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CYCLOMETALLATION OF *N,N*-DIMETHYL-2-BROMOTHIOBENZAMIDE AND SOME RELATED THIOAMIDES WITH PALLADIUM(0) AND PALLADIUM(II)

MATSUO NONOYAMA*

Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya, 464-01, Japan

KIYOHIKO NAKAJIMA

Department of Chemistry, Aichi University of Education, Igaya, Kariya, 448, Japan

and

MASAKAZU KITA

Naruto University of Education, Takashima, Naruto-cho, Naruto-shi, Tokushima, 772, Japan

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Abstract—*N,N*-Dimethyl-2-X-thiobenzamide [X=Cl (abbreviated as Hcbt) and Br (Hbbt)] and *N,N*-dimethyl-2-(2-bromophenyl) thioacetamide (Hbpt) were cyclopalladated at one of the N-methyl groups upon reaction with lithium tetrachloropalladate(II), while oxidative addition took place at the aryl–halogen bond of Hbbt, Hbpt and *N,N*-dimethyl-2-iodothiobenzamide (Hibt) upon reaction with bis(dibenzylideneacetone)palladium(0). The reaction products, and their tri-*n*-butylphosphine (PBu_3) and 4-tert-butylpyridine (tbp) derivatives, were characterized by IR and NMR spectroscopies. All the complexes were composed of a palladathiaheterocycle with sulphur coordination of a thioamide group. The structure of (*N,N*-dimethylthiobenzamido) (*N,N*-diethyldithiocarbamato)palladium(II) was determined by X-ray analysis. There is steric hindrance between one of the N—CH_3 groups and one benzene ring hydrogen atom. This should result in disfavoured benzene ring cyclopalladation of *N,N*-dimethylthiobenzamide (Hbt) with lithium tetrachloropalladate(II) and induce N—CH_3 cyclopalladation.

An *N,N*-dimethylthiocarbamoyl group is a good ancillary substituent promoting cyclopalladation of furan and thiophene rings with palladium(II) (for example, *N,N*-dimethyl-2 and 3-furan- and -thiophenecarbothioamides),[1,2] but the group bound to a benzene ring is cyclopalladated at its own N-methyl group, leaving the benzene ring intact.[3] The complex of *N,N*-dimethylthiobenzamide (Hbt) with a cyclopalladated benzene ring corresponding to the complexes of the furan and thiophene thioamides is thus not obtained using a similar method. It is intriguing to study cyclopalladated Hbt complexes in comparison with the corresponding heterocyclic complexes. We have hence prepared several *N,N*-dimethylthiocarbamoyl-substituted benzene derivatives (Table 1 and structures **I** and **II**, where abbreviations are shown) and investigated their reaction with lithium tetrachloropalladate(II) and bis(dibenzylideneacetone)palladium(0).

* Author to whom correspondence should be addressed.

Table 1. Yields, melting points, analytical results and IR spectra of the ligands and complexes

Compound[a]	M.p.[b] (°C)	Yield (%)	Analysis: Found, % (Calc., %) C	H	N	IR (cm^{-1})[c] ν(C—N)	ν(Pd—Cl)
Hcbt	109–110	30	53.8 (54.1)	5.0 (5.1)	6.9 (7.0)	1522	
Hbbt	127–129	13	44.1 (44.3)	4.3 (4.1)	5.5 (5.7)	1518	
Hbbs	89–91	25	37.3 (37.1)	3.5 (3.5)	4.5 (4.8)	1527	
Hibt	112–113	58	37.1 (37.1)	3.4 (3.5)	4.8 (4.8)	1517	
Hbpt	93–94	18	46.5 (46.5)	4.6 (4.7)	5.5 (5.4)	1528	
PdBr(bt)	196(dec)	70	30.9 (30.8)	2.9 (3.0)	3.5 (4.0)	1566	
PdI(bt)	223(dec)	87	27.7 (27.2)	2.5 (2.5)	3.5 (3.5)	1554	
$PdBr(bt)(PBu_3)$	132–134	9	45.4 (45.6)	6.5 (6.7)	2.6 (2.5)	1560	
PdBr(bt)(tbp)	205(dec)	23	44.4 (44.5)	4.7 (4.8)	5.8 (5.8)	1544	
Pd(bt)(edc)	171–172	31	40.2 (40.1)	4.7 (4.8)	6.7 (6.7)	1548	
$PdCl_2(Hbbt)$	235(dec)	84	25.4 (25.7)	2.4 (2.4)	3.1 (3.3)	1554	341,298
PdCl(cbt)	265(dec)	88	31.6 (31.7)	2.6 (2.7)	4.1 (4.1)	1613	268,230
PdCl(bbt)	260(dec)	94	27.8 (28.1)	2.4 (2.4)	3.6 (3.6)	1611	258,229
$PdCl(bbt)(PBu_3)$	147–149	50	42.9 (42.9)	6.0 (6.2)	2.5 (2.4)	1597	251
PdCl(bbt)(tbp)	263(dec)	35	41.6 (41.6)	4.3 (4.3)	5.4 (5.4)	1609	280
PdBr(pt)	128(dec)	91	32.8 (32.9)	3.2 (3.3)	3.8 (3.8)	1563	
PdCl(bpt)	225(dec)	90	30.1 (30.1)	2.8 (2.8)	3.5 (3.5)	1598	258,230
$PdCl(bpt)(PBu_3)$	144–145	74	43.9 (43.9)	6.2 (6.4)	2.4 (2.3)	1579	257

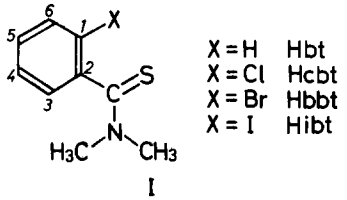
[a] Abbreviations are as follows: Hcbt = *N*,*N*-dimethyl-2-chlorothiobenzamide; Hbbt = *N*,*N*-dimethyl-2-bromothiobenzamide; Hbbs = *N*,*N*-dimethyl-2-bromoselenobenzamide; Hibt = *N*,*N*-dimethyl-2-iodothiobenzamide; Hbpt = *N*,*N*-dimethyl-2-(2-bromophenyl)thioacetamide; PBu_3 = tri-*n*-butylphosphine; tbp = 4-tert-butylpyridine; edc = *N*,*N*-diethyldithiocarbamate ion.

[b] dec = decomposition.

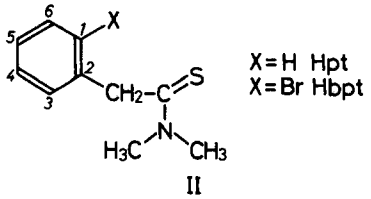
[c] Measured in Nujol mull.

RESULTS AND DISCUSSION

The substituted thiobenzamides and phenylthioacetamides were all prepared from appropriate aldehydes and ketones by the literature method,[4] except Hibt, which was obtained by thiation of the parent carboxamide with Lawesson's Reagent.[5] The thioamides were characterized by elemental analysis, and IR and NMR spectra (Tables 1–3; numbering of the benzene ring is shown in structures **I** and **II**). The characteristic IR band of ν(C—N) of a thioamide group is observed at *ca* 1520 cm^{-1}. In the ^1H NMR spectra there are two N-methyl signals between 3.0 and 3.7 ppm and in the $^{13}C\{^1H\}$ spectra the two N-methyl signals are in the range 42–46 ppm and the C=S signal in the range 196–201 ppm. The chemical shifts of C(1) normally depend upon X (**I**; X=H, Cl, Br and I) and X also has some effect on the other carbon resonances [e.g. C(2) and C=S]. This point was not investigated further. The selenoamide, Hbbs, obtained by selenation of the parent amide with dichlorophenylphosphine selenide,[6] has similar spectral features to those of Hbbt and the ^{13}C signal of the C=Se group shows $^1J(^{77}Se-^{13}C) = 209.3$ Hz.



I



II

The reaction of lithium tetrachloropalladate(II) with Hbt in refluxing methanol has been reported to result in cyclopalladation of the N—CH_3 group and PdCl(bt) without a palladium–benzene ring bond is obtained.[3] We performed accordingly the oxidative addition reaction of bis(dibenzylideneacetone)palladium(0) with Hbbt and obtained the expected complex PdBr(bt) with a pal-

Table 2. ^{1}H NMR chemical shifts of the ligands and complexes (δ ppm against tetramethylsilane)[a]

Compound	Solvent[b]	N—CH_3	N—CH_2	C—CH_2	Others
Hbt[c]	$CDCl_3$	3.05, 3.50			7.26
Hcbt	$CDCl_3$	3.07, 3.56			7.27m
Hbbt	$CDCl_3$	3.10, 3.59			7.1–7.6m
Hbbs	$CDCl_3$	3.03, 3.68			7.1–7.6m
Hibt	$CDCl_3$	3.08, 3.58			6.8–7.5m
Hpt[c]	$CDCl_3$	3.18, 3.48		4.30	7.30m
Hbpt	$CDCl_3$	3.18, 3.53		4.32	7.0–7.6m
PdBr(bt)	DMSO-d_6	3.56, 3.73			7.08m, 7.35m, 8.08br
PdI(bt)	DMSO-d_6	3.58, 3.75			7.08m, 7.37m, 8.20m
PdBr(bt)(PBu_3)	$CDCl_3$	3.58, 3.69			6.8–7.4m
PdBr(bt)(tbp)	$CDCl_3$	3.55, 3.72			8.58br, 6.51br, 6.8–7.3m
Pd(bt)(edc)	$CDCl_3$	3.64br			6.8–7.5m
PdCl(cbt)	DMSO-d_6	3.09	4.49		7.4–7.7m
PdCl(bbt)	DMSO-d_6	3.07	4.48		7.4–7.9m
PdCl(bbt)(PBu_3)	$CDCl_3$	3.06	4.25dd (12.9) [2.9] 4.05dd (12.9) [4.0]		7.2–7.7m
PdCl(bbt)(tbp)	$CDCl_3$	3.02	4.75d (13.0) 4.58d (13.0)		7.3–7.7m
PdBr(pt)	DMSO-d_6	3.47, 3.65		4.36	7.50dd (5.6, 3.2), 6.8–7.2m
PdCl(bpt)	DMSO-d_6	3.40	4.34	4.09	7.68dt (6.8, 1.3), 7.2–7.6m
PdCl(bpt)(PBu_3)	$CDCl_3$	3.20	4.04[d]	4.04[d]	7.55dt (7.5, 1.1), 7.0–7.4m

[a] Signals are singlets unless otherwise noted. Figures in parentheses are J(H–H) and those in square brackets J(P–H) in Hz. m = multiplet, d = doublet, t = triplet and br = broad.

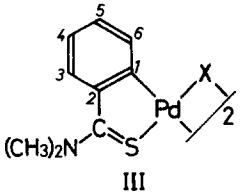
[b] DMSO-d_6 = dimethyl sulphoxide-d_6.

[c] Hbt = *N*,*N*-dimethylthiobenzamide and Hpt = *N*,*N*-dimethyl-2-phenylthioacetamide.

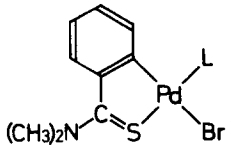
[d] An overlapped signal (with a shoulder at a lower field).

ladium–benzene ring bond (Table 1). Hibt reacted similarly to give PdI(bt), but the reaction with Hcbt did not proceed smoothly in similar conditions and was not studied further. Similarly to Hbbt, the homologous Hbpt reacted with palladium(0) giving PdBr(pt) with a low decomposition temperature (Table 1). The N-methyl group of these thioamides was cyclopalladated with lithium tetrachloropalladate in refluxing methanol as reported for the above mentioned Hbt[3] (Table 1), except Hibt, which gave an intractable black precipitate. For the selenoamide, Hbbs, no definite complex has so far been obtained from the reaction either with the palladium(0) or palladium(II) species used above. At room temperature no cyclopalladation occurred with lithium tetrachloropalladate: e.g. Hbbt yielded $PdCl_2$(Hbbt).

In the ^{1}H NMR spectra of PdX(bt) (X = Br, I; Table 2), the two N-methyl signals shift to a lower field with retention of their intensities, suggesting that the N-methyl groups are not palladated, and one aromatic proton signal is observed at a much lower field compared with the signal region of free ligands. The weak $^{13}C\{^1H\}$ signal of C(1) of PdBr(bt) is deshielded compared with that of free Hbt, suggesting that C(1) is bonded to an element with a deshielding effect.[7] The IR spectra show a higher frequency shift of ν(C—N) bands, suggesting sulphur coordination of a thioamide group.[8]



III



IV trans-(C, Br)

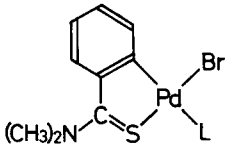
Table 3. $^{13}C\{^1H\}$ NMR chemical shifts of the ligands and complexes (δ ppm against tetramethylsilane)[a]

Compound	N—CH_3	N—CH_2	C—CH_2	C(1)	C(2)	C=S	Others
Hbt	42.5, 43.4			127.4	142.6	199.8	127.6, 124.9
Hcbt	42.1, 42.6			127.7	141.6	196.1	129.1, 129.0, 127.3, 126.9
Hbbt	42.2, 42.9			117.3	143.8	197.5	132.5, 129.1, 127.6, 127.2
Hbbs	43.8, 46.1			115.9	146.0	201.2[b]	132.2, 129.1, 127.3, 126.4
Hibt	42.3, 43.1			92.1	147.8	200.1	139.0, 128.9, 128.4, 126.2
Hpt	42.2, 44.7		50.8	127.9[c]	135.5	200.3	128.6,[c] 126.7
Hbpt	42.2, 44.6		50.3	124.2	135.6	199.7	132.6, 129.3, 128.4, 127.7
PdBr(bt)	45.0, 46.9			154.3	146.1	197.3	137.7, 130.8, 127.1, 123.2
PdI(bt)	44.9, 46.8			[d]	[d]	197.4	[d] 131.0, 127.1, 123.0
PdBr(bt)(PBu_3)	44.8, 46.4			160.1	149.8	202.3	137.9, 130.0, 126.3, 122.2
				(3.8)	(0.7)	(2.4)	(12.4) (5.5)
PdBr(bt)(tbp)[e]	45.2, 47.2			157.9	146.8	203.1	142.5, 131.4, 126.6, 122.6
				154.6	146.0	201.6	135.4, 130.9, 122.4
Pd(bt)(edc)	45.5, 47.0			161.2	146.0	204.9	137.1, 130.9, 126.7, 122.1
PdCl(cbt)	43.8	62.3		128.8	134.0	188.6	132.2, 129.6, 128.8, 127.8
PdCl(bbt)	43.9	62.4		118.4	136.2	190.0	132.8, 132.3, 128.7, 128.3
PdCl(bbt)(PBu_3)	44.7	55.2		118.8	138.2	192.4	132.8, 131.2, 128.6, 127.8
		(4.2)			(2.1)	(2.1)	
PdCl(bbt)(tbp)	43.6	54.9		119.2	137.1	190.8	133.0, 131.6, 128.5, 127.8
PdCl(bpt)	43.1	62.1	42.9	124.6	134.0	193.0	132.3, 132.0, 129.5, 127.7
PdCl(bpt)(PBu_3)	43.9	55.9	44.3	124.4	133.6	194.1	132.6, 130.1, 129.0, 127.8
		(4.5)	(3.1)			(2.4)	

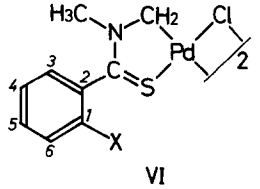
[a] Solvents are the same as those for ^1H NMR. Figures in parentheses are $J(^{31}P-^{13}C)$ in Hz.
[b] $J(^{13}C-^{77}Se) = 209.3$ Hz.
[c] The assignment may be reversed.
[d] Could not be detected because of the low solubility.
[e] Two isomers are present in a $CDCl_3$ solution.

These facts suggest that PdX(bt) has structure **III** (X = Br, I). The deshielded aromatic ^1H signals at 8.08 (X = Br) and 8.20 ppm (I) are assigned to H(6) near to X because X has a deshielding effect on a proton close to it.[7] One of the origins of the downfield shifts of the N-methyl signals [from 3.05 and 3.50 ppm of free Hbt to 3.56 and 3.73 ppm of PdBr(bt)] should result from the fact that the benzene ring of free Hbt is perpendicular rather than co-planar to the thioamide plane[9] and one N-methyl group hence lies in the shielding region of the benzene ring, but upon complex formation the amide plane is forced to be in the coordination plane to form a chelate ring and the shielding effect of the benzene ring is no longer effective.

The more soluble complex PdBr(bt)(PBu_3) also shows the N-methyl signals in a similar region but there is no lower field aromatic proton signal. The small value (3.8 Hz) of $J(^{13}C-^{31}P)$ of C(1) suggests that PBu_3 is coordinated *cis* to C(1) and structure **IV** is proposed for the complex (L = PBu_3), where H(6) is far away from bromine and the chemical shift is not affected by the deshielding effect of the bromine atom. The NMR spectrum of PdBr(bt)(tbp) in $CDCl_3$ is complicated (there appears to be about twice the number of ^{13}C peaks compared to the number of carbon atoms of the complex), suggesting the presence of isomers [*trans*-



V cis-(C, Br)

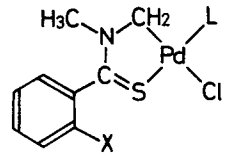


VI

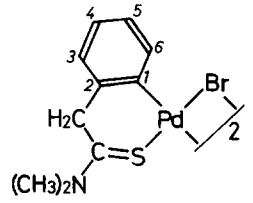
(C, Br) (**IV**) and *cis*-(C, Br) (**V**)]. The two isomers exist in nearly equal abundance based on the ^{1}H NMR spectral intensities; e.g. the t-butyl signals of tbp at 1.30 and 1.34 ppm are nearly equal in intensity. The ^{1}H NMR spectrum shows two unique signals at 6.51 and 8.58 ppm. The shielded signal is assigned to H(6) of the *trans* isomer because the proton lies in the shielding region of the pyridine ring of tbp, while the deshielded signal is assigned to H(6) of the *cis* one because the proton lies in proximity to the bromine atom with a deshielding effect on the nearby proton.[7] No assignment of the individual ^{13}C signals to the isomers is possible so far.

In comparison of the isomerism with that found for similar complexes of *N*,*N*-dimethyl-2-thiophenecarbothioamide (Hatt),[1] the cyclopalladated bt ligand is shown to prefer a *trans*-(C,X) arrangement to a greater extent than the cyclopalladated att ligand. To elucidate the origin, an X-ray structural analysis was desired for the bt complexes, but no suitable crystals have so far been obtained. Suitable crystals for X-ray analysis were instead obtained for Pd(bt)(edc) (see below). The two ethyl groups of edc of Pd(bt)(edc) are not equivalent, as expected; ^{13}C signals are at 12.4, 12.5 (CH_3); 44.6, 44.8 (CH_2); 209.6 ppm (C=S). Other signals are similar to the PBu_3 and tbp derivatives (Table 3). In the IR spectrum, two strong bands at 347 and 372 cm^{-1} may be due to Pd—S (edc) bonds, the two bands being absent in the IR spectra of the above complexes.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of PdCl(cbt) and PdCl(bbt) are very different from those discussed above. The single N-methyl ^{1}H signal (intensity 3H) is in a similar region to the higher field one of the N-methyl groups of free Hbbt or Hcbt and a new signal (intensity 2H) appears at a much lower field (at 4.48 ppm). In agreement with the ^{1}H NMR spectrum, the ^{13}C peak at 43.9 ppm is assigned to N—CH_3 and that at 62.4 ppm to Pd—CH_2—N. The chemical shift of C(1) is close to that of free Hbbt or Hcbt, indicating no interaction of the benzene ring with palladium. In the IR spectrum, two bands are observed at 258 and 229 cm^{-1}, assignable to ν(Pd—Cl), and sulphur coordination of the thioamide group is supported by the higher frequency shift of the ν(C—N) band[8] (Table 1). Structure **VI** (X = Cl, Br) is proposed for PdCl(bbt) and PdCl(cbt). The shielding of the N-methyl ^{1}H signal mentioned above is due to the fact that in **VI** the N-methyl group is in the shielding region of the benzene ring of bbt, the ring being assumed to be nearly perpendicular to the thioamide group, as in free Hbbt,[9] and a similar conformation of a phenyl group having been found by X-ray analysis in Pd(bt)(acac) (acac = acetylacetonato; **VII**: X = H and Cl, L = acac).[10]



VII



VIII

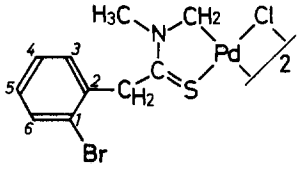
The ^{1}H NMR spectra of PdCl(bbt)(PBu_3) and PdCl(bbt)(tbp) show that the two protons of Pd—CH_2—N are not equivalent. This indicates that the rotation of the bromophenyl group is inhibited: the bromo substituent is fixed above or below the plane of coordination on the NMR time scale to allow no plane of symmetry. The small J(^{1}H–^{31}P) and J(^{13}C–^{31}P) values suggest structure **VII** for this complex: a similar structure (**VII**, X = H; L = PEt_3) has been reported previously for PdCl(bt)(PEt_3).[3] The assignment of the CH_3 and CH_2 signals is confirmed in the NMR spectrum of PdCl(bbt)(tbp): in the ^{13}C spectrum without ^{1}H decoupling, the signal at 43.6 ppm is a quartet [J(C–H) = 140.9 Hz, CH_3] and that at 54.9 ppm a triplet [J(C–H) = 147.5 Hz, CH_2]. The low frequency ν(Pd—Cl) band at 280 cm^{-1} suggests the *trans* Cl—Pd—CH_2 arrangement: the strong *trans* influence of the carbon donor weakens the Pd—Cl bond.

Exchange of cyclometallated ligands in palladium(II) complexes has been reported to proceed in organic solvents in the presence of an acid to give a thermodynamically stable product:[11] a metal centre formally migrates from one ligand to another or, alternatively, there is substitution of a leaving cyclometallated ligand by an incoming one. To find the thermodynamical stability of the aryl-palladated [PdBr(bt)] (**III**; X = Br), the complex was subjected to a similar reaction. When the complex, dissolved in DMSO-d_6, was heated at 100°C for 8 h, the solution became dark and the ^{1}H NMR signals of the starting material completely disappeared. The resulting ^{1}H NMR spectrum showed main peaks at 3.21(s), 4.5 (s) and 7.56(m) ppm, accompanied by many weak signals. The main peaks are close in chemical shift to the ^{1}H NMR

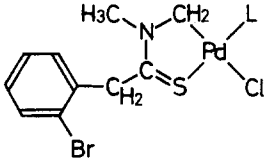
signals of the N—CH_3 palladated [PdCl(bt)] in DMSO-d_6 [3.20(s), 4.48(s) and 7.55(m) ppm] and the main product should be the N—CH_3 palladated [PdBr(bt)] (cf. **VI**; X = H). The reaction proceeds mainly via metallation-site exchange (from aryl to N—CH_3) but not cleanly, as shown by the appearance of many additional ^{1}H NMR peaks. The preliminary result shows that the N—CH_3 palladated complex should be thermodynamically favourable.

The DMSO-d_6 solution of PdBr(pt), derived formally from *N,N*-dimethyl-2-phenylthioacetamide (Hpt), was not stable at room temperature and decomposed within 2 h. In the ^{1}H NMR spectrum measured immediately after dissolution (several minutes after dissolution), peaks of decomposition products began to appear and no ^{13}C NMR spectrum was available. In the ^{1}H NMR spectrum (Table 2) the two N-methyl signals retain a 3H intensity and a separate aromatic proton signal is observed at 7.50 ppm, which may be due to H(6) *ortho* to a Pd—C bond.[7] The IR spectrum suggests sulphur coordination of the thioamide group.[8] Structure **VIII** is proposed or PdBr(pt), where the C—Br bond of Hbpt adds oxidatively to palladium(0) in the same way as Hbbt. The resulting six-membered chelate ring should be less stable than a similar five-membered one and PdBr(pt) may decompose easily. This complex has not been studied further.

The spectroscopic properties of PdCl(bpt) and PdCl(bpt)(PBu_3) (Tables 1–3) are similar to those of the above complexes of bbt except that in the bpt complexes the two protons of N—CH_2—Pd are equivalent because there is no barrier to motion of the bromophenyl group: a flexible CH_2 group is present between thioamide and bromophenyl



IX



X

groups. Structures **IX** and **X** respectively are proposed for the two complexes.

The X-ray analysis of Pd(bt) (edc) showed that the asymmetric unit contained two independent molecules with similar geometry (Table 4) and in the following, one of the two is discussed (Fig. 1). The distorted square planar structure is consistent with the above spectroscopic results. The two Pd—S(edc) bond lengths clearly reflect the *trans* influences of the two different donor atoms of bt: Pd—S(12) *trans* to C(1) is 2.406(3) Å, while Pd—S(11) *trans* to S(13) is 2.311(3) Å.

In free Hbt, the dihedral angle between the thioamide group and the benzene ring is reported to be 63°, avoiding steric repulsion among the *ortho* ring-hydrogens and the nearly planar thioamide group.[12] A dihedral angle of 69.1(2)° (mean) has been found in $Cd(Hbt)_4(ClO_4)_2 \cdot H_2O$, where Hbt is coordinated only through the sulphur atom.[13] Upon chelation of Hbt to a palladium atom through the sulphur and *ortho*-carbon atoms, the thioamide group is forced to lie in a coordination plane; if there is no steric hindrance, the above dihedral angle would be zero. In the complex Pd(bt)(edc), there are significant distortions: the angle between the benzene ring and the N(11)—C(7)—S(13) plane is 22.1(4)° and the dimethyl amino group is turned by 18.6(8)° around the C(7)—N(11) axis, relieving approach of the H[C(5)] atom and the C(9)H_3 methyl group. The interfering groups are, however, not sufficiently separated even by the distortion, the C(9)–H[C(5)] distance being *ca* 2.5 Å, shorter than the sum of van der Waals radii [CH_3 (2.0 Å) and H (1.2 Å)].

The disfavoured cyclopalladation of the benzene ring of Hbt compared with the N—CH_3 group should be partially based on these facts. The cyclopalladation of N—CH_3 causes no significant steric constraint and the dimethylthioamide group retains the original planar geometry, as has been shown by the X-ray structure of Pd(bt)(acac).[10] The above-mentioned thermal isomerization of the benzene ring palladated complex to the N—CH_3 palladated one should support the discussion. The preferred ring cyclopalladation of *N,N*-dimethylthioamides of five-membered furan and thiophene[1,2] is explained in terms of the fact that the angle corresponding to C(5)—C(6)—C(7) is widened in the five-membered derivatives, resulting in relaxation of the above steric restriction.

EXPERIMENTAL

Measurements

Measurements were carried out by the methods reported previously.[1,2]

Table 4. Selected bond lengths (Å) and angles (°) of Pd(bt)(edc)

Molecule A		Molecule B	
Pd(1)—S(11)	2.311(3)	Pd(2)—S(21)	2.317(3)
Pd(1)—S(12)	2.406(3)	Pd(2)—S(22)	2.395(4)
Pd(1)—S(13)	2.294(3)	Pd(2)—S(23)	2.286(3)
Pd(1)—C(1)	2.00(1)	Pd(2)—C(21)	2.01(1)
S(11)—C(10)	1.71(1)	S(21)—C(30)	1.71(1)
S(12)—C(10)	1.72(1)	S(22)—C(30)	1.74(1)
S(13)—C(7)	1.72(1)	S(23)—C(27)	1.71(1)
N(11)—C(7)	1.32(1)	N(21)—C(27)	1.33(1)
N(12)—C(10)	1.34(1)	N(22)—C(30)	1.31(1)
C(6)—C(7)	1.48(2)	C(26)—C(27)	1.48(2)
S(11)—Pd(1)—S(12)	74.5(1)	S(21)—Pd(2)—S(22)	74.9(1)
S(11)—Pd(1)—S(13)	176.9(1)	S(21)—Pd(2)—S(23)	175.6(1)
S(11)—Pd(1)—C(1)	97.8(3)	S(21)—Pd(2)—C(21)	99.0(3)
S(12)—Pd(1)—S(13)	102.5(1)	S(22)—Pd(2)—S(23)	100.8(1)
S(12)—Pd(1)—C(1)	172.1(3)	S(22)—Pd(2)—C(21)	172.6(3)
S(13)—Pd(1)—C(1)	85.3(3)	S(23)—Pd(2)—C(21)	85.3(3)
C(5)—C(6)—C(7)	122.0(9)	C(25)—C(26)—C(27)	124(1)

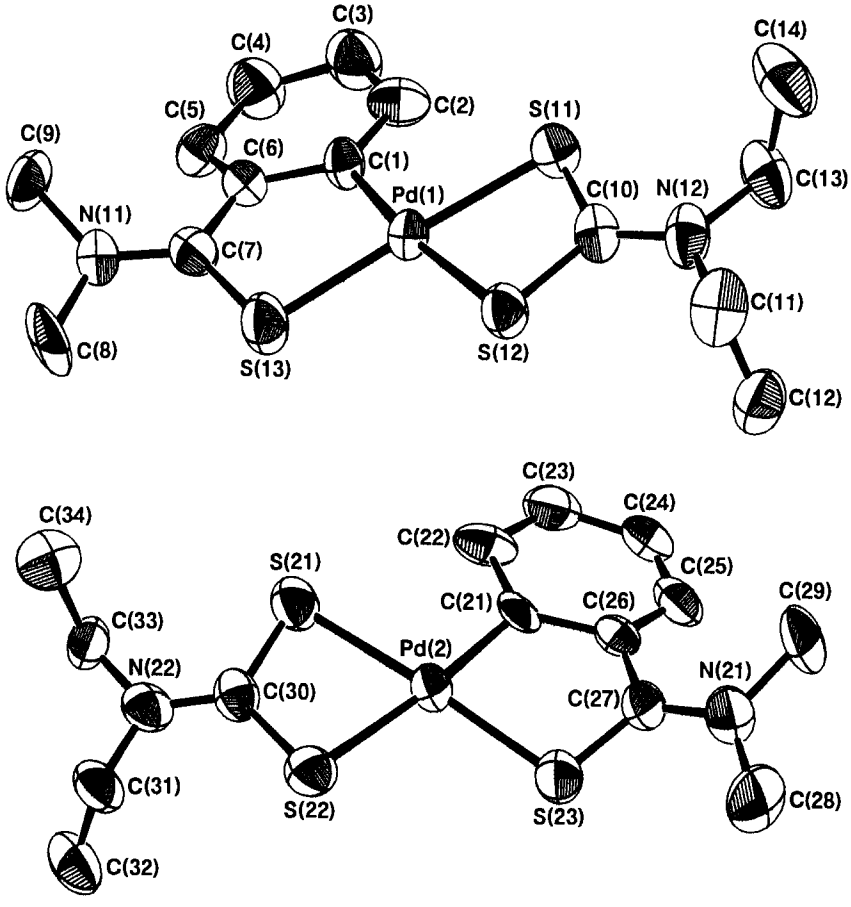


Fig. 1. ORTEP drawing and atomic numbering scheme of two independent molecules (A and B) of Pd(bt)(edc).

Preparation of the ligands

Yields, melting points and analytical results of new compounds are given in Table 1. Faintly yellow Hbt, Hcbt, Hbbt, Hpt and Hbpt were prepared from appropriate aldehydes or ketones by the literature method.[4] Yellow Hbbs was prepared by selenation of the corresponding carboxamide with phenyldichlorophosphine selenide[6] and faintly yellow Hibt by thiation of the corresponding carboxamide with Lawesson's reagent.[5] IR spectra (Nujol mull): ν(C—N) of the thioamide group of Hbt is at 1528 cm^{-1}, that of Hpt at 1523 cm^{-1} and those of the others are given in Table 1.

Preparation of the complexes

PdBr(bt). A mixture of 1 mmol of Hbbt and 1 mmol of bis(dibenzylideneacetone)palladium(II) in 30 cm^3 of toluene was stirred for 1 day at room temperature. A brown precipitate was collected, washed with toluene and dried in air. PbBr(pt) and PdI(bt) were similarly prepared from Hbpt and Hibt, respectively, by stirring for 3 and 1 h.

PdCl(bbt). A methanol solution (30 cm^3) of lithium tetrachloropalladate, prepared *in situ* from 1 mmol of palladium(II) and 2 mmol of lithium chloride, was mixed with 1 mmol of Hbbt and the mixture was refluxed with stirring for 1 day. After cooling, a grey–brown precipitate was filtered, washed with methanol and dried in air. PdCl(cbt) and PdCl(bpt) were obtained in a similar manner from Hcbt and Hbpt, respectively. When the above reaction was carried out at room temperature $PdCl_2$ (Hbbt) was the product.

PBu_3 *and* tbp *derivatives*. To a suspension of 1 mmol of the complex prepared above in 30 cm^3 of dichloromethane was added 1 mmol of PBu_3 or 2 mmol of tbp and the mixture stirred until it became clear. To the filtered solution was added 30 cm^3 of n-hexane and the resulting mixture concentrated to a small volume to give a white or yellow precipitate, which was collected, washed with n-hexane and dried in air.

Pd(bt)(edc). A mixture of 1 mmol of PdBr(bt) and 1 mmol of sodium *N*,*N*-diethyldithiocarbamate in 30 cm^3 of acetone was stirred for 3 h on a hot plate. The solution was evaporated to dryness under reduced pressure and the residue was extracted a few times with dichloromethane. The combined extracts were filtered, mixed with n-hexane and concentrated to a small volume to precipitate a yellow powder, which was collected, washed with n-hexane and dried in air. The powder was recrystallized from dichloromethane–n-hexane.

X-ray analysis of Pd(bt)(edc)

Slow evaporation at room temperature of a toluene–hexane solution of Pd(bt)(edc) gave a crystal

Table 5. Crystallographic data for Pd(bt)(edc)

Complex	Pd(bt)(edc)
Formula	$C_{14}H_{20}N_2PdS_3$
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	17.533 (4)
b (Å)	8.550 (4)
c (Å)	23.036 (4)
β (°)	95.76 (2)
Z	8
V (Å^3)	3436(2)
μ(Mo-K_α) (cm^{-1})	14.09
Crystal colour	Colourless
Crystal habit	Prismatic
Crystal size (mm^3)	$0.2 \times 0.4 \times 0.3$
Scan type	θ–2θ
$2\theta_{max}$ (°)	50
Reflections measured	$\pm h, +k, +l$
No. of reflections measured	6725
No. of reflections observed [$\|F_o\| > 6\sigma(\|F_o\|)$]	2497
R	0.0457
R_w	0.0512
Weighting scheme	$w = [\sigma^2_{count} + (0.020\|F_o\|)^2]^{-1}$
GOF	1.55

suitable for X-ray analysis. Diffraction data were collected on a Rigaku AFC-5R diffractometer with graphite monochromatized Mo-K_α radiation (λ = 0.71073 Å). Crystallographic data are given in Table 5. Unit cell parameters and the orientation matrix were determined from 25 reflections in the range $20° < 2\theta < 25°$. No significant variation in intensities was observed for three standard reflections during data collection. Data were corrected for Lorentz and polarization effects, and empirical absorption corrections were applied on the basis of the average relative intensity curve of azimuthal scan data for three reflections ($75° < \chi < 90°$). The calculations were carried out on a HITAC M-680H computer at the Computer Center of the Institute for Molecular Science using the Universal Crystallographic System UNICS III.[14] The locations of the metals were determined by a direct method using MULTAN-78[15] and the other non-hydrogen atoms were found by the usual Fourier methods. The hydrogen atoms were generated in calculated positions. All non-hydrogen atoms were anisotropically refined. Supplementary material (complete lists of bond lengths and angles, atomic parameters, anisotropic thermal parameters for non-hydrogen atoms, and F_0 and F_c tables) is available from the authors on request.

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