	N(1B)—C(8B)—C(9B)	105.0(3)
C(8A)—C(9A)—C(10A)	103.3(3)	C(8B)—C(9B)—C(10B)	104.4(3)

Table 7.—*continued.*

C(9A)—C(10A)—C(11A)	103.6(3)	C(9B)—C(10B)—C(11B)	104.4(3)
N(1A)—C(11A)—C(10A)	104.1(3)	N(1B)—C(11B)—C(10B)	103.9(3)
S(2A)—C(12A)—N(2A)	117.2(2)	S(2B)—C(12B)—N(2B)	117.1(2)
S(2A)—C(12A)—C(6A)	116.2(2)	S(2B)—C(12B)—C(6B)	116.6(2)
N(2A)—C(12A)—C(6A)	126.6(3)	N(2B)—C(12B)—C(6B)	126.2(3)
N(2A)—C(13A)—C(14A)	104.4(2)	N(2B)—C(13B)—C(14B)	103.9(3)
C(13A)—C(14A)—C(15A)	103.1(3)	C(13B)—C(14B)—C(15B)	103.1(3)
C(14A)—C(15A)—C(16A)	104.5(3)	C(14B)—C(15B)—C(16B)	103.9(3)
N(2A)—C(16A)—C(15A)	104.6(2)	N(2B)—C(16B)—C(15B)	103.5(3)

1 mmol (177 mg) of palladium(II) chloride and 2 mmol (85 mg) of lithium chloride, was added 1.2 mmol (246 mg) of Hpr to produce an orange suspension. The suspension was stirred for 2 days at room temperature to give a yellow precipitate, which was washed with methanol and dried in air.

PdCl (ppr): A mixture of 1 mmol (177 mg) of palladium(II) chloride and 1.2 mmol (246 mg) of Hpr in 10 cm^3 of hexamethylphosphoric triamide (HMPA) was heated with stirring at 80°C for 2 h and cooled to room temperature. The red solution was poured into 20 cm^3 of water and the mixture was stirred for 10 min. The fine yellow brown precipitate was collected by a centrifuge and the supernatant solution was decanted. The residual was agitated well with 20 cm^3 of methanol and re-centrifuged. The precipitate was suspended in 20 cm^3 of dichloromethane, filtered, and dried in air to yield a yellow powder (0.18 g). The red dichloromethane mother liquor was subjected to a silica gel column chromatography. The column was eluted with a 5 : 1 mixture of benzene and acetone, and the first eluted yellow band was collected and evaporated to dryness under reduced pressure. The yellow residue was suspended in methanol, collected by filtration and dried in air (0.10 g). The two portions were combined.

PdCl (mpr): A mixture of 1 mmol (304 mg) of Hmpr and 1 mmol of lithium tetrachloropalladate (prepared as above) in 30 cm^3 of methanol was refluxed for 2 h to yield a yellow precipitate. The product was filtered, washed with methanol, and dried in air. Recrystallization from hot dimethylsulfoxide gave crystals suitable for X-ray analysis. ^1H NMR (dmso-d_6): 4.22 t, 3.98 t (α-CH_2), 2.09 q (β-CH_2), 7.12 t (H-5), 7.72 d (H-4,6) ppm. $^{13}H\{^1H\}$: 23.0, 25.6 (β-C), 55.0 (α-C), 120.1 (C-5), 128.5 (C-4,6), 146.1 (C-1,3), 171.9 (C—Pd), 195.1 (C=S) ppm.

Pd (acac) (bpr): To a methanol solution (20 cm^3) of 1.0 mmol (122 mg) of sodium acetylacetonate was added 0.84 mmol (290 mg) of PdCl (bpr) and the mixture was stirred at room temperature for 1 h to give a light yellow precipitate. The precipitate was collected, dissolved in dichloromethane, and the solution was filtered. Upon addition of hexane the filtrate yielded yellow crystals and concentration of the mother liquor gave further crystals. Slow evaporation of a dichloromethane–hexane solution afforded crystals suited to X-ray analysis.

The two complexes Pd (acac) (ppr) and Pd (acac) (ppi) were prepared by this method from PdCl (bpr) and PdCl (ppi), respectively.

PdCl (bpr) (tbp): Addition of 1.1 mmol (149 mg) of tbp to a suspension of 0.48 mmol (166 mg) of PdCl (bpr) in 20 cm^3 of dichloromethane resulted in a yellow clear solution. The solution was filtered, concentrated to 5 cm^3, and mixed with 10 cm^3 of *n*-hexane to precipitate yellow crystals. The product was collected, washed with *n*-hexane, and dried in air.

The other tbp complexes (Table 1) were prepared by this method and the PBu_3 derivatives were similarly prepared by use of a stoichiometric amount of PBu_3 instead of tbp. If the reaction solution was dirty-colored, the solution was treated with Florisil. Metathesis of the chloro complexes with excess lithium bromide or iodide in acetone afforded the corresponding bromo or iodo derivatives, respectively; to suppress dissociation of tbp, two drops of tbp was added during the metathesis of the tbp complexes.

X-ray analysis

Crystal data, intensity collection information, and structure refinement parameters for Hnr, Pd (acac) (bpr), and PdCl (mpr) are provided in Table 8. Diffraction data were collected on a Rigaku AFC-5R diffractometer using graphite-monochromatized Mo-K_α radiation ($\lambda = 0.71073$ Å). The θ–2θ scan mode was employed. The intensities of three representative reflections measured after every 150 reflections remained constant throughout the data collection indicating the crystal stability.

Table 8. Crystallographic data and experimental details of Hnr, Pd (acac) (bpr), and PdCl (mpr)

Compound	Hnr	Pd (acac) (bpr)	PdCl (mpr)
Formula	$C_{15}H_{15}NS$	$C_{17}H_{21}NO_2PdS$	$C_{16}H_{19}ClN_2PdS_2$
fw	241.36	409.85	445.34
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1$ (No. 4)	$P2_1/a$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	6.048(1)	8.621(3)	12.314(2)
b, Å	9.7188(9)	12.840(3)	12.616(2)
c, Å	10.9129(8)	15.618(3)	12.113(2)
α, °			101.53(1)
β, °	98.538(9)	100.89(2)	105.28(1)
γ, °			103.21(1)
Z	2	4	4
V, Å^3	634.3(1)	1697.7(7)	1698.2(5)
μ(Mo-K_α), cm^{-1}	2.21	12.02	14.71
Transm factor		0.863–0.905	0.621–0.759
Crystal color	pale yellow	pale yellow	yellow
Crystal habit	prismatic	prismatic	prismatic
Crystal size, mm^3	$0.2\times0.3\times0.4$	$0.1\times0.1\times0.4$	$0.2\times0.3\times0.4$
d_x (g/cm^3)	1.26	1.60	1.74
F(000)	256	832	896
T, K	298	298	298
Scan range, °	$1.207+0.5\tan\theta$	$1.260+0.5\tan\theta$	$1.575+0.5\tan\theta$
Scan speed (°/min)	8	8	8
2θ max,°	60	55	55
Reflections measured	$0\leqslant h\leqslant 9$	$0\leqslant h\leqslant 11$	$0\leqslant h\leqslant 17$
	$0\leqslant k\leqslant 14$	$0\leqslant k\leqslant 16$	$-18\leqslant k\leqslant 18$
	$-15\leqslant l\leqslant 15$	$-20\leqslant l\leqslant 20$	$-17\leqslant l\leqslant 17$
No. of reflections measured	2129	4144	8154
No. of reflections observed $[\|F_o\| > 3\sigma(\|F_o\|)]$	1389	2027	6197
No. of parameters refined	153	199	397
R	0.049	0.062	0.027
R_w	0.050	0.062	0.031
s	1.59	1.67	1.24
Largest diff. peak (e/Å^3)	0.26	0.88	0.35
Largest diff. hole (e/Å^3)	−0.21	−0.65	−0.56

$R = \Sigma\|\|F_o\|-|F_c\|\|/\Sigma|F_o|$.
$R_w = [\Sigma w\|\|F_o\|-|F_c\|^2/\Sigma w|F_o|^2]^{1/2}$, $w = [\sigma^2(F_o)+\{0.015(F_o)\}^2]^{-1}$.

Absorption corrections were made by the Gaussian numerical integration method[12] for Pd (acac) (bpr) and PdCl (mpr). The structures were solved by direct methods with the program SHELXS-86,[13] which gave the positions of all non-hydrogen atoms for Hnr and those of palladium atoms for Pd (acac) (bpr) and PdCl (mpr). The remaining non-hydrogen atoms of Pd (acac) (bpr) and PdCl (mpr) were located by the subsequent Fourier syntheses. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms of Pd (acac) (bpr) were not located, and those of Hnr and PdCl (mpr) were placed at calculated positions with isotropic thermal parameters of the bonded carbon atoms. The Fourier syntheses and the full-matrix least-squares refinement were carried out using the Xtal 3.2 software.[14]

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