Cyclometallation of *N,N*-dimethylbenzo[*b*]furan-2-carbothio (and seleno) amides with palladium(II), ruthenium(II) and rhodium(III)

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Abstract

N,N-Dimethylbenzo[*b*]furan-2-carbothio (and seleno) amides (abbreviated as Hzft and Hzfs) were prepared from the corresponding carboxamide upon reaction with Lawesson's reagent and phenyldichlorophosphine selenide, respectively. Both Hzft and Hzfs were cyclopalladated with lithium tetrachloropalladate(II) and cyclorhodated with hexachlorotetrakis(tri-n-butylphosphine)dirhodium(III), while cycloruthenation with tetrachlorohexacarbonyldiruthenium(II) occurred only with Hzft These cyclometallated products were spectroscopically characterized. The benzofuran ring was metallated at position 3 and the amide groups were coordinated through the sulfur or selenium atom to form a five-membered metallathia (or selena) heterocycle The corresponding benzo[*b*]thiophene (thianaphthene) analogues were not cyclometallated under similar conditions The structures of Hzfs, [PdCl(zfs)(PBu_3)], and [RuCl(zft)$(CO)_2$(PBu_3)] were determined by X-ray analysis

Key words: Crystal structures; Palladium complexes, Rhodium complexes, Ruthenium complexes, Cyclometallated complexes

Introduction

N,N-Dimethylthio- and -selenocarbamoyl groups are revealed to be good auxiliary substituents for promoting cyclometallation of furan and thiophene rings with Pd(II), Ru(II) and Rh(III) [1, 2]. The *N,N*-dimethylthiocarbamoyl substituent bonded to a benzene ring is, however, reported to be unable to promote cyclometallation of the benzene ring but the N-methyl group is, instead, cyclometallated with Pd(II) [3]. The interesting difference in cyclometallation reactivity between the benzene and the five-membered heterocycles should be based on the fact that furan and thiophene are generally more reactive than benzene [4]. Reduction in reactivity of these five-membered heterocycles is expected to disfavor ring metallation. We are interested in this aspect and have investigated cyclometallation of the thio- and selenoamides of benzologues of furan and thiophene (Fig. 1); reactivities of the benzologues are, in general, significantly reduced compared with those of the parents [4]. *N,N*-Dimethylbenzo[*b*]furan-2-carbothio (and seleno) amides (abbreviated as Hzft and Hzfs, respectively) are cyclometallated at the furan ring but *N,N*-dimethylbenzo[*b*]thiophene(thianaphthene)-2-carbothio (and seleno) amide (Htnt and Htns) are cyclometallated at neither the ring nor the N-methyl group under similar conditions

Results and discussion

N,N-Dimethylbenzo[*b*]furan-2-carboxamide (Hzfo) was obtained by the one-pot reaction of salicylaldehyde with *N,N*-dimethyl-2-chloroacetamide in the presence of potassium carbonate in refluxing dimethylformamide. Hzfo reacted with Lawesson's reagent [5] in hexamethylphosphorictriamide and phenyldichlorophosphine selenide [6] in xylene and 100 °C for several hours to give Hzft and Hzfs, respectively, (Table 1), which were spectroscopically characterized. Hzfs has further been confirmed by X-ray analysis (see below). In the IR spectra (Nujol mull), ν(C–N) of a thio (or seleno) amide group [7] was observed at 1516 (Hzft)

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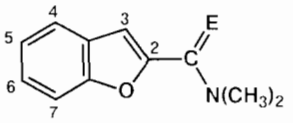
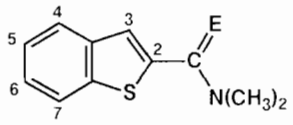
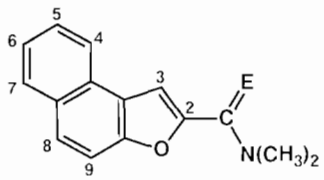


E =	O	S	Se
Abbre	Hzfo	Hzft	Hzfs



E =	O	S	Se
Abbre	Htno	Htnt	Htns



E =	O	S	Se
Abbre	Hnfo	Hnft	Hnfs

Fig 1 Amides and their abbreviations

and 1520 (Hzfs) cm^{-1} and in the $^{13}C\{^1H\}$ NMR spectra (in $CDCl_3$), δ (^{13}C) of the group at 185.4 (Hzft) and 188.7 (Hzfs) ppm ($J(^{13}C-^{77}Se) = 208$ Hz) [8]. *N,N*-Dimethylbenzo[*b*]thiophene-2-carboxamide (Htno) was obtained from 2-nitrobenzaldehyde and methyl mercaptoacetate via benzo[*b*]thiophene-2-carboxylic acid. Htno was thiated and selenated as previously described to give *N,N*-dimethylbenzo[*b*]thiophene-2-carbothio (and seleno) amides (Htnt and Htns), respectively.

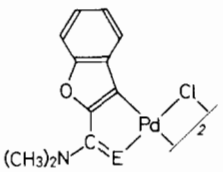
The benzo[*b*]furan derivatives (collectively abbreviated as Hbf), Hzft and Hzfs, reacted with lithium tetrachloropalladate in methanol at room temperature for 1 day to give PdCl(bf) (Table 2). The scarcely soluble complexes were converted to the soluble adducts with tri-n-butylphosphine (PBu_3) and 4-tert-butylpyridine(tbp), [PdCl(bf)L] (L = PBu_3 and tbp) (Table 2).

The ^1H NMR spectra of PdCl(zft) and PdCl(zfs) in dimethylsulfoxide-d_6 (dmso-d_6) (a dmso-d_6 complex may form) showed that the integration of the aromatic proton resonances is reduced by one proton unit but that the integration of the N-methyl signals is retained. In the ^{13}C spectra, the 3-C signals significantly shift to lower field. These facts indicate ring cyclometallation. Structure I (E = S, Se) is proposed for the two; the higher frequency shift of ν(C–N) of the amide groups (Tables 3 and 4) supports the S and Se coordination of the amide groups [7] and the presence of the ν(Pd–Cl) bands coordination of Cl

TABLE 1 Yields, melting points, and analytical results for the amides[a]

Compound	Yield (%)	m.p. (°C)	Anal. Found (calc.) (%)		
			C	H	N
Hzfo	63	78–79	69.79	5.95	7.48
			(69.83)	(5.86)	(7.40)
Hzft	75	91–92	64.09	5.39	6.75
			(64.36)	(5.40)	(6.75)
Hzfs	59	77–78	52.51	4.55	5.62
			(52.39)	(4.40)	(5.55)
Hnfo	77	156–158	75.29	5.35	5.90
			(75.35)	(5.48)	(5.85)
Hnft	82	185–186	70.61	5.06	5.63
			(70.56)	(5.13)	(5.49)
Hnfs	84	171–172	59.95	4.37	4.47
			(59.61)	(4.33)	(4.64)
Htno	76	103–104	64.32	5.44	6.75
			(64.36)	(5.40)	(6.82)
Htnt	93	132–133	59.79	5.00	6.26
			(59.69)	(5.01)	(6.33)
Htns	54	128–129	49.31	4.21	5.27
			(49.26)	(4.13)	(5.22)

[a]Abbreviations: Hzfo = *N,N*-dimethylbenzofuran-2-carboxamide, Hzft = *N,N*-dimethylbenzofuran-2-carbothioamide; Hzfs = *N,N*-dimethylbenzofuran-2-carboselenoamide, Hnfo = *N,N*-dimethylnaphthofuran-2-carboxamide, Hnft = *N,N*-dimethylnaphthofuran-2-carbothioamide, Hnfs = *N,N*-dimethylnaphthofuran-2-carboselenoamide, Htno = *N,N*-dimethylthianaphthene-2-carboxamide, Htnt = *N,N*-dimethylthianaphthene-2-carbothioamide, Htns = *N,N*-dimethylthianaphthene-2-carboselenoamide



I PdCl(C–E)

The benzo[*b*]thiophene derivatives (Hbt), Htnt and Htns, gave $PdCl_2$(Hbt) upon reaction with lithium tetrachloropalladate under similar conditions (Table 2). The composition reveals that the amide ligands are neutral, that is, no replacement of a hydrogen atom of Hbt with a palladium atom takes place. The ^1H NMR spectra of $PdCl_2$(Hbt) (Table 4) support the situation; the 3-H signal remains and the N–CH_3 signals change in chemical shifts without loss of integration intensity suggesting S or Se coordination of the amide groups. In the IR spectra of the complexes the ν(C–N) bands shifted to higher frequencies also indicating S and Se coordination [7] while the appearance of ν(Pd–Cl) bands suggests Cl coordination. The reaction in refluxing methanol precipitated no complex with a definite composition; if cyclopalladation took place, PdCl(bt) would be obtained. The benzo[*b*]thiophene

TABLE 2 Yields, melting points, and analytical results for the complexes[a]

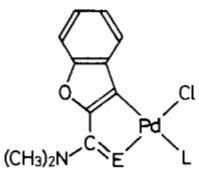
Complex	Yield (%)	m.p. (°C)	Anal. (%) Found (calc.)		
			C	H	N
PdCl(zft)	95	265 (dec.)	38.64 (38.17)	2.71 (2.91)	4.02 (4.05)
PdI(zft)	92	268 (dec.)	30.17 (30.19)	2.20 (2.30)	3.06 (3.20)
PdCl(zft)(PBu_3)	71	133–136	50.12 (50.37)	6.61 (6.80)	2.49 (2.55)
PdCl(zft)(tbp)	79	265 (dec.)	49.91 (49.91)	4.74 (4.82)	5.79 (5.82)
Pd(zft)(acac)	68	217 (dec.)	46.81 (46.90)	4.13 (4.18)	3.37 (3.42)
$RhCl_2$(zft)(PBu_3)$_2$	54	209–213	53.65 (53.71)	8.21 (8.24)	1.80 (1.79)
RuCl(zft)(CO)$_2$	81	250 (dec.)	39.58 (39.35)	2.61 (2.54)	3.37 (3.53)
RuCl(zft)(CO)$_2$(PBu_3)	80	183–185	49.91 (50.12)	6.26 (6.22)	2.27 (2.34)
Ru(zft)(acac)(CO)$_2$	87	198 (dec.)	46.89 (46.95)	3.80 (3.72)	2.95 (3.04)
PdCl(zfs)	99	257 (dec.)	33.60 (33.62)	2.60 (2.56)	3.67 (3.56)
PdCl(zfs)(PBu_3)	61	149–153	46.22 (46.40)	6.22 (6.26)	2.42 (2.35)
PdCl(zfs)(tbp)	69	250 (dec.)	45.02 (45.47)	4.39 (4.39)	5.39 (5.30)
$RhCl_2$(zfs)(PBu_3)$_2$	73	177–179	50.38 (50.67)	7.84 (7.78)	1.52 (1.69)
$RuCl_2$(CO)$_2$(Hzfs)$_2$	50	210 (dec.)	39.08 (39.36)	3.05 (3.03)	3.69 (3.82)
PdCl(nft)	97	245 (dec.)	45.70 (45.47)	3.22 (3.05)	3.55 (3.54)
PdCl(nft)(PBu_3)	68	142–144	53.97 (54.18)	6.45 (6.57)	2.29 (2.34)
PdCl(nft)(tbp)	83	265 (dec.)	54.08 (54.24)	4.79 (4.74)	5.12 (5.27)
$RuCl_2$(CO)$_2$(Hnft)$_2$	62	203 (dec.)	51.98 (52.03)	3.76 (3.55)	3.51 (3.79)
$PdCl_2$(Htnt)	98	250 (dec.)	33.37 (33.14)	2.69 (2.78)	3.48 (3.51)
$PdCl_2$(Htns)	99	193 (dec.)	29.75 (29.65)	2.63 (2.49)	3.09 (3.14)

[a]Abbreviations: PBu_3 = tri-n-butylphosphine; tbp = 4-tert-butylpyridine, acac = acetylacetonato ion. The abbreviations of the amides are given in Table 1.

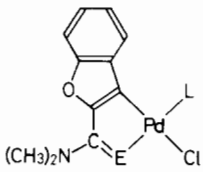
derivatives are therefore, less reactive toward cyclopalladation than the benzo[*b*]furan derivatives.

[Pd(zft)(acac)] was easily prepared (Table 2) and spectroscopically characterized (Tables 4 and 5). The amide ligand is coordinated as in the parent complex and the acac group has the usual O–O chelating mode; one low frequency ν(Pd–O) band may result from strong *trans* influence of the palladated 3-C atom. The 4-H chemical shift is used as a standard value in the following discussion.

The ^{1}H, ^{13}C and ^{31}P NMR spectra of [PdCl(zft)(PBu_3)] reveal the presence of two isomers in a $CDCl_3$ solution: a major isomer (81%) (to this is assigned a *cis*-(C,Cl) geometry, Structure II) and a minor one (19%) (a *trans*-(C,Cl), Structure III). The crystals consist of a pure *cis*-(C,Cl) isomer (confirmed by X-ray: see below) and dissolution results in an equilibrium between the two isomers in solution. The 4-H signal of the major isomer is strongly deshielded, in structure II 4-H being in the proximity of the *cis* Cl with deshielding effect [9]. The large $J(^{31}P–^{13}C)$ value of 3-C is consistent with a *trans* 3-C–Pd–P arrangement. The shielding of δ (^{31}P) of the major isomer is due to a strong *trans* influence [10] of the *trans* carbon donor (3-C). On the other hand, $\delta(^{31}P)$ of the minor is relatively deshielded suggesting that the *trans* donor is the one with a weaker *trans* influence, namely an S donor.



II *cis*-(C,Cl)



III *trans*-(C,Cl)

The NMR spectra of the seleno derivative, [PdCl(zfs)(PBu_3)], are nearly identical to those of the major isomer of the above thio analogue suggesting structure II for this complex. The *cis*-(C,Cl) arrangement has been confirmed by X-ray (see below). In the NMR spectra, in addition to the main signals, there are,

TABLE 3 ^{1}H and ^{13}C{^{1}H} NMR (in $CDCl_3$ and ppm vs tetramethylsilane) and IR (Nujol mull: cm^{-1}) spectra of the amides

Amide	^{1}H NMR[a]		^{13}C NMR				IR
	N–CH_3	3-H	N-CH_3	C(=E)[b]	2-C	3-C	ν(C–N)
Hzfo	3.17	7.26	37.0	160.5	148.9	111.3	1633[c]
Hzft	3.53 3.42	7.29d (0.9)	44.1	185.4	153.2	111.8	1516
Hzfs	3.58 3.29	7.40	48.2 45.5	188.7 [208]	156.0	112.8	1520
Hnfo	3.29	7.83d (0.9)	37.8	160.7	148.7	112.5	1630[c]
Hnft	3.56	7.91d (0.9)	44.4	186.0	152.0	112.3	1510
Hnfs	3.65 3.40	8.08d (0.8)	48.8 45.8	188.4 [206]	155.8	114.1	1512
Htno	3.15	7.48	37.9	164.5	137.5	125.3	1611[c]
Htnt	3.48	7.25d (0.7)	44.2	191.7	143.9	122.2	1527
Htns	3.57 3.24	7.21d (0.7)	48.1 45.3	194.0 [208]	147.2	120.8	1529

[a]Signals are singlet unless otherwise noted. d = doublet. Figures in parentheses are $J(^1H–^1H)$ in Hz. [b]E = O, S and Se. Figures in square brackets are $J(^{77}Se–^{13}C)$ in Hz. [c]ν(C=O)

TABLE 4 ^{1}H NMR (ppm vs. tetramethylsilane) and IR (Nujol mull· cm^{-1}) spectra of the complexes

Complex	Solvent	^{1}H NMR[a]		IR	
		N–C^{1}H$_3$	4-H	ν(C–N)	ν(M–Cl)
PdCl(zft)	dmso-d$_6$	3 84	8 74d	1583	301
		3 58	(7.7)		218
PdCl(zft)(PBu$_3$)	CDCl$_3$			1565	299
trans (C,Cl)		3 78	7 58d		
		3 55d	(7 5)		
		(0 7)			
cis(C,Cl)		3 81	9 11d		
		3 47	(7 5)		
PdCl(zft)(tbp)	CDCl$_3$			1571	310
trans (C,Cl)		3 82	5 82d		
		3 57	(7 8)		
cis (C,Cl)		3 82	9 11d		
		3 51	(8.6)		
Pd(zft)(acac)	CDCl$_3$	3 83	8 55d[b]	1567	443[c]
		3 58	(7 5)		213
RhCl$_2$(zft)(PBu$_3$)$_2$	CDCl$_3$	3 89	9 11d	1547	286
		3 57	(7.8)		236
RuCl(zft)(CO)$_2$	dmso-d$_6$	3 67	7 94d[d]	1550	278br[e]
		3 94	(7.1)		
RuCl(zft)(CO)$_2$(PBu$_3$)	CDCl$_3$	3 90	8 13d	1553	288[f]
		3 65	(7.3)		
Ru(zft)(acac)(CO)$_2$	CDCl$_3$	3 89	8 03d	1551	509[g]
		3 61	(7 3)		427
PdCl(zfs)	dmso-d$_6$	3 85	8 86d	1586	294
		3 65	(7.4)		258
PdCl(zfs)(PBu$_3$)	CDCl$_3$	3.75	9 28d	1579	303
		3.39	(7.6)		
PdCl(zfs)(tbp)	CDCl$_3$			1567	299
trans (C,Cl)		3 83	5 82d		
		3 62	(8.4)		
cis (C,Cl)		3 84	9 24d		
		3 60	(7.8)		
RhCl$_2$(zfs)(PBu$_3$)$_2$	CDCl$_3$	3.85	9 29d	1551	271
		3.58	(8 1)		211
RuCl$_2$(Hzfs)$_2$(CO)$_2$	CDCl$_3$	3 77	[h]	1549	294[i]
		3.31			268
PdCl(nft)	dmso-d$_6$	3 75	8 64[k]	1604	277
		4 62[j]			222
PdCl(nft)(PBu$_3$)	CDCl$_3$	3 68	8 06[k]	1577	260
		4 29d[j]			
		{3 2}[l]			
PdCl(nft)(tbp)	CDCl$_3$	3 67	8 11[k]	1603	256
		4 78[j]			
RuCl$_2$(Hnft)$_2$(CO)$_2$	CDCl$_3$	3 34	8.10[k]	1534	286
		3 73			270
PdCl$_2$(Htnt)	CD$_3$NO$_2$	3 91	7.84[k]	1571	328br
		3 69			315
PdCl$_2$(Htns)	CD$_3$NO$_2$	3 91	7.79[k]	1576	322br
		3 75			308

[a]Signals are singlet unless otherwise noted d = doublet. Figures in parentheses are J(^{1}H–^{1}H) in Hz. [b]Signals due to acac 2.00, 2 17 and 5.44 ppm. [c]These bands are assigned to ν(Pd–O) Bands due to acac. 1577 and 1518 cm^{-1} [d]Accompanied with weak signals [e]br = broad ν(CO): 1961 and 2040 cm^{-1} [f]ν(CO) 1957 and 2029 cm^{-1}. [g]These bands may be due to ν(Ru–O). ν(CO): 1956 and 2030; ν(acac). 1583 and 1515 cm^{-1} Signals due to acac 1.85, 2 05 and 5 32 ppm [h]Not found [i]ν(CO) 1963 and 2032 cm^{-1}. [j]Signals of a CH$_2$ group. [k]3-H [l]J(^{1}H–^{31}P) in Hz

however, very weak peaks (intensities less than 5%) at chemical shifts close to those of the minor isomer {*trans*-(C,Cl), structure III} of the above thio analogue, e.g. δ(^{31}P) = 13.3 ppm. This fact indicates that the selenoamide is more inclined to form a *cis*-(C,Cl) isomer than the thioamide The preferred formation of the

TABLE 5 $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra of the complexes[a]

Complex	$\delta(^{13}C)$ (ppm) (J[b] (Hz))				$\delta(^{31}P)$ (ppm)[b]
	N-CH_3	C(=E)	2-C	3-C	
PdCl(zft)	42.8 43.9	178.9	148 5	136.1	
PdCl(zft)(PBu_3)					
trans-(C,Cl)	43.5 44.8d (3 1)	183 1d (3.1)	154 0d (2.1)	[c]	15.3
cis-(C,Cl)	43 5 44 4	182 1d (10 4)	155.3d (9.7)	153 7d (149.9)	2 6
Pd(zft)(acac)[d]	43 2 44.2	181 8	153.9	141.2	
$RhCl_2$(zft)(PBu_3)$_2$	43.4 43.6	180 1	148 8d [4 0]	159 4dt [33 7] (10 3)	2 8d {85 9}
RuCl(zft)(CO)$_2$(PBu_3)[e]	43 8 45 4	182 9d (8.8)	156 0d (5.9)	166 9d (77.7)	4 2
Ru(zft)(acac)(CO)$_2$[f]	44 1 45 4	183 1	155 1	162.5	
PdCl(zfs)	43 8	180 5	151 0	138.0	
PdCl(zfs)(PBu_3)	44.6 47.6	180 3d (11 7)	155 7d (8 8)	156.2d (149 5)	2 6
$RhCl_2$(zfs)(PBu_3)$_2$	44 1 46 9	180 3	151 7d [4 4]	161.4dt [33 7] (10 3)	2 3d {87.2}
PdCl(nft)	45.6 64.8[g]	176 3	146 5	114.2	
PdCl(nft)(PBu_3)	46.2 57 9d[g] (4 4)	178 8d (2.9)	148 2d (2.9)	114.8	12.4
PdCl(nft)(tbp)	45.2 57.4[g]	177 2	147 4	113 6	

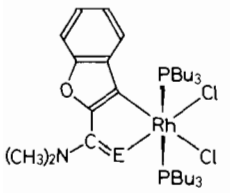
[a]Solvents are the same as those used for the ^1H NMR spectra [b]Figures in parentheses are $J(^{31}P–^{13}C)$, those in brackets $J(^{103}Rh–^{13}C)$, and those in braces $J(^{103}Rh–^{31}P)$ in Hz. [c]Not detected. [d]Signals due to acac: 26.9, 27 8, 100 0, 185 5, 187 2 ppm [e]$\delta(^{13}CO)$: 198.0d ppm (10.3 Hz), 194.6d (10.3) [f]$\delta(^{13}CO)$: 196 4, 196.6 ppm Signals due to acac 28.0, 28 2, 99 7, 187 7, 188 8 ppm [g]The signal is due to a Pd–CH_2 group.

cis-(C,Cl) isomers is in great contrast to the fact that the parent *N*,*N*-dimethylfuran-2-carbothio (or seleno) amide (Haft or Hafs) principally forms *trans*-(C,Cl)-[PdCl(aft or afs)(PBu_3)].

For [PdCl(bf)(tbp)] (bf=zft and zfs), the presence of two isomers in $CDCl_3$ solutions is evident from the ^1H NMR spectra (Table 4); the spectra of the major isomer (75%) (*cis*-(C,Cl)) of [PdCl(zft)(tbp)] and of that (64%) of [PdCl(zfs)(tbp)] are mutually very similar and the spectra of the minor isomer (25%) (*trans*-(C,Cl)) of the former and of that (36%) of the latter are also very similar to each other. The 4-H chemical shifts of the majors resemble that of *cis*-(C,Cl)-[PdCl(bf)(PBu_3)] and for the majors structure II (L=tbp) is proposed where 4-H is close to Cl. The 4-H signals of the minors show a marked upfield shift which results from an anisotropic shielding effect of the pyridine ring of tbp which is coordinated perpendicularly to the coordination plane because of steric restraint [2] (structure III, L=tbp). The isomer ratios are different from those found for the above PBu_3 complexes. The ratios have, however, a similar trend to that found for [PdCl(aft or afs)(tbp)] of the parent furan-2-derivatives. One of the factors affecting the ratios should be the relative *trans* influences of the four coordinating donors around the central Pd atom. The steric bulk of the ligands may also be a factor.

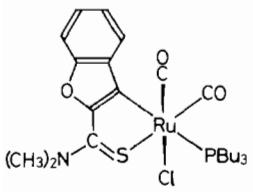
Both Hzft and Hzfs (Hbf) reacted with $Rh_2Cl_6(PBu_3)_4$ in refluxing toluene to produce [$RhCl_2$(bf)(PBu_3)$_2$] (Table 2). The ^1H NMR spectra (Table 4) show a low field doublet of 4-H and the origin is the same as that for *cis*-(C,Cl)-[PdCl(bf)(PBu_3)]. The ^{31}P NMR spectra (Table 5) reveal that the two PBu_3 groups are equivalent and mutually *trans*; the coupling constants $J(^{103}Rh–^{31}P)$ are indicative of a *trans* disposition of the phosphines [11]. Structure IV is assigned to [$RhCl_2$(bf)(PBu_3)$_2$]. The splitting pattern of 3-C, a doublet ($J(^{103}Rh–^{13}C)$) of triplets ($J(^{31}P–^{13}C)$), and the J(P–C) values are

consistent with structure IV where the 3-C and P atoms are mutually *cis*. Coordination of Cl is evident from the ν(Rh–Cl) bands



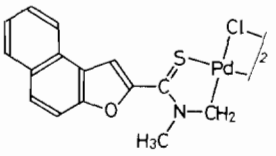
IV

The reaction of $Ru_2Cl_4(CO)_6$ with Hbf gave a different type of complex: $RuCl_2(Hzfs)_2(CO)_2$ or $RuCl(zft)(CO)_2$ (Table 2). The ^1H NMR spectrum of $RuCl_2(Hzfs)_2(CO)_2$ shows that all the hydrogen atoms of Hzfs remain intact revealing non-cyclometallation and the IR spectrum shows the Se coordination of the amide group. *Cis*-coordination of the two Cl and CO groups is also suggested. In the ^1H NMR spectrum of $RuCl(zft)(CO)_2$, the integration of the aromatic protons is, however, reduced by one proton unit like the above palladium complexes. To obtain ^{13}C NMR spectra more soluble derivatives, $[RuCl(zft)(CO)_2(PBu_3)]$ and $[Ru(zft)(acac)(CO)_2]$, were prepared (Table 2). The spectra show that cyclometallation occurs at 3-C (Table 5) and that the two CO groups are not equivalent. The large $J(^{13}C–^{31}P)$ of 3-C of the former suggests a *trans* 3-C–Ru(II)–P geometry and the small $J(^{13}C–^{31}P)$ values of CO suggest a *cis* P–Ru–CO arrangement. Structure V is proposed, which was confirmed by X-ray analysis. The NMR signals of acac of $[Ru(zft)(acac)(CO)_2]$ suggest a normal O–O chelation and a possible structure for this is the one where the acac ligand spans the Cl and PBu_3 positions of structure V.



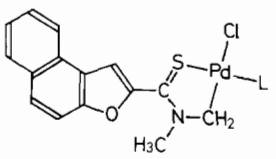
V

The above results show that 4-H of cyclometallated bf interferes with a *cis*-coordinating ligand in the same plane. For instance, when the ligand is Cl, 4-H is deshielded while when it is tbp, 4-H is shielded. To render the hydrogen closer to the *cis* ligand in expectation of intensifying the effect, *N,N*-dimethylnaphtho[2,1-*b*]furan-2-carbothioamide (Hnft) was prepared and the reaction with palladium(II) chloride was studied (Tables 1, 2 and 3). The reaction of Hnft with lithium tetrachloropalladate at room temperature gave an intractable precipitate but under more forceful conditions PdCl(nft) was obtained The seleno analogue, Hnfs, was decomposed under the same conditions. The ^1H NMR spectrum (Table 4) of the product shows that one of the N–CH_3 groups of the free Hnft is converted to an N–CH_2 group: a significant downfield shift (4.62 ppm) and a reduced integration intensity (2 H) [3]. The aromatic proton integration is retained. The ^{13}C NMR spectrum (Table 5) also shows the presence of an N–CH_2 group (64.8 ppm) and no participation of the naphthofuran ring in the coordination. Structure VI is a reasonable one.



VI

To certify the supposition, two derivatives were prepared: $[PdCl(nft)(PBu_3)]$ and [PdCl(nft)(tbp)]. In the ^1H and $^{13}C\{^1H\}$ NMR spectra, although the signals of the N–CH_2 group of the latter are singlets, those of the former are a doublet due to $J(^1H–^{31}P)$ or $J(^{13}C–^{31}P)$ and the values indicate that the C and P donors are in a *cis* relation. $\delta(^{31}P)$ is similar to that of the *trans*-(C,Cl) isomer of the above palladium complexes; PBu_3 is coordinated *trans* to the amide-S atom. Structure VII is proposed for [PdCl(nft)L] (L = PBu_3 and tbp).



VII

The metallation of the N–CH_3 group is definite. The above ^{13}C assignment of the CH_2 and CH_3 groups is distinctly supported by the ^1H-coupled ^{13}C NMR spectrum of $[PdCl(nft)(PBu_3)]$: $\delta(CH_3) = 46.2$ ppm (quartet, $J(^{13}C–^1H) = 140.7$ Hz) and $\delta(CH_2) = 57.9$ ppm (triplet of doublets, $J(^{13}C–^1H) = 142.9$ and $J(^{13}C–^{31}P) = 4.4$ Hz). The steric obstruction of the additional benzene ring prevents palladium from metallating 3-C; 4-H of the additional ring would be brought very close to a *cis* ligand if Hnft is metallated at 3-C. To avoid this disadvantage, the N–CH_3 group is interpreted to be cyclopalladated. Reaction of Hnft with $Rh_2Cl_6(PBu_3)_4$ in refluxing toluene resulted only in recovery of the starting materials and formation of $RuCl_2(CO)_2(Hnft)_2$ indicates no ruthenation of Hnft. The reactivity of Hnft is, therefore, reduced when compared with that of Hzft. One reason for this could be due to the steric hindrance of the added benzene ring.

X-ray analysis has confirmed the formation of Hzfs, which is depicted in Fig. 2. The selected bond distances and angles are given in Table 6 (numbering of atoms

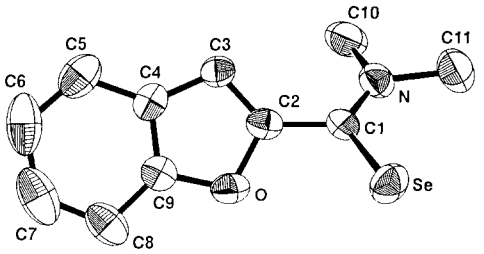


Fig 2 ORTEP drawing of Hzfs with atom-numbering scheme

TABLE 6. Bond distances (Å) and bond angles (°) of Hzfs with e s d.s in parentheses

Distances			
Se–C1	1 827(9)	N–C1	1 31(1)
N–C10	1.45(1)	N–C11	1 47(1)
C1–C2	1 51(1)	C2–C3	1.32(1)
C2–O	1.38(1)	O–C9	1 38(1)
C3–C4	1 39(1)	C4–C9	1 37(1)
C4–C5	1 44(2)	C5–C6	1 40(2)
C6–C7	1.38(2)	C7–C8	1 42(2)
C8–C9	1.36(1)		
Angles			
C10–N–C11	110.3(8)	C10–N–C1	129.3(8)
C11–N–C1	120.3(8)	N–C1–Se	125 3(7)
N–C1–C2	116.9(8)	C2–C1–Se	117 8(6)
C1–C2–C3	130.7(8)	C1–C2–O	116 3(7)
C3–C2–O	112.6(8)	C2–C3–C4	106 1(8)
C2–O–C9	104.7(6)	C3–C4–C9	108 1(8)
C3–C4–C5	136(1)	C4–C5–C6	119(1)
C5–C6–C7	120(1)	C6–C7–C8	123(1)
C7–C8–C9	113(1)	C8–C9–C4	128 4(9)
C8–C9–O	123.0(8)	C4–C9–O	108 6(8)
C9–C4–C5	116.4(9)		

is shown in Fig. 2). The planar selenoamide group makes a dihedral angle of 44.4° with respect to the furan ring and the Se and O atoms are approximately in a *cis* relation. The C–Se length of the amide group is between the single and double C–Se bond distances and a little shorter than that of *N,N,N′,N′*-tetramethylselenourea (1.863(4) Å) [12].

Upon forming [PdCl(zfs)(PBu_3)] by cyclopalladation, the structure of which is shown in Fig. 3 and the bond distances and angles in Table 7, Hzfs rotates the amide group about 180° around the C(1)–C(2) axis resulting in a *trans* relation of the Se and O atoms. Significant changes occur in the bond distances upon formation of a chelate ring: Se–C(1) is lengthened from 1.830(9) to 1.880(5) Å and C(2)–C(3) from 1.31(1) to 1.369(6) Å while C(1)–C(2) is shortened from 1.50(1) to 1.428(6) Å. Hence, the two bonds, Se–C(1) and C(2)–C(3), result in the approach to a single bond but the C(1)–C(2) approaches a double bond; the partial structure Se=C(1)–C(2)=C(3) shifts upon chelation to some extent to Se–C(1)=C(2)–C(3)–Pd.

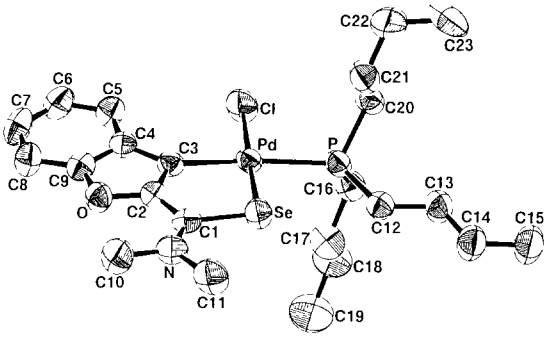


Fig 3. ORTEP drawing of PdCl(zfs)(PBu_3) with atom-numbering scheme.

TABLE 7 Bond distances (Å) and bond angles (°) of [PdCl(zfs)(PBu_3)] with e.s.d.s in parentheses

Distances			
Pd–Se	2.374(1)	Pd–Cl	2.362(2)
Pd–P	2.329(1)	Pd–C3	2.042(4)
Se–C1	1.880(5)	C1–N	1.315(6)
N–C10	1.474(8)	N–C11	1.474(7)
C1–C2	1.418(6)	C2–C3	1.369(6)
C2–O	1.406(6)	O–C9	1 369(6)
C3–C4	1.429(6)	C4–C9	1.402(7)
C4–C5	1.425(7)	C5–C6	1.355(8)
C6–C7	1.398(8)	C7–C8	1 349(9)
C8–C9	1.395(7)	P–C12	1 834(5)
P–C16	1 823(5)	P–C20	1 821(5)
C12–C13	1.516(7)	C13–C14	1 506(8)
C14–C15	1.510(9)	C16–C17	1 523(8)
C17–C18	1.50(1)	C18–C19	1.50(1)
C20–C21	1.560(8)	C21–C22	1 479(9)
C22–C23	1.50(1)		
Angles			
Se–Pd–Cl	177.87(4)	Se–Pd–P	92 57(4)
Se–Pd–C3	84.7(1)	Cl–Pd–P	86.32(5)
Cl–Pd–C3	96.5(1)	P–Pd–C3	175.7(1)
Pd–Se–C1	98.6(1)	Pd–P–C12	118.2(2)
Pd–P–C16	112 0(2)	Pd–P–C20	111.6(2)
C12–P–C16	104.0(2)	C12–P–C20	104 6(2)
C16–P–C20	105.4(2)	C1–N–C10	125.3(4)
C1–N–C11	121.2(4)	C10–N–C11	113.4(4)
Se–C1–N	120.9(3)	Se–C1–C2	112.3(3)
N–C1–C2	126.8(4)	C1–C2–C3	125.1(4)
C2–O–C9	104.3(4)	O–C2–C1	121.5(4)
O–C2–C3	113.4(4)	Pd–C3–C2	119.1(3)
Pd–C3–C4	136.5(3)	C2–C3–C4	104.1(4)
C3–C4–C5	135.8(4)	C3–C4–C9	107.8(4)
C5–C4–C9	116.5(4)	C4–C5–C6	119.2(5)
C5–C6–C7	121.7(5)	C6–C7–C8	121.9(6)
C7–C8–C9	116.5(5)	O–C9–C4	110.5(4)
O–C9–C8	125.4(5)	C4–C9–C8	124 2(5)
P–C12–C13	116.4(4)	C12–C13–C14	115.0(5)
C13–C14–C15	113.7(5)	P–C16–C17	112.2(4)
C16–C17–C18	113 3(5)	C17–C18–C19	116.4(6)
P–C20–C21	111 6(4)	C20–C21–C22	113.4(5)
C21–C22–C23	111.4(6)		

The geometry around the square planar Pd atom is different from that found for the related [PdCl(bts)(PBu_3)] (Hbts = *N*,*N*-dimethyl-3-thiophenecarboselenoamide) in that the coordination sites of Cl and PBu_3 are reversed relative to the Se and palladated C atoms between the two complexes. The coordination bond distances are accordingly different between the two, and distinctly reflect the *trans* influence of each donor atom: Se–Pd *trans* to Cl is 2.374(1) Å in [PdCl(zfs)(PBu_3)] while Se–Pd *trans* to P is 2.415(1) Å in [PdCl(bts)(PBu_3)] and C–Pd is 2.042(4) Å in the former (*trans* to P) while it is 1.979(6) Å in the latter (*trans* to Cl). The factors controlling the geometries of the complexes are intriguing but not yet clear. In [PdCl(zfs)(PBu_3)], the short non-bonding distance of Cl–H(5) (2.58(4) Å) and the wide angle of Cl–Pd–C(3) (96.5(1)°) should show that the coordination site of the Cl is already crowded. A more bulky PBu_3 is hence unfavorable to occupy the coordination site near H(5). This may be one of the reasons.

The structure of [RuCl(zft)($CO)_2$(PBu_3)] was determined by X-ray analysis to eliminate ambiguity from the spectroscopically proposed structure, a structure with reversed coordination sites of Cl and PBu_3 being previously proposed for [RuCl(bfs)($CO)_2$(PBu_3)] (Hbfs = *N*,*N*-dimethylfuran-3-carboselenoamide) [1]. The distorted octahedral structure is depicted in Fig. 4 and the bond parameters are given in Table 8. The coordination bond distances clearly reflect the *trans* influences of the respective donor atoms and the structural features of the chelating amide ligand are similar to those previously described for [PdCl(zfs)(PBu_3)]. In free *N*-(4,6-dimethylpyridin-2-yl)benzothioamide [13], a C=S distance is, for instance, reported to be 1.650(2) Å and a C(amide)–C(benzene-*ipso*) one 1.487(3) Å; the former is elongated but the latter shortened in the Ru complex (S–C(1) = 1.712(5), C(1)–C(2) = 1.434(7) Å). The angle C(3)–Ru–C(13) looking up at H(5) is opened out to 96.3(2)° as in the Pd complex.

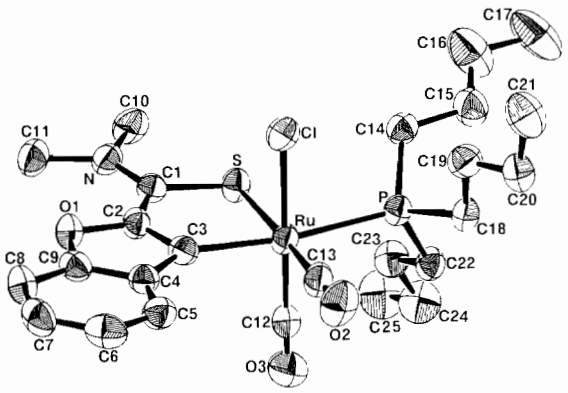


Fig 4. ORTEP drawing of RuCl(zft)($CO)_2$(PBu_3) with atom-numbering scheme

TABLE 8 Bond distances (Å) and bond angles (°) of [RuCl(zft)($CO)_2$(PBu_3)] with e s d s in parentheses

Distances			
Ru–Cl	2.441(2)	Ru–S	2 434(2)
Ru–P	2.414(2)	Ru–C3	2.091(5)
Ru–C12	1.879(6)	Ru–C13	1 886(6)
S–C1	1.712(5)	P–C14	1.807(6)
P–C18	1.841(6)	P–C22	1 827(6)
O1–C2	1.403(6)	O1–C9	1 358(7)
O2–C13	1.132(8)	O3–C12	1.099(8)
N–C1	1 323(7)	N–C10	1.460(8)
N–C11	1 470(8)	C1–C2	1.433(7)
C2–C3	1 362(8)	C3–C4	1.442(8)
C4–C5	1.405(8)	C4–C9	1.400(8)
C5–C6	1 385(9)	C6–C7	1.39(1)
C7–C8	1.37(1)	C8–C9	1 393(9)
C14–C15	1 537(9)	C15–C16	1 42(1)
C16–C17	1.50(1)	C18–C19	1 526(8)
C19–C20	1 505(9)	C20–C21	1 52(1)
C22–C23	1 524(8)	C23–C24	1 49(1)
C24–C25	1 52(1)		
Angles			
Cl–Ru–S	89 07(5)	Cl–Ru–P	87 47(5)
Cl–Ru–C3	88 3(2)	Cl–Ru–C12	179 4(2)
Cl–Ru–C13	89 1(2)	S–Ru–P	90 63(5)
S–Ru–C3	80 6(2)	S–Ru–C12	91 4(2)
S–Ru–C13	176 4(2)	P–Ru–C3	170 3(2)
P–Ru–C12	92 8(2)	P–Ru–C13	92 4(2)
C3–Ru–C12	91 5(2)	C3–Ru–C13	96 3(2)
C12–Ru–C13	90 4(3)	Ru–S–C1	101 7(2)
Ru–C12–O3	179 5(6)	Ru–C13–O2	179 5(5)
Ru–P–C14	113.1(2)	Ru–P–C18	116 3(2)
Ru–P–C22	114.1(2)	C14–P–C18	105 9(3)
C14–P–C22	104.0(3)	C18–P–C22	102 1(3)
C2–O1–C9	104 3(4)	C1–N–C10	120 0(5)
C1–N–C11	125.4(5)	C10–N–C11	114 6(5)
S–C1–N	119.8(4)	S–C1–C2	114 3(4)
N–C1–C2	125.9(5)	O1–C2–C1	122 1(5)
O1–C2–C3	113 7(5)	C1–C2–C3	124 2(5)
Ru–C3–C2	119 0(4)	Ru–C3–C4	137 0(4)
C2–C3–C4	103 9(5)	C3–C4–C5	134 7(5)
C3–C4–C9	107 1(5)	C5–C4–C9	118 2(5)
C4–C5–C6	118 2(6)	C5–C6–C7	121 9(6)
C6–C7–C8	121 4(7)	C7–C8–C9	116 7(6)
O1–C9–C4	111.1(5)	O1–C9–C8	125 3(5)
C4–C9–C8	123 7(5)	P–C14–C15	117 2(4)
C14–C15–C16	117 4(6)	C15–C16–C17	116 5(8)
P–C18–C19	116 2(4)	C18–C19–C20	111 7(5)
C19–C20–C21	112.7(6)	P–C22–C23	114 5(4)
C22–C23–C24	113 9(5)	C23–C24–C25	112 4(6)

In both the [PdCl(zfs)(PBu_3)] and [RuCl(zft)-($CO)_2$(PBu_3)] complexes, the phosphine ligands are similarly oriented to relieve the steric strain for Cl which is coordinated *cis* to the PBu_3. Torsion angles around the P–Pd (or Ru) bond are as follows: Cl–Pd–P–C(16) = 62.2(2) and Cl–Pd–P–C(20) = 55.7(2)°; Cl–Ru–P–C(14) = 49 5(2) and Cl–Ru–P–C(18) = 73.4(2)°.

Experimental

Measurements

Measurements were carried out using previously reported methods [1, 2]. IR spectra were measured on Nujol mulls. Chemical shifts of ^{1}H and ^{13}C NMR spectra are given against internal tetramethylsilane and those of ^{31}P against external 85% H_3PO_4.

Syntheses

Yields, melting points, and analytical results of the amides are summarized in Table 1 and those of the complexes in Table 2.

Preparation of the amides

N,N-Dimethylbenzofuran-2-carboxamide (Hzfo). This amide was prepared by the literature method [14]. To a mechanically stirred mixture of 0.1 mol (12.2 g) salicylaldehyde and 0.1 mol potassium carbonate (13.8 g) in 120 cm^3 *N,N*-dimethylformamide (DMF) protected from moisture was dropwise added 0.11 mol (13.5 g) *N,N*-dimethyl-2-chloroacetamide. The mixture was refluxed for 75 min. After cooling, the solid was filtered off and washed with a small amount of DMF. Most of the combined solvent was evaporated under reduced pressure and to the concentrated solution were added 100 cm^3 water to precipitate the powder, which was filtered, washed with water, and dried in air. The powder was dissolved in 100 cm^3 dichloromethane and the solution was treated with active charcoal, filtered, concentrated to a small volume, and mixed with n-hexane to precipitate white crystals. The crystals were filtered, washed with n-hexane, and dried in air (yield 11.5 g).

N,N-Dimethylnaphthofuran-2-carboxamide (Hnfo) The amide was similarly prepared as above from 2-hydroxy-1-naphthaldehyde. The refluxing time was 2 h and instead of n-hexane ether was used to precipitate the pure crystals.

N,N-Dimethylbenzothiophene-2-carboxamide (Htno). Methyl benzothiophene-2-carboxylate, prepared by the literature method [15], was hydrolyzed with aqueous sodium hydroxide followed by acidification with concentrated hydrochloric acid to give the free carboxylic acid. A mixture of 60 mmol (10.7 g) of the acid and 30 mmol (5.4 g) hexamethylphosphoramide was heated at 190 °C for 3 h. The cooled mixture was then extracted with dichloromethane. The extract was mixed with ether and washed a few times with aqueous 10% potassium carbonate to remove any unreacted free acid. The organic phase was treated with active charcoal, filtered, and concentrated to a small volume to give a white powder, which was filtered, washed with ether, and dried in air (yield 9.4 g).

Thioamides and selenoamides. Thiation and selenation of these carboxamides were carried out by the literature methods [5, 6]. The reaction times were as follows: Hzft, 6; Htnt, 6; Hnft, 7; Hzfs, 5; Htns 48; Hnfs, 48 h The thioamides were obtained as yellow crystals and the selenoamides as orange–red crystals.

Preparation of the complexes

PdCl(bf) and $PdCl_2$(Hbt). To a methanol solution (30 cm^3) of lithium tetrachloropalladate, prepared *in situ* from 1 mmol palladium(II) chloride and 2 mmol lithium chloride, was added 1 mmol of the amide. The mixture was stirred for 24 h at room temperature. The resulting yellow–brown precipitate was filtered, washed with methanol, and dried in air.

PdCl(nft). The mixture, prepared as above, was refluxed for 48 h and similarly treated.

PdCl(zft)L, PdCl(zfs)L and PdCl(nft)L (L = PBu_3 and tbp). To a suspension of 1 mmol PdCl(zft), PdCl(zfs) or PdCl(nft) in 30 cm^3 dichloromethane was added 1 mmol PBu_3 or 2 mmol tbp. The mixture was stirred until it became clear. The mixture was filtered and to the concentrated filtrate was added n-hexane to precipitate the yellow product, which was filtered, washed with n-hexane, and dried in air.

Pd(zft)(acac). A mixture of 1 mmol PdCl(zft) and 1 mmol lithium acetylacetonate in a mixed solvent of 20 cm^3 dichloromethane and 20 cm^3 ethanol was stirred on a hot plate for 2 h. The mixture was then concentrated to dryness under reduced pressure. The residue was extracted two times with 20 cm^3 dichloromethane and the combined extracts were filtered, concentrated to a small volume, and mixed with n-hexane to afford yellow crystals, which were filtered, washed with n-hexane, and dried in air.

$RhCl_2$(zft)$(PBu_3)_2$ and $RhCl_2$(zfs)$(PBu_3)_2$. A mixture of 0.5 mmol hexachlorotetrakis(tri-n-butylphosphine)dirhodium(III) and 1 mmol Hzft or Hzfs in 30 cm^3 toluene was refluxed with stirring for 8 h and the solvent was evaporated off under reduced pressure. The residue was dissolved in 50 cm^3 dichloromethane, treated with Florisil, filtered, concentrated to a small volume, and mixed with n-hexane. Precipitated yellow crystals were filtered, washed with n-hexane, and dried in air.

RuCl(zft)$(CO)_2$, $RuCl_2(CO)_2(Hzfs)_2$ and $RuCl_2(CO)_2(Hnft)_2$. A mixture of 0.5 mmol tetrachlorohexacarbonyldiruthenium(II) and 1 mmol Hzft, Hzfs or Hnft in 30 cm^3 2-methoxyethanol was stirred on a hot plate for 4 h and the solution was evaporated to a small

TABLE 9 Crystal data

Complex	zfs	PdCl(zfs)(PBu_3)	RuCl(zft)$(CO)_2(PBu_3)$
Formula	$C_{11}H_{11}OSe$	$C_{23}H_{37}NClOPPdSe$	$C_{25}H_{37}NClO_3PRuS$
Crystal system	orthorhombic	triclinic	monoclinic
Space group	$P2_12_12_1$	$P\bar{1}$	$P2_1/a$
a (Å)	12 487(3)	10.758(1)	14 292(2)
b (Å)	12 587(2)	12.909(1)	20 489(2)
c (Å)	6 704(1)	9.965(1)	9 895(2)
α (°)		91 88(1)	
β (°)		106 93(1)	91 90(1)
γ (°)		90 07(1)	
Z	4	2	4
V (Å^3)	1053 7(4)	1323 2(3)	2895 8(7)
μ(Mo Kα) (cm^{-1})	34 84	22.29	7.71
Crystal color	orange	orange	pale yellow
Crystal habit	prismatic	prismatic	prismatic
Crystal size (mm)	0 6×0.5×0 2	0.2×0.2×0 4	0 2×0.2×0 3
Scan type	θ–2θ	θ–2θ	θ–2θ
Scan speed (°/min)	4	12	6
Scan width (°)	1 155+0 500 tanθ	1.050+0 500 tanθ	1.103+0 500 tanθ
$2\theta_{max}$ (°)	60	55	55
Reflections measured	$+h$, $+k$, $+l$	$\pm h$, $\pm k$, $+l$	$\pm h$, $+k$, $+l$
No reflections measured	1806	6426	7225
No reflections observed [$\|F_o\| > 3\sigma(\|F_o\|)$]	1262	4356	4197
R	0 0497	0.0418	0 0557
R_w	0 0599	0 0507	0 0538
GOF	3 47	2 22	1 78
Weighting scheme, w	$[\sigma_{count}^2 + (0\ 020\|F_o\|)^2]^{-1}$	$[\sigma_{count}^2 + (0.020\|F_o\|)^2]^{-1}$	$[\sigma_{count}^2 + (0\ 020\|F_o\|)^2]^{-1}$

volume under reduced pressure. Upon addition of ethanol (50 cm^3) to the concentrated solution, a yellow precipitate was obtained, which was filtered, washed with ethanol, and dried in air.

RuCl(zft)$(CO)_2(PBu_3)$ and Ru(zft)(acac)$(CO)_2$. These two complexes were similarly prepared to the above corresponding palladium complexes. The former is light yellow and the latter is yellow crystals.

X-ray analysis

Crystals of Hzfs, PdCl(zfs)(PBu_3) and RuCl(zft)-$(CO)_2(PBu_3)$ suitable for structure determination were obtained by slow evaporation of a dichloromethane–hexane solution of each compound at room temperature. Diffraction data were collected on a Rigaku AFC-5R diffractometer with graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). Crystal data and experimental details are listed in Table 9. 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 collections. 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 using a HITAC M-680H computer at the Computer Center of the Institute for Molecular Science. The locations of the metals were determined by the direct method using SHELXS-86 [16] and the other non-hydrogen atoms were found by the usual Fourier methods using the Universal Crystallographic Computation Program System UNICS III [17]. The hydrogen atoms were generated in calculated positions. All non-hydrogen atoms were anisotropically refined. The atomic parameters of non-hydrogen atoms are listed in Table 10.

The space group of Hzfs was non-centrosymmetric. The final R/R_w values for the structure presented here were calculated to be 0.0497/0.0599 and those for its inversion to be 0.0632/0.0789. The presented structure is significant at the 0.005 level when Hamilton's R factor test [18] is applied.

Supplementary material

The anisotropic thermal parameters for the non-hydrogen atoms, hydrogen atomic parameters, and the complete lists of the $|F_o|$ and $|F_c|$ values of Hzfs, RuCl(zft)$(CO)_2(PBu_3)$ and PdCl(zfs)(PBu_3) are available from the authors on request.

TABLE 10 Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors of Hzfs, [PdCl(zfs)(PBu_3)] and [RuCl(zft)$(CO)_2(PBu_3)$]

Atom	x	y	z	B_{eq}[a] (Å^2)
Hzfs				
Se	−1317(1)	−6696(1)	−2319(1)	4 6
O	−3324(3)	−8214(3)	−2711(6)	3.6
N	−2429(4)	−6623(4)	1289(8)	3.7
C1	−2290(5)	−7101(5)	−419(10)	3.2
C2	−2929(5)	−8080(5)	−800(9)	3 4
C3	−3105(5)	−8934(5)	320(10)	3.2
C4	−3640(5)	−9664(4)	−889(10)	3.4
C5	−4034(6)	−10720(6)	−629(14)	5.1
C6	−4527(5)	−11224(6)	−2254(18)	6 4
C7	−4637(6)	−10680(7)	−4065(15)	6 5
C8	−4259(5)	−9636(6)	−4371(12)	4 9
C9	−3769(4)	−9211(5)	−2732(10)	3 4
C10	−3275(6)	−6790(6)	2755(10)	5 1
C11	−1733(6)	−5738(6)	1904(13)	5 3
[PdCl(zfs)(PBu_3)]				
Pd	1841 9(3)	7068 4(3)	637 5(3)	3.7
Se	−422 9(4)	7344.9(4)	−297.9(5)	4.6
Cl	4101(1)	6786(1)	1483(2)	6 0
P	2367(1)	8456(1)	−541(1)	4 0
O	−229(3)	5062(2)	2523(3)	4 7
N	−2276(3)	6224(3)	540(4)	4.6
C1	−1026(4)	6344(3)	699(5)	3 9
C2	4(4)	5799(3)	1615(4)	3 8
C3	1293(4)	5926(3)	1723(4)	3 7
C4	1932(4)	5202(3)	2747(4)	4 1
C5	3242(5)	4897(4)	3369(5)	4.9
C6	3495(5)	4180(4)	4373(6)	5.7
C7	2506(5)	3735(4)	4823(6)	6 2
C8	1249(5)	3996(4)	4281(6)	5 5
C9	981(4)	4712(3)	3219(5)	4.4
C10	−2856(5)	5436(4)	1220(7)	6.4
C11	−3246(5)	6864(5)	−430(6)	6 6
C12	1043(4)	9268(4)	−1540(5)	4 6
C13	1430(5)	10166(4)	−2282(6)	5 7
C14	325(5)	10841(4)	−3045(6)	6 1
C15	749(6)	11753(4)	−3722(6)	7 1
C16	3190(4)	8035(4)	−1822(5)	4 8
C17	2356(6)	7289(4)	−2942(6)	6 3
C18	3030(7)	6901(5)	−3983(7)	8 6
C19	3243(7)	7672(6)	−4985(7)	8 4
C20	3490(5)	9361(4)	659(5)	5 0
C21	2899(5)	9824(5)	1801(6)	6.2
C22	3820(6)	10493(5)	2870(6)	7.1
C23	3202(7)	10937(6)	3924(7)	8 7
[RuCl(zft)$(CO)_2(PBu_3)$]				
Ru	6234 4(3)	6552 5(2)	3134.0(4)	3 6
Cl	5315(1)	6965(1)	1195(2)	4 7
S	6399(1)	5518(1)	1958(1)	4 2
P	7604(1)	6975(1)	2069(1)	3 8
O1	3974(2)	5224(2)	3736(4)	4 3
O2	5902(3)	7826(2)	4575(5)	7.1
O3	7349(3)	6061(2)	5519(4)	7.0
N	5193(3)	4546(2)	1830(4)	4 2
C1	5389(3)	5125(3)	2362(5)	3 8
C2	4820(3)	5476(3)	3280(5)	3 9
C3	5029(3)	6081(3)	3774(5)	3 8
C4	4255(3)	6232(3)	4619(5)	3 9
C5	4008(4)	6771(3)	5409(6)	5 0
C6	3169(4)	6747(3)	6070(6)	5 7
C7	2580(4)	6206(4)	5979(7)	5 8
C8	2807(4)	5669(3)	5231(6)	5 3
C9	3645(4)	5698(3)	4553(5)	4 2
C10	5844(4)	4241(3)	914(6)	5.4
C11	4346(5)	4162(3)	2072(7)	5 8
C12	6935(4)	6240(3)	4639(6)	4 5
C13	6025(4)	7347(3)	4039(6)	4 6
C14	7674(4)	6735(3)	318(6)	4 5
C15	8555(4)	6939(3)	−425(7)	6.0
C16	8753(7)	6601(4)	−1632(9)	9.1
C17	9651(7)	6777(4)	−2292(8)	9.6
C18	7750(4)	7868(3)	2094(6)	4 2
C19	7076(4)	8256(3)	1176(6)	5 1
C20	7209(4)	8980(3)	1354(7)	5 6
C21	6642(5)	9376(3)	323(8)	7.4
C22	8712(3)	6696(3)	2843(6)	4 3
C23	8893(4)	5967(3)	2698(6)	5 1
C24	9806(5)	5748(4)	3314(8)	6 9
C25	9979(5)	5023(4)	3105(9)	8 3

[a] $B_{eq} = 4/3\{\Sigma_i \Sigma_j B_{ij} \boldsymbol{a}_i \boldsymbol{a}_j\}$.

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