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Formation and structures of Pd(II) *N,S*-heterocyclic carbene-pyridyl mixed-ligand complexes

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ABSTRACT

Mononuclear mixed-ligand complexes of Pd(II) containing a *N,S*-heterocyclic carbene (NSHC) with a secondary alkyl *N*-substituent and pyridyl ligand, with the general formula $[PdI_2(C_{10}H_{11}NS)L]$ ($C_{10}H_{11}NS$ = 3-isopropylbenzothiazolin-2-ylidene; L = pyridine, 2-aminopyridine, 3-iodopyridine and 4-*tert*-butyl-pyridine) have been synthesized and characterized by X-ray single-crystal crystallography. Both solution and solid-state structures, as evident from their ^{1}H NMR spectra and X-ray structures, show anagostic γ-hydrogen interactions of metal with methine of the substituent on the carbene or pyridyl ligand giving 5-membered-chelate-like structures.

1. Introduction

The growing interest of the organometallic and catalytic chemistry of *N*-heterocyclic (NHC) carbenes [1–4] has led to the emergence of carbenes that are stabilized by different types of heterocycles [5–12], notably *N,S*-heterocyclic (NSHC) carbenes [13–22]. Presence of sulfur without an exocyclic substituent offers an alternative in catalyst design to the use of bulky substituents on nitrogen in NHC ligands. Accordingly, a series of Pd(II) NSHC complexes [23,24] and their use as precursors to NSHC-based mixed-ligand complexes have been reported [25,26]. Introduction of a second hetero-ligand provides a simple and versatile means to tune the electronic and steric properties of the resultant complex and its chemical and catalytic behaviors. Similar development is witnessed in the mixed-ligand NHC complexes [27–35] especially in pyridyl carbene complexes. In our earlier report, 3-substituted benzothiazolium salts are conveniently prepared from benzothiazole and suitable primary alkyl halides [23–26]. We herein report an extension of this methodology to secondary alkyl halides and the structural features of the resultant series of carbene-pyridyl complexes. The use of pyridyl as a second ligand to enhance the catalytic activities is probably best represented by the PEPPSI™ system [36–42]. It is common knowledge that the nature of the alkyl/aryl substituent would influence the catalytic performance whereas many highly active catalysts are found in NHC ligands that bear a sterically hindered substituent to facilitate the reductive elimination step [2,43–49].

2. Results and discussion

2.1. Neat synthesis of benzothiazolium salt **A**

3-Isopropylbenzothiazolium tri-iodide $C_{10}H_{12}NS^+I_3^-$, **A**, forms readily from the reaction of benzothiazole in neat 2-iodopropane (excess). Unlike the related 1,3-diisopropylbenzimidazolin-2-ylidene analogue, *i*Pr_2-bimyH$^+$I$^-$ [50], it is isolated in its tri-iodide form, presumably from iodide and iodine addition reaction. The formation of iodine, which notably appears as a purple solid on the wall of the condenser at the conclusion of the reaction, could be traced to photo-activation of alkyl iodide giving alkyne and iodine in a radical mechanism [51]. The somewhat unsatisfactory yield (32%) is attributed to base-assisted Hofmann elimination of 3-isopropylbenzothiazolium iodide to propene and benzothiazole (Scheme 1). The yield of **A** can be raised to 44% when iodine is added to the reaction. The product as a salt is soluble in common organic solvents (e.g. halogenated solvents, ROH, THF, CH_3CN, DMSO, DMF) and water, and generally more soluble than 3-benzyl-, 3-(2-propenyl)- and 3-propylbenzothiazolium bromides [23–26].

The thiazolium proton (SC*H*N) resonance is characteristically downfield shifted (11.52 ppm). It is also more deshielded compared to *i*Pr_2-bimyH$^+$I$^-$ (10.79 ppm) [50] which is expected. The downfield-shift of the thiazolium carbon (δC = 163.1 ppm)

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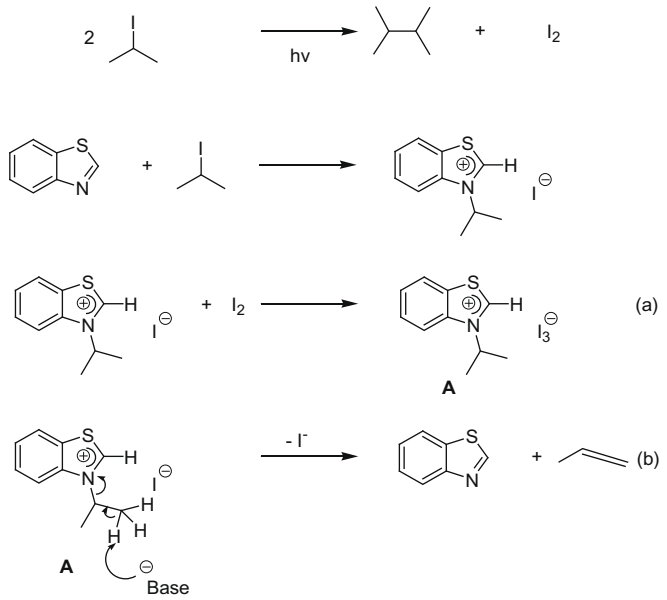


Scheme 1. Proposed formation pathway of benzothiazolium salt A and side products.

by ~20 ppm compared to the azolium carbon in iPr$_2$-bimyH$^+$X$^-$ (X = I, 139.5 [50]; X = Br, 140.7 ppm [52]) is also within expectation. The positive mode ESI mass spectrum shows a principal peak at m/z = 178 corresponding to the thiazolium cation. X-ray single-crystal diffraction of **A** confirmed the identity of the 3-isopropyl substituted benzothiazolium cation with the linear tri-iodide anion (Fig. 1).

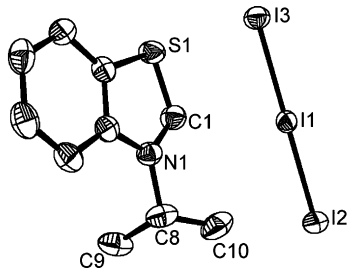


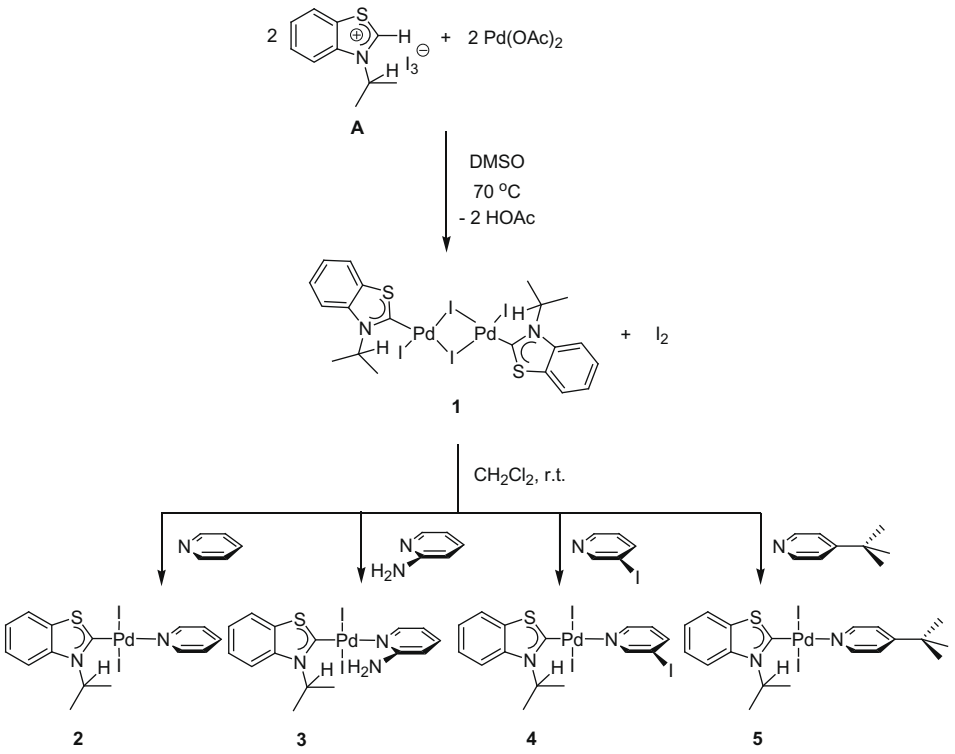
Fig. 1. ORTEP representation of **A** with 50% thermal ellipsoids and labeling scheme; hydrogen atoms are omitted for clarity.

2.2. Synthesis of mononuclear palladium(II) mixed-ligand complexes via the dinuclear complex

A 1:1 mixture of molar of Pd(OAc)$_2$ and **A** stoichiometrically reacts to give [PdI(μ-I)(C$_{10}$H$_{11}$NS)]$_2$ (**1**), using a modified procedure reported for [PdBr(μ-Br)(NSHC)]$_2$ [NSHC = 3-benzylbenzothiazolin-2-ylidene] [23]. The disappearance of the downfield SCHN proton resonance infers successful complexation. This is substantiated by the carbenoid resonance (^{13}C) at 184.0 ppm which was not detected in [PdBr(μ-Br)(NSHC)]$_2$ [NSHC = 3-benzyl- and 3-propylbenzothiazolin-2-ylidene] [23,25], due to lower solubility of the latter.

The isopropyl methine proton (6.22 ppm) is significantly downfield shifted (Δ 0.71 ppm) compared to **A** (5.51 ppm), which could be explained by an intramolecular electrostatic anagostic C–H···Pd interaction, which is substantiated by the solid-state structure described below.

Using the reported method [23–26], mononuclear Pd(II) complexes **2–5** with mixed-ligands can be easily prepared through a bridge–cleavage reaction in 70–90% yields from **1** with addition



Scheme 2. Synthesis of palladium(II) carbene-pyridyl complexes **1–5**.

Table 1
Comparison of selected spectroscopic and structural data of benzothiazolium **A** and its complexes **1–5**.

	A	1	2	3	4	5
δ (^{1}H): C*H*(CH$_3$)$_2$ (ppm)	5.51[b]	6.22[c]	6.57[b]	6.54[b]	6.53[b]	6.58[b]
δH (Δδ*H*)[a] (ppm)	–	0.71	1.06	1.03	1.02	1.07
δ (^{13}C): C$_{carbene}$ (ppm)	163.1[b]	184.0[c]	189.4[b]	191.6[b]	187.8[b]	189.0[b]
d (C–H···Pd) (Å)		2.66	2.68	2.67	2.66	2.64, 2.70
θ (C–H···Pd) (°)		122.6	122.6	123.0	123.0	123.2 122.5

[a] Δδ*H* = δH(CHMe$_2$ in complex) − δH(CHMe$_2$ in **A**).
[b] Recorded in CDCl$_3$.
[c] Recorded in DMSO-d_6.

of donors, *viz*. pyridine, 2-aminopyridine, 3-iodopyridine and 4-*tert*-butyl-pyridine (Scheme 2). The isopropyl methine protons of **2–5** (6.53–6.58 ppm) show similar shifts compared to **A** (Δ*H* = 1.02–1.07 ppm) (Table 1). The pendant amine on the pyridine ring in **3** gives a broad singlet at 5.38 ppm downfield shifted from the free ligand (broad singlet, 4.69 ppm), possibly attributed to restricted C–NH$_2$ free rotation due to intramolecular H-bonding [64]. The ^{13}C NMR signals (CDCl$_3$) of the carbenoid carbons of **2–5** (**2**: 189.4, **3**: 191.6, **4**: 187.8 and **5**: 189.9 ppm) (Table 1) are deshielded compared to the parent complex **1**. This could be explained by the inductive effect of the *N*-donor ligand that lowers the Lewis-acidity of the Pd(II) center.

2.3. Molecular structures

X-ray single-crystal diffraction studies were carried out on **1–5** (Figs. 2–6 and Tables 2 and 3). Complex **1,** which crystallizes as CH$_2$Cl$_2$ solvate (**1** · CH$_2$Cl$_2$), is a dinuclear planar Pd(II) complex with doubly bridging iodide (Fig. 2). The two NHC carbenes across the coordination plane are *anti* to each other. The carbene ring planes are almost perpendicular to the [Pd$_2$C$_2$I$_4$] coordination plane with a dihedral angle measured at 88.6°. The two *N*-isopropyl substituents are on the opposite sides of the metal coordination plane, thus minimizing any inter-ligand contacts. The Pd–I bonds can be divided into three types with significantly different lengths. The terminal Pd–I is understandably the shortest (2.5856(6) Å) whereas the bridged bonds that are *trans* to the carbenes are the longest (2.6594(7) Å), due to the strong *trans* influence of the NSHC carbene. In agreement with the ^{1}H NMR data, the isopropyl CH groups are orientated toward the metal center with C–H···Pd at 2.66 Å and C–H···Pd angles 122.6°, which lie within the broad range of 2.3–2.9 Å and 110–170° respectively reported for weak anagostic interactions [53–63]. Such electrostatic contact in sq planar d^8 system could involve interaction of the Pd(II) filled d_z^2- or $d_{xz/yz}$ orbital and the C–H σ^* orbital [53–63]. Albinati, Pregosin and co-workers have reported such C–H···M (M = Pt^{II} or Pd^{II}) interactions in non-carbene systems [64–66]. Similar phenomena have also been observed in a Rh(I) complex with a six or seven-membered NHC ring [7,67,68] and d^8 NHC complexes [50,53–58,69].

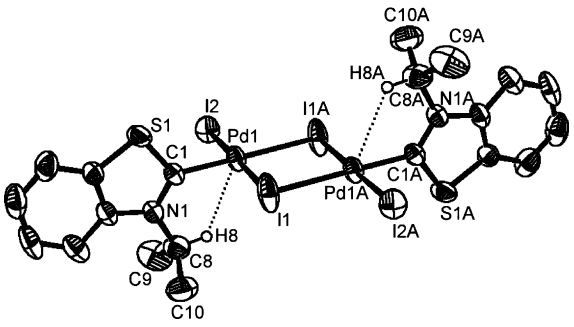


Fig. 2. ORTEP representation of compound **1** with 50% thermal ellipsoids and labeling scheme. The hydrogen atoms except those involved in metal interactions are removed to improve clarity.

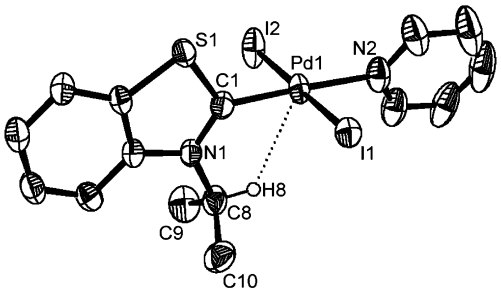


Fig. 3. ORTEP representation of compound **2** with 50% thermal ellipsoids and labeling scheme. The hydrogen atoms except that involved in metal interaction are removed to improve clarity.

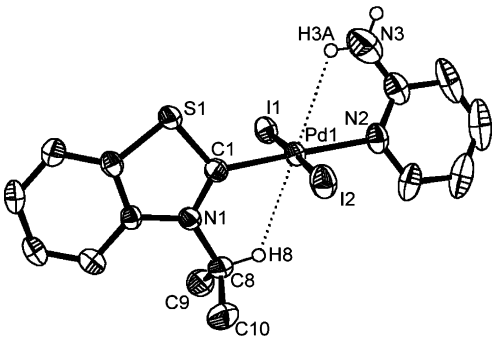


Fig. 4. ORTEP representation of complex **3** with 50% thermal ellipsoids and labelling scheme. The hydrogen atoms except those involved in metal interactions are removed to improve clarity.

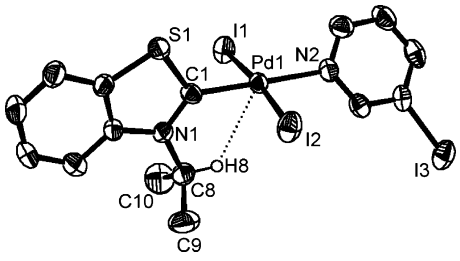


Fig. 5. ORTEP representation of compound **4** with 50% thermal ellipsoids and labeling scheme. The hydrogen atoms except that involved in metal interaction are removed to improve clarity.

As expected, all complexes **2–5** are isostructural and mononuclear, with *trans*-configuration for pyridyl and carbene ligands in an essentially sq planar Pd(II) sphere (Figs. 3–6). The Pd–C bond in **2** [1.954(4) Å] and that in [PdBr$_2$(NHC)(pyridine)] (NHC = 1,3-diisopropylbenzimidazolin-2-ylidene) [1.953(4) Å] are comparable (Fig. 3) [70]. The shorter Pd–N$_{pyridine}$ [2.088(4) Å] in **2** (compared to 2.113(3) Å in the Pd-benzimidazolyl analogue) [70] however could reflect a slightly lower *trans*-influence of NHSC compared to NHC ligands.

The 2-aminopyridyl ring of **3** is twisted away from coplanarity with the coordination plane such that one of the protons of the pendant amine shows H-bonding interaction with the metal (N–H(3A)···Pd(1) 2.67 Å) above the metal plane (Fig. 4). Below the plane, the isopropyl proton γ-interacts with the metal (C8–H8···Pd(1) 2.67 Å), thus effectively resulting in a [4 + 2]

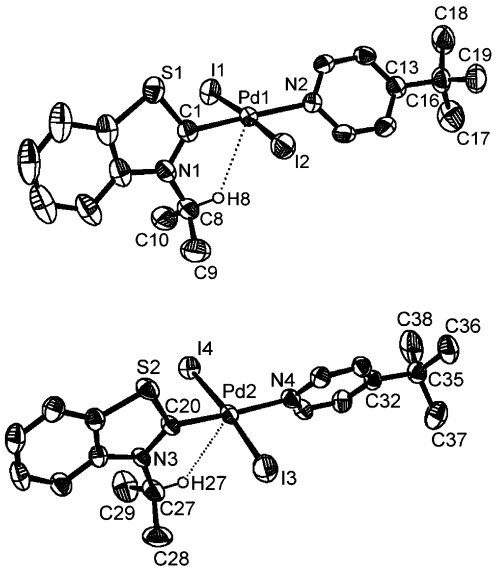


Fig. 6. ORTEP representation of both independent molecules in the asymmetric unit cell of **5** with 50% thermal ellipsoids and labeling scheme. The hydrogen atoms except that involved in metal interactions are removed to improve clarity.

pseudo-octahedral structure for Pd(II). The C–N bond (1.319(8) Å) of amine on the pyridine ring is significantly shorter than a normal amine C–N(H_2) single bond (~1.44 Å), indicating substantial π character arising from electron delocalization of the amine lone pair to the pyridyl ring [71].

Similar anagostic interactions between the isopropyl proton and metal is invariably found in **2–5** (2.64–2.70 Å). This is supported by the decrease of the C1–N1–C8 angle from 124.40(2)° in **A** to 120.30(5)–121.00(5)° in **1–5** despite the replacement of H by a much larger Pd atom (Table 2). The persistent anagostic interactions in solution and solid-state represents a structural feature of this series of complexes. The pertinent spectroscopic and structural data that support these interactions are listed in Table 1.

The carbene ring planes of complexes **2** and **4–5** are twisted out of the {$PdCNI_2$} coordination planes to give near-perpendicular (89.2–91.8°) dihedral angles in order to minimize steric conflict. The Pd–$C_{carbene}$ bonds (1.938(5)–1.956(4) Å) of complexes **2–5** are slightly shorter and presumably stronger than those in the precursor complex **1** (1.968(6) Å) indicating the higher *trans* influence of iodide than pyridyl. The Pd–N bonds (2.086(4)–2.108(5) Å) of **2–5** are within the range but generally slightly shorter than those found in the analogous PEPPSI-IPr and PEPPSI with *N/O*-functionalized NHCs [2.089(3)–2.137(2) Å] [36,46]. This is also suggestive of higher *trans* influence of NHC compared to NSHC ligands.

Table 2
Selected bond lengths (Å) and angles (°) of **A** and **1–5**.

Bond lengths (Å)	**A**	**1**	**2**	**3**	**4**	**5**		
						Molecule a	Molecule b	
Pd1–C1	–	1.968(6)	1.954(4)	1.956(4)	1.948(6)	1.946(6)	Pd2–C20	1.938(5)
Pd1–N2	–	–	2.088(4)	2.095(4)	2.108(5)	2.106(5)	Pd2–N4	2.086(4)
Pd1–I1	–	2.659(7)	2.604(5)	2.603(4)	2.594(7)	2.589(6)	Pd2–I4	2.6088(6)
Pd1–I1#2	–	2.619(6)	–	–	–	–		
Pd1–I2	–	2.586(6)	2.610(5)	2.615(5)	2.611(7)	2.603(7)	Pd2–I3	2.6091(6)
Pd1#2–I1	–	2.620(2)	–	–	–	–		
S1–C1	1.681(3)	1.691(6)	1.717(5)	1.716(5)	1.715(6)	1.711(6)	S2–C20	1.709(5)
N1–C1	1.311(4)	1.325(7)	1.329(6)	1.329(5)	1.329(8)	1.335(7)	N3–C20	1.334(6)
N1–C8	1.498(3)	1.478(8)	1.495(6)	1.491(5)	1.488(8)	1.485(8)	N3–C27	1.495(7)
C8–C9	1.519(4)	1.531(11)	1.512(7)	1.502(7)	1.514(12)	1.514(10)	C27–C28	1.514(10)
C8–C10	1.514(5)	1.545(12)	1.518(8)	1.524(6)	1.535(11)	1.520(10)	C27–C29	1.500(9)
C12–N3	–	–	–	1.319(8)	–	–		
C13–C16	–	–	–	–	–	1.534(8)	C32–C35	1.525(8)
C16–C17	–	–	–	–	–	1.525(11)	C35–C37	1.545(9)
C16–C18	–	–	–	–	–	1.515(10)	C35–C38	1.522(10)
C16–C19	–	–	–	–	–	1.509(10)	C35–C36	1.525(9)
I3–C12	–	–	–	–	2.090(7)	–		
Angles (°)								
C1–Pd1–N2	–	–	178.03(2)	178.41(2)	178.80(2)	179.10(2)	C20–Pd2–N4	175.7(2)
C1–Pd1–I1	–	128.87(2)	88.25(1)	87.50(1)	86.78(2)	86.62(2)	C20–Pd2–I4	88.56(17)
C1–Pd1–I2	–	87.89(2)	89.84(1)	89.60(1)	88.45(2)	87.19(2)	C20–Pd2–I3	86.08(17)
C1–Pd1–I1#2	–	91.79(2)	–	–	–	–		
I1–Pd1–I2	–	92.67(2)	177.07(2)	176.96(2)	174.18(3)	173.78(2)	I4–Pd3–I3	174.41(2)
I1#2–Pd1–I1	–	87.67(2)	–	–	–	–		
I2–Pd1–I1#2	–	178.84(3)	–	–	–	–		
I1–Pd1–N2	–	–	90.41(1)	91.52(1)	93.50(2)	94.15(1)	I4–Pd2–N4	91.50(13)
I2–Pd1–N2	–	–	91.56(1)	91.39(1)	91.34(2)	92.04(1)	I3–Pd2–N4	93.97(13)
I2–I1–I3	177.95(8)	–	–	–	–	–		
N1–C1–S1	115.00(2)	112.10(4)	111.40(3)	111.30(3)	111.00(4)	111.50(4)	N3–C20–S2	110.9(4)
N1–C1–Pd1	–	127.50(4)	128.50(3)	128.40(3)	128.30(4)	127.30(4)	N3–C20–Pd2	129.7(4)
S1–C1–Pd1	–	120.50(3)	120.10(2)	120.3(2)	120.70(3)	121.10(3)	S2–C20–Pd2	119.4(3)
C1–N1–C8	124.40(2)	121.00(5)	120.90(4)	120.60(4)	120.30(5)	120.80(5)	C20–N3–C27	120.5(5)
C9–C8–C10	112.90(3)	115.10(7)	115.90(5)	114.90(4)	114.20(7)	115.00(6)	C28–C27–C29	116.1(6)
N1–C8–C9	109.10(2)	110.60(6)	110.70(4)	111.60(4)	111.30(6)	111.00(6)	N3–C27–C28	110.4(5)
N1–C8–C10	111.30(2)	110.30(7)	111.10(4)	111.20(4)	111.40(6)	111.70(5)	N3–C27–C29	111.6(5)
N2–C12–N3	–	–	–	118.40(5)	–	–		
C13–C12–N3	–	–	–	119.70(6)	–	–		
C17–C16–C13	–	–	–	–	–	110.00(6)	C37–C35–C32	107.9(5)
C18–C16–C13	–	–	–	–	–	112.00(6)	C38–C35–C32	112.3(5)
C18–C16–C17	–	–	–	–	–	108.80(7)	C38–C35–C37	107.9(6)
C19–C16–C13	–	–	–	–	–	108.10(6)	C36–C35–C32	108.9(5)
C19–C16–C17	–	–	–	–	–	108.90(6)	C36–C35–C37	110.0(6)
C19–C16–C18	–	–	–	–	–	109.00(7)	C36–C35–C38	109.8(6)

Table 3
Selected crystallographic data of **A** and **1–5**.

	A	1	2	3	4	5
Formula	$C_{10}H_{12}I_3N_1S_1$	$C_{21}H_{24}I_4N_2S_2Pd$	$C_{15}H_{16}I_2N_2S_1Pd$	$C_{15}H_{17}I_2N_3S_1Pd$	$C_{15}H_{15}I_3N_2S_1Pd$	$C_{19}H_{24}I_2N_2S_1Pd$
Formula weight	558.97	1124.39	616.56	631.58	742.45	672.66
Color, habit	Red, block	Red, block	Orange, block	Yellow, plate	Orange, block	Orange, block
Crystal size (mm^3)	0.40 × 0.38 × 0.18	0.22 × 0.12 × 0.10	0.36 × 0.12 × 0.10	0.26 × 0.12 × 0.06	0.44 × 0.28 × 0.12	0.36 × 0.30 × 0.14
Temperature (K)	293(2)	223(2)	223(2)	223(2)	295(2)	223(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	*P*2(1)/*n*	*C*2/*c*	*P*2(1)/*n*	*P*2(1)/*n*	*Pbca*	*P*2(1)/*n*
a (Å)	11.8255(5)	13.5986(12)	9.9163(6)	9.8906(6)	16.2344(7)	9.2994(12)
b (Å)	9.8827(5)	13.2155(12)	12.5278(8)	12.6917(8)	14.9728(7)	14.6385(17)
c (Å)	13.5113(6)	18.1317(16)	15.3999(9)	15.6072(10)	16.8210(8)	33.984(4)
α (°)	90	90	90	90	90	90
β (°)	105.5350(10)	94.571(2)	91.4490(10)	90.075(2)	90	96.611(3)
γ (°)	90	90	90	90	90	90
V ($Å^3$)	1521.35(12)	3248.1(5)	1912.5(2)	1959.1(2)	4088.8(3)	4595.5(10)
Z	4	4	4	4	8	8
$D_{calcd.}$ (g cm^{-3})	2.440	2.299	2.141	2.141	2.412	1.944
Radiation used	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
μ (mm^{-1})	6.274	5.133	4.303	4.205	5.538	3.590
θ range (°)	2.04–27.50	2.15–27.50	2.10–27.50	2.07–27.49	2.21–27.50	1.52–27.50
Unique data	19172	11334	13099	13656	27562	32411
[$R_{(int)}$]	0.0217	0.0252	0.0272	0.0347	0.0435	0.0386
Maximum, minimum transmission	0.3980, 0.1881	0.6278, 0.3981	0.6729, 0.3065	0.7865, 0.4078	0.5562, 0.1943	0.6333, 0.3581
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0206, wR_2 = 0.0497	R_1 = 0.0463 wR_2 = 0.1234	R_1 = 0.0384 wR_2 = 0.0864	R_1 = 0.0348 wR_2 = 0.0788	R_1 = 0.0523 wR_2 = 0.1100	R_1 = 0.0502 wR_2 = 0.1090
R indices (all data)	R_1 = 0.0226 wR_2 = 0.0606	R_1 = 0.0647 wR_2 = 0.1340	R_1 = 0.0474 wR_2 = 0.0903	R_1 = 0.0494 wR_2 = 0.0840	R_1 = 0.0604 wR_2 = 0.1134	R_1 = 0.0672 $wR2$ = 0.1154
Goodness-of-fit (GOF) on F^2	1.097	1.050	1.062	0.983	1.242	1.104
Peak/hole (e $Å^{-3}$)	0.706/−0.718	2.300/−1.243	2.132/−0.935	1.138/−0.437	1.505/−0.618	1.368/−0.921

3. Conclusion

Introduction of a secondary alkyl on nitrogen in the benzothiazolium ring or an amine at the α-position to a pyridyl invariably gives rise to γ-hydrogen interactions with the metal resulting in 5-membered-ring chelate-like structures. The d^8 sq planar Pd(II) thus takes up a pseudo-sq pyramidal or octahedral geometry. Although anagostic interactions are usually found in d^8 metals, they are occasionally associated with other systems such as Cu(II) (d^9) [72,73]. There are emerging discussions on the significance of such bonding [63] and possible applications in bio-active systems [74]. This provides an impetus for us to examine if such dual γ-interactions from a mixed-ligand motif can be applied to stabilize non-d^8 systems. Work is ongoing in this direction.

4. Experimental

4.1. General procedures

Unless otherwise stated, all manipulations were performed without taking precautions to exclude air and moisture. All solvents were used as received. Benzothiazole was purchased from Sigma–Aldrich® and distilled prior to use. 2-Iodo-propane, 2-aminopyridine, 3-iodopyridine, 4-*tert*-butyl-pyridine and $Pd(OAc)_2$ were purchased from Sigma–Aldrich® and used as received. ^1H and ^{13}C NMR spectra were recorded on Bruker AMX 500 spectrometers using Me_4Si as an internal standard. ESI mass spectra were obtained using a Finnigan MAT 731 LCQ spectrometer. Elemental analyses were performed on a Perkin–Elmer PE 2400 elemental analyzer at the Department of Chemistry, National University of Singapore.

4.2. 3-Isopropylbenzothiazolium tri-iodide (*A*)

A mixture of neat benzothiazole (3.74 g, 27.65 mmol) and 2-iodo-propane (15.33 g, 90.16 mmol) was stirred at 100 °C for 2 days. The brown oil thus obtained was washed several times with ethyl acetate to afford yellow solid. Diffusion of Et_2O into a concentrated CH_2Cl_2 solution yielded transparent crystals suitable for X-ray diffraction studies. Yield: 4.91 g (8.78 mmol, 32%). ^1H NMR (500 MHz, $CDCl_3$): δ 11.52 (s, 1H, NCHS), 8.54 (d, $^3J_{HH}$ = 8.20 Hz, 1H, Ar-H), 8.24 (d, $^3J_{HH}$ = 8.80 Hz, 1H, Ar-H), 7.90 (t, $^3J_{HH}$ = 7.90 Hz, 1H, Ar-H), 7.80 (t, $^3J_{HH}$ = 7.88 Hz, 1H, Ar-H), 5.51 (m, $^3J_{HH}$ = 6.63 Hz, 1H, $CH(CH_3)_2$), 1.93 (d, $^3J_{HH}$ = 6.90 Hz, 6H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 163.1 (s, NCHS), 140.1, 131;6, 130.3, 129.2, 125.8, 117.1 (s, Ar-C), 57.4 (s, $CH(CH_3)_2$), 23.6 (s, $CH(CH_3)_2$). MS (ESI, positive mode) *m/z* (%): 178 (100) $[M - I_3]^+$. Anal. Calc. for $C_{10}H_{12}I_3NS$ (M = 558.99): C, 21.49; H, 2.16; N, 2.51; S, 5.74. Found: C, 21.81; H, 2.16; N, 2.54; S, 5.12%.

4.3. Diiodo(μ-diiodo)bis(3-isopropylbenzothiazolin-2-ylidene)-dipalladium(II) (*1*)

Complex **1** was prepared based on a literature method [29] from **A** (559 mg, 1 mmol) and $Pd(OAc)_2$ (225 mg, 1 mmol). Purification by column chromatography using CH_2Cl_2 as effluent gave **1** as a red solid. Slow evaporation of a concentrated CH_2Cl_2 solution yielded red crystals suitable for X-ray diffraction studies. Yield: 193 mg (0.18 mmol, 36%). ^1H NMR (500 MHz, DMSO-d_6): δ 8.24 (d, $^3J_{HH}$ = 8.20 Hz, 2H, Ar-H), 8.10 (d, $^3J_{HH}$ = 8.20 Hz, 2H, Ar-H), 7.56 (t, $^3J_{HH}$ = 7.55 Hz, 2H, Ar-H), 7.50 (t, $^3J_{HH}$ = 7.55 Hz, 2H, Ar-H), 6.22 (m, $^3J_{HH}$ = 6.95 Hz, 2H, $CH(CH_3)_2$), 1.80 (d, $^3J_{HH}$ = 6.95 Hz, 12H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6): δ 184.0 (s, NCS), 140.7, 137.9, 127.4, 125.6, 123.2, 116.9 (s, Ar-C), 55.4 (s, $CH(CH_3)_2$), 18.7 (s, $CH(CH_3)_2$). MS (ESI, positive mode) *m/z* (%): 1019 (100) $[M-I+CH_3OH+CH_3CN]^+$. Anal. Calc. for $C_{20}H_{22}I_4N_2S_2Pd_2$ (M = 1074.99): C, 22.35; H, 2.06; N, 2.61; S, 5.97. Found: C, 22.67; H, 2.02; N, 2.51; S, 6.30%.

4.4. trans-Diiodo(3-isopropylbenzothiazolin-2-ylidene)-(pyridine)palladium(II) (*2*)

Pyridine (5 mL) was added to complex **1** (602 mg, 0.056 mmol) and the mixture was stirred overnight at r.t. The clear yellow solution thus obtained was evaporated to dryness under vacuum. The

solid product **2** was redissolved in CH_2Cl_2 onto which was layered Et_2O to give yellow single-crystals upon standing. Yield: 678 mg (0.11 mmol, 98%). ^1H NMR (500 MHz, $CDCl_3$): δ 9.06 (d, $^3J_{HH}$ = 6.30 Hz, 2H, 2,6-py-H), 7.89 (d, $^3J_{HH}$ = 8.15 Hz, 1H, 4-py-H), 7.75 (m, 2H, 3,5-py-H), 7.44 (t, $^3J_{HH}$ = 7.90 Hz, 1H, Ar-H), 7.38–7.33 (m, 3H, Ar-H), 6.57 (m, $^3J_{HH}$ = 7.10 Hz, 1H, $CH(CH_3)_2$), 1.92 (d, $^3J_{HH}$ = 6.95 Hz, 6H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 189.4 (s, NCS), 154.1, 141.3, 138.9, 137.8, 126.0, 124.6, 122.2, 115.8 (s, py-C and Ar-C), 63.4 (s, $CH(CH_3)_2$), 19.2 (s, $CH(CH_3)_2$). MS (ESI, positive mode) *m/z* (%): 587 (100) $[M-I+3CH_3OH]^+$. Anal. Calc. for $C_{15}H_{16}I_2N_2SPd$ (M = 616.59): C, 29.22; H, 2.62; N, 4.54; S, 5.20. Found: C, 30.95; H, 2.66; N, 4.72; S, 5.64%.

4.5. trans-Diiodo(3-isopropylbenzothiazolin-2-ylidene)(2-aminopyridine)palladium(II) (**3**)

A mixture of **1** (110 mg, 0.102 mmol) and 2-aminopyridine (19 mg, 0.204 mmol) was suspended in CH_2Cl_2 (5 mL) and stirred overnight at r.t. Upon solvent evaporation under vacuum, the yellow solid was washed with Et_2O several times. Diffusion of Et_2O into a concentrated CH_2Cl_2 solution yielded yellow crystals suitable for X-ray diffraction studies. Yield: 100 mg (0.158 mmol, 77%). ^1H NMR (500 MHz, $CDCl_3$): δ 7.90 (d, $^3J_{HH}$ = 8.20 Hz, 1H, 2-py-H), 7.78 (m, 1H, 3-py-H), 7.55-7.49 (m, 1H, Ar-H), 7.47–7.42 (m, 2H, Ar-H), 7.41–7.37 (m, 1H, Ar-H), 6.67 (m, 1H, 4-py-H), 6.59 (d, $^3J_{HH}$ = 8.20 Hz, 1H, 5-py-H), 6.54 (m, $^3J_{HH}$ = 7.25 Hz, 1H, $CH(CH_3)_2$), 5.38 (s br, 2H, NH_2), 1.94 (d, $^3J_{HH}$ = 7.55 Hz, 6H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 191.6 (s, NCS), 157.9, 149.7, 141.4, 138.5, 137.7, 126.1, 124.6, 122.4, 115.9, 114.1, 108.6 (s, py-C and Ar-C), 63.3 (s, $CH(CH_3)_2$), 19.4 (s, $CH(CH_3)_2$). MS (ESI, positive mode) *m/z* (%): 504 (50) $[M-I]^+$, 1042 (100) $2[M-I]^+ + CH_3OH$. Anal. Calc. for $C_{15}H_{17}I_2N_3SPd$ (M = 631.63): C, 28.52; H, 2.71; N, 6.65; S, 5.08. Found: C, 28.92; H, 2.69; N, 6.54; S, 5.06%.

4.6. trans-Diiodo(3-isopropylbenzothiazolin-2-ylidene)(3-iodopyridine)palladium(II) (**4**)

Complex **4** was prepared as a yellow solid in analogy to **3** from **1** (56 mg, 0.052 mmol) and 3-iodopyridine (24 mg, 0.117 mmol). Yellow single-crystals of **4** were obtained from a diffusion of Et_2O into a concentrated CH_2Cl_2 solution. Yield: 49 mg (0.065 mmol, 62%). ^1H NMR (500 MHz, $CDCl_3$): δ 9.32 (s, 1H, 2-py-H), 9.06 (d, $^3J_{HH}$ = 5.05 Hz, 1H, 5-py-H), 8.07 (d, $^3J_{HH}$ = 8.20 Hz, 1H, Ar-H), 7.90 (d, $^3J_{HH}$ = 8.20 Hz, 1H, Ar-H), 7.77 (d, $^3J_{HH}$ = 7.55 Hz, 1H, 4-py-H), 7.45 (t, $^3J_{HH}$ = 7.58 Hz, 1H, Ar-H), 7.38 (t, $^3J_{HH}$ = 7.25 Hz, 1H, Ar-H), 7.14 (t, $^3J_{HH}$ = 6.60 Hz, 1H, 3-py-H), 6.53 (m, 1H, $^3J_{HH}$ = 6.95 Hz, $CH(CH_3)_2$), 1.92 (d, $^3J_{HH}$ = 6.95 Hz, 6H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 187.8 (s, NCS), 159.6, 152.7, 146.3, 141.2, 138.8, 126.1, 125.5, 124.6, 122.2, 115.9, 91.9 (s, py-C and Ar-C), 63.5 (s, $CH(CH_3)_2$), 19.2 (s, $CH(CH_3)_2$). MS (ESI, positive mode) *m/z* (%): 583 (100) $[M-I-CH_3OH]^+$, 742 (50) $[M+H]^+$. Anal. Calc. for $C_{15}H_{15}I_3N_2SPd.CH_2Cl_2$ (M = 827.42): C, 23.23; H, 2.07; N, 3.39; S, 3.88. Found: C, 22.72; H, 1.90; N, 3.38; S, 4.66%. The elemental analysis remained unsatisfactory despite repeated purification and analysis, possibly due to complex solvation.

4.7. trans-Diiodo(3-isopropylbenzothiazolin-2-ylidene)(4-tert-butylpyridine)palladium(II) (**5**)

Complex **5** was prepared as a yellow solid in analogy to **3** from **1** (140 mg, 0.13 mmol) and 4-*tert*-butyl-pyridine (35 mg, 0.26 mmol). Yellow single-crystals of **5** were obtained from a diffusion of Et_2O into a concentrated CH_2Cl_2 solution. Yield: 96 mg (0.14 mmol, 15%). ^1H NMR (500 MHz, $CDCl_3$): δ 8.93 (d, $^3J_{HH}$ = 6.90 Hz, 2H, 2, 6-py-H), 7.89 (d, $^3J_{HH}$ = 8.20 Hz, 1H, Ar-H), 7.76 (d, $^3J_{HH}$ = 7.60 Hz, 1H, Ar-H), 7.44 (t, $^3J_{HH}$ = 7.58 Hz, 1H, Ar-H), 7.37 (t, $^3J_{HH}$ = 7.55 Hz, 1H, Ar-H), 7.31 (d, $^3J_{HH}$ = 6.90 Hz, 2H, 3, 5-py-H), 6.58 (m, $^3J_{HH}$ = 7.09 Hz, 1H, $CH(CH_3)_2$), 1.92 (d, $^3J_{HH}$ = 6.95 Hz, 6H, $CH(CH_3)_2$), 1.32 (S, 9H, $(CH_3)_3$). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 189.9 (s, NCS), 162.4, 153.6, 149.6, 141.3, 138.9, 126.0, 124.5, 122.2, 121.8, 115.8 (s, py-C and Ar-C), 63.3 (s, $CH(CH_3)_2$), 35.1 $(CH_3)_3$, 30.3 $(CH_3)_3$, 19.2 (s, $CH(CH_3)_2$). MS (ESI, positive mode) *m/z* (%): 544 (20) $[M-I]^+$, 819 (100) $[M-I]^+ + 2$[*tert*-butyl-pyridine], 948 (80) $[M-I]^+ + 3$[*tert*-butyl-pyridine]. Anal. Calc. for $C_{19}H_{25}I_2N_2SPd$ (M = 673.71): C, 33.87; H, 3.74; N, 4.16; S, 4.76. Found: C, 34.42; H, 3.50; N, 4.11; S, 5.39%.

4.8. X-ray diffraction studies

Single-crystals of complex **1** were obtained by slow evaporation of a concentrated CH_2Cl_2 solution, while those of complexes **2–5** were obtained by diffusion of Et_2O into CH_2Cl_2 solutions. The crystal of **5** contains two independent molecules in the asymmetric unit of the cell. Suitable crystals were mounted on quartz fibers and X-ray data collected on a Bruker AXS APEX diffractometer, equipped with a CCD detector, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The collecting frames of date, indexing reflection and determination of lattice parameters and polarization effects were done with the SMART suite programs [75]. The integration of intensity of reflections and scaling was done by SAINT. The empirical absorption correction was done by SADABS [76]. The space group determination, structure solution and least-squares refinements on $|F|^2$ were carried out with the SHELXTL [77]. The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms. Anisotropic thermal parameters were refined for the rest of the non-hydrogen atoms. The hydrogen atoms were placed in their ideal positions. A selected summary of crystal data for complexes **1–5** are summarized in Tables 2 and 3.

Supplementary material

Crystallographic data for salt **A** and **1–5** in CIF format. This material is available free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: mailto: deposit@ccdc.cam.ac.uk) or at www.ccdc.cam.ac.uk/conts/retrieving.html.

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