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Benzothiazolin-2-ylidene and Azole Mixed-Ligand Complexes of Palladium

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Dedicated to commemorate the 80th anniversary of chemistry research and education in Singapore

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A series of mixed-ligand, mononuclear complexes *trans*-[PdX_2(NSHC)(azole)] [NSHC = N,S-heterocyclic carbene; azole = imidazole, 1-(2,4,6-trimethylphenyl)-1*H*-imidazole, benzimidazole, benzothiazole and benzoxazole] have been prepared and characterised by X-ray single-crystal diffraction. These complexes catalyse the sp^2–sp^3 cross-coupling of fluoroaryl halides with arylboronic acid to give diarylmethanes with good yields and high turnovers.

Introduction

The development of N-heterocyclic carbene complexes and their catalytic applications is a vibrant area of current research.[1] Our recent isolation of dinuclear benzothiazole-based carbene complexes[2] has provided a ready access to a range of hybrid carbene complexes. The introduction of a second ligand with a different nature at the metal core could present a synthetically convenient strategy for tuning the electronic and steric properties of the coordination sphere. This approach is appealing as many of these complexes are catalytically active, although their efficacies often depend strongly on the electronic and steric state of the metal atom and hence the ligands it carries. We shall develop this idea further herein by preparing a range of N,S-heterocyclic carbene (NSHC) complexes[2–4] containing an azole as the second ligand (**A**–**D** in Figure 1). These azoles are inexpensive commercial reagents, which, despite having similar structural motifs to the thiazole-based carbene, are fundamentally different as they are sp^2-hybridised N-donors whose strength varies with the heteroatom in the ring. Mixed carbene/azole complexes are rare in the literature, although one reported example concerns a Sonogashira-active carbomoyl-substituted NHC-(3-methyl-1*H*-imidazole)palladium(II) complex.[5] To the best of our knowledge, no NSHC analogue is known. Azole complexes, such as the catalytically active imidazole,[6] imidazoline[7] and benzoxazole[8] complexes of Cu, Ir, Ru and Pd, are, however, more common. Herein we demonstrate the catalytic potential of this type of complexes by describing their sp^2–sp^3 cross-coupling activities with benzylic halides and an organoboronic acid to give pharmacologically active diarylmethanes.[9] This type of reaction is known to be catalysed by Pd complexes of phosphanes[10] and mixed oxides,[11] palladacycles[12,13] and NHC[14] complexes of Pd but is not known for NSHC complexes. A broad range of polyfunctionalized benzylzinc reagents also undergo smooth cross-coupling reactions catalyzed by $Ni(acac)_2$ and PPh_3.[15]

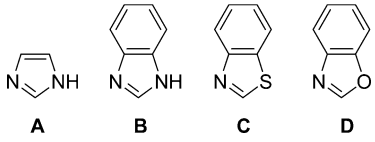

Figure 1. Azole ligands with different heteroatoms.

Results and Discussion

Dinuclear Pd^{II} complexes containing 3-benzyl-, 3-propyl- and 3-isopropylbenzothiazolium-2-ylidene ligands[2] undergo facile stoichiometric bridge-cleavage with an azole [imidazole, 1-(2,4,6-trimethylphenyl)imidazole, benzimidazole, benzothiazole, benzoxazole] to give the mononuclear mixed-ligand complexes **1**–**7** in 53–89% yield (Scheme 1, Table 1). ^{1}H NMR analysis of the products suggested monodentate N-coordination of the azole, with the C-2 proton [NC(H)E] (E = NH, NR, S, O) still in place. Coordination in **1** and **2** occurs preferentially at the sp^2-nitrogen atom, and the oxygen and sulfur atoms of the heterocycle in **4**–**7** are pendant. The two ligands (C-bonded benzothiazolin-2-ylidene and N-bonded benzothiazole) in **4**, **6** and **7** share a common five-membered [C_3NS] thiazole ring. The

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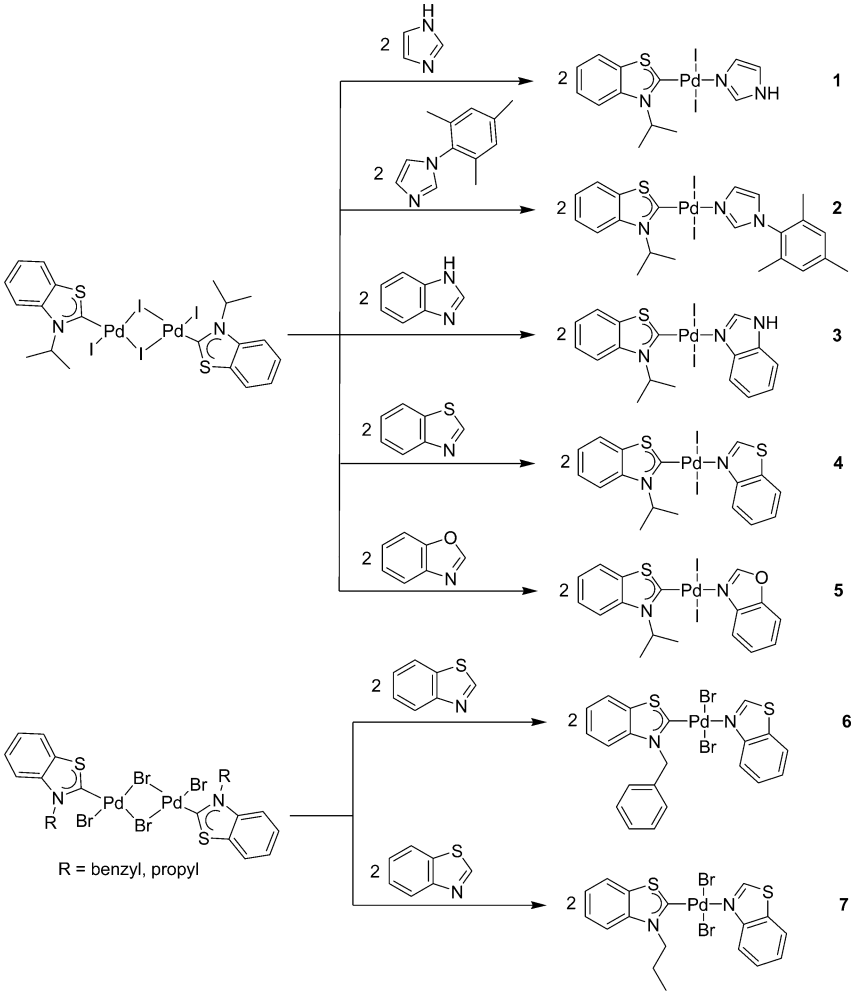
signal of the isopropyl methine proton of **1**–**5** (δ = 6.57–6.68 ppm) is significantly downfield shifted ($\Delta\delta$ = 1.06–1.17 ppm) with respect to that in the benzothiazolium substrate (δ = 5.51 ppm).[2c] This is attributed to an intramolecular anagostic C–H···Pd interaction, as discussed previously.[2c,16–18] The ^{13}C NMR resonances of the carbenic carbon atom of **1**–**7** (δ = 189.0–195.9 ppm) are deshielded with respect to the *trans*-carbamoyl-substituted NHC-(3-methyl-1*H*-imidazole)palladium(II) complex (δ = 151.57 ppm).[5]

Complexes **1**–**7** were subjected to X-ray single-crystal diffraction analysis. They are all mononuclear with a square-planar palladium centre coordinated by the NSHC, azole and two halide ligands. The azole and carbene are invariably *trans*-oriented in this series of isostructural complexes (Figures 2 and 3 and Figures S1–S5 in the Supporting Information; see also Tables 2 and 5). The *cis* complexes are obtained when the incoming ligand (e.g. PR_3) has a higher *trans* influence than the halide.[2b]



Scheme 1. Synthesis of mixed NSHC/azole Pd^{II} complexes **1**–**7**.

Table 1. Comparison of selected spectroscopic and structural data for complexes **1**–**7**.

	1	**2**	**3**	**4**	**5**	**6**	**7**
δ(^{1}H): C*H*(CH$_3$)$_2$ [ppm]	6.57[a]	6.58[a]	6.58[b]	6.68[a]	6.62[b]	–	–
$\Delta\delta$ [ppm][c]	1.06	1.07	1.07	1.17	1.11	–	–
δ(^{1}H): NCHS [ppm]	–	–	–	9.46[a]	–	9.41[a]	9.44[a]
δ(^{1}H): NCHO [ppm]	–	–	–	–	8.74[b]	–	–
δ(^{1}H): NCHN [ppm]	8.41[a]	8.27[a]	8.78[b]	–	–	–	–
δ(^{13}C): $C_{carbene}$ [ppm]	191.0[a]	190.3[a]	192.8[b]	189.9[a]	189.0[b]	195.9[a]	193.6[a]
d(C–H···Pd) [Å]	2.69, 2.76	2.65	2.75	2.75	2.65	–	–
θ(C–H···Pd) [°]	122.30, 121.60	123.50	121.50	121.10	122.90	–	–
d(Pd–C) [Å]	1.948(4), 1.952(4)	1.943(6)	1.946(4)	1.956(9)	1.957(4)	1.952(4)	1.950(3)

[a] Measured in $CDCl_3$. [b] Measured in [D_6]DMSO. [c] $\Delta\delta$ = δH(C*H*Me$_2$ in complex) – δH(C*H*Me$_2$ in 3-isopropylbenzothiazolium-2-ylidene ligand).

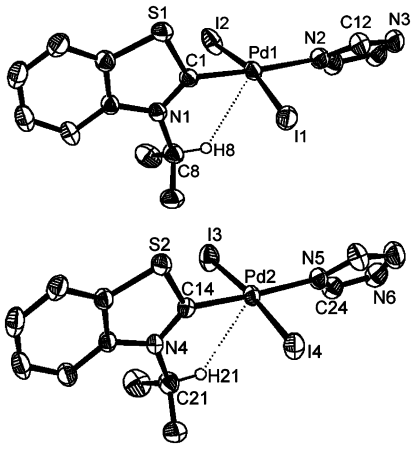


Figure 2. ORTEP representation of two independent molecules in the asymmetric unit cell of **1** with 50% thermal ellipsoids and labelling scheme. All hydrogen atoms, except that involved in metal interaction, have been omitted for clarity.

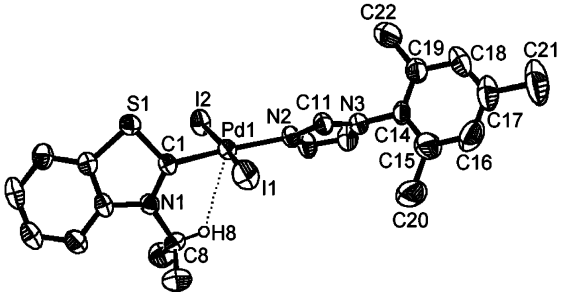


Figure 3. ORTEP representation of complex **2** with 50% thermal ellipsoids and labelling scheme. All hydrogen atoms, except that involved in metal interaction, have been omitted for clarity.

The Pd–$C_{carbene}$ bond lengths [1.943(6)–1.957(4) Å] are within the range observed in other Pd^{II} complexes of benzothiazolin-2-ylidene with a solvent molecule at the *trans* position[2a,3b] but are shorter than in their iodide-bridged precursor [1.968(6) Å],[2c] probably due to the weaker *trans* influence of the azole ligand. The Pd–N_{azole} bond lengths [2.075(3)–2.114(5) Å] are similar to those in other mixed-ligand NHC/azole complexes of Pd^{II}.[5,19] The shortest, and presumably strongest, Pd–C bond in complexes **1**–**5**, which contain the same carbene ligand, is found in **2** together with the longest, and presumably weakest, Pd–N bond, whereas the weakest Pd–C and strongest Pd–N bonds are found in **5**. The carbene ring planes are almost orthogonal (80.30–87.50°) to the metal coordination plane [$PdCNX_2$] (X = Br, I). The angle between the azole and the metal coordination planes in **1**–**7** varies over a wide range (36.6–83.5°).

Metal coordination at the carbon atom in benzothiazolin-2-ylidene complexes **4**, **6** and **7** leads to a contraction of the N–C–S angle [110.60(3)–112.00(7)°],[4a] and greater deviation from sp^2 hybridisation, compared to those complexes containing a benzothiazoly ligand [116.30(3)° or 115.50(7)–116.30(3)°]. The benzo rings of the azole ligands are generally *anti* to the N-substituent of the carbene ring (as in **3**, **5**, **6** and **7**) with **4**, which has a *syn* configuration, the notable exception. The anagostic interactions between the isopropyl CH groups and the metal atom found in solution are also witnessed in the solid-state structures (C–H···Pd 2.65–2.76 Å for **1**–**5**; Table 1). The decrease of the C1–N1–C8 angle from 124.40(2)° in 3-isopropylbenzothiazolium triiodide[2c] to 120.20(3)–122.00(5)° in **1**–**5**, despite the replacement of H by a much larger Pd atom, also supports these intramolecular γ-hydrogen interactions.

The stoichiometric cross-coupling of benzyl halides and arylboronic acids was examined in different solvents at 60 °C at a low catalyst loading of 1 mol-%. Complex **6** was chosen as a representative model as it has the same benzothiazole motif in both ligands and a sterically less demanding N-substituent (Table 3). The use of dmf as solvent (Table 3, Entries 3 and 8) tends to give the highest yields, possibly due to the presence of reducing formic acid.[20] Addition of H_2O to the organic solvent increases the yields significantly (Table 3, Entries 6–9), with a 1:1 mixture of dmf/H_2O giving a quantitative yield with all bases (NaOH, K_2CO_3, Cs_2CO_3) used (Table 3, Entries 8, 10 and 11).

Under optimized conditions in dmf/H_2O (1:1) with K_2CO_3 as the common base, all the complexes are Suzuki-active toward the formation of pharmacologically active diarylfluoromethanes (Table 4).[9] As the complexes are air-stable, these catalytic preparations can be carried out in standard glassware in air. They invariably give quantitative yields for benzyl bromide (Table 4, Entries 1–7) and near-quantitative yields for 2-fluorobenzyl (Table 4, Entries 8–14), 2,4-difluorobenzyl (Table 4, Entries 15–21) and 2,6-difluorobenzyl bromides (Table 4, Entries 22–28) at 60 °C within 2 h (Table 4). A previous report on the use of *trans*-[$PdBr(N\text{-succ})(PPh_3)_2$] (1 mol-%; *N*-succ = *N*-halosuccinimides) with 4-fluorobenzyl bromide gave 91% yield,[21] with a lower yield (69%) being obtained for the formation of 1-benzyl-3,5-difluorobenzene.

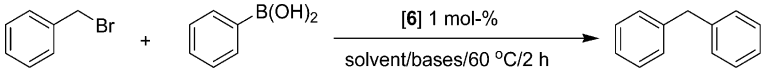
The complexes begin to show some differences when the strongly electron-withdrawing 2-(trifluoromethyl)benzyl bromide is used as the substrate. Thus, complex **1** performs best, giving a near-quantitative yield, followed by **3**, **4**, **5** and **2** (Table 4, Entries 29–35), thereby emphasising the advantage of the isopropyl substituent at the nitrogen atom. Complexes **2**, **3** and **6** also give high yields with 2,3,4,5,6-pentafluorobenzyl bromide (Table 4, Entries 36–42). This system is also active towards benzyl chloride, with the best yields obtained for **2**, **3** and **1** (in decreasing order). In general, complexes with an isopropyl substituent on the NSHC ring and a second ligand of a (benz)imidazole type tend to perform best in this type of benzylic coupling. Benzoxazole or benzothiazole ligands are less favourable as a co-ligand.

Since **3** is among the best performers in this system, we examined its turnover numbers (TONs) with different fluoroaryl bromides and found that the yields are essentially quantitative at 0.01 mol-% catalyst loading, with TONs in the range of 8800–10000. These results are summarized in Scheme 2.

Table 2. Selected bond lengths [Å] and angles [°] for complexes **1**–**7**.

Bond Lengths [Å]	**1** Molecule a	Molecule b		**2**	**3**	**4**	**5**	**6**	**7**
Pd1–C1	1.948(4)	Pd2–C14	1.952(4)	1.943(6)	1.946(4)	1.956(9)	1.957(4)	1.952(4)	1.950(3)
Pd1–N2	2.113(4)	Pd2–N5	2.075(3)	2.114(5)	2.082(4)	2.098(8)	2.096(3)	2.081(3)	2.090(3)
Pd1–Br1								2.438(11)	2.436(4)
Pd1–Br2								2.424(11)	2.423(5)
Pd1–I1	2.611(4)	Pd2–I3	2.616(4)	2.608(6)	2.603(5)	2.611(10)	2.608(4)		
Pd1–I2	2.622(5)	Pd2–I4	2.613(4)	2.608(6)	2.607(5)	2.605(10)	2.612(4)		
S1–C1	1.715(4)	S2–C14	1.717(4)	1.708(6)	1.712(5)	1.697(9)	1.710(4)	1.717(4)	1.711(3)
S2–C11						1.733(9)			1.710(4)
S2–C15								1.717(4)	
O1–C11							1.353(5)		
N1–C1	1.328(5)	N4–C14	1.326(5)	1.338(7)	1.334(6)	1.331(12)	1.330(5)	1.328(5)	1.335(4)
N1–C8	1.501(5)	N4–C21	1.499(5)	1.480(8)	1.489(6)	1.489(12)	1.491(5)	1.476(4)	1.480(4)
N2–C11				1.314(7)	1.301(6)	1.280(12)	1.284(5)		1.297(4)
N2–C12	1.329(6)	N5–C24	1.305(5)						
N2–C15								1.298(5)	
N3–C11				1.341(8)	1.338(6)				
N3–C12	1.342(6)	N6–C24	1.327(6)						
N3–C14				1.444(8)					
Angles [°]									
C1–Pd1–N2	175.86(15)	C14–Pd2–N5	175.80(15)	176.80(2)	174.73(18)	176.60(4)	178.55(14)	179.14(13)	177.01(12)
C1–Pd1–Br1								89.87(10)	90.94(9)
C1–Pd1–Br2								88.38(10)	88.46(9)
N1–C1–S1	111.20(3)	N4–C14–S2	111.50(3)	111.40(4)	111.90(3)	112.00(7)	111.5(3)	110.60(3)	110.80(2)
N2–Pd1–Br1								90.57(8)	92.04(8)
N2–Pd1–Br2								91.20(8)	88.55(8)
Br1–Pd1–Br2								177.89(19)	177.77(17)
C1–Pd1–I1	88.00(12)	C14–Pd2–I3	87.40(12)	87.40(16)	89.82(14)	88.00(3)	87.45(11)		
C1–Pd1–I2	84.43(12)	C14–Pd2–I4	89.08(12)	85.52(16)	86.14(14)	89.00(3)	89.02(11)		
N2–Pd1–I1	92.72(10)	N5–Pd2–I3	93.26(10)	93.32(13)	92.12(11)	93.60(2)	93.59(9)		
N2–Pd1–I2	95.42(10)	N5–Pd2–I4	90.58(10)	94.02(13)	92.06(11)	89.50(2)	89.98(9)		
I1–Pd1–I2	168.90(16)	I3–Pd2–I4	174.23(16)	171.46(3)	175.58(18)	176.37(4)	175.86(15)		
C1–N1–C8	120.20(3)	C14–N4–C21	121.00(3)	122.00(5)	120.70(4)	121.70(8)	120.50(3)	122.30(3)	123.70(3)
C11–N2–Pd1				128.60(4)	130.00(3)	123.00(6)	124.60(3)		122.50(2)
C12–N2–Pd1	128.90(3)	C24–N5–Pd2	127.70(3)						
C15–N2–Pd1								125.40(3)	
N1–C1–Pd1	129.20(3)	N4–C14–Pd2	131.00(3)	126.40(4)	131.00(3)	129.40(7)	127.50(3)	127.90(3)	129.80(2)
N2–C11–S2						115.50(7)			116.30(3)
N2–C15–S2								116.30(3)	
N2–C11–O1							115.60(4)		
N2–C11–N3				110.70(6)	112.00(5)				
N2–C12–N3	110.20(5)	N5–C24–N6	110.80(4)						
Dihedral angle ($PdCNX_2$/azole)	39.60	–	52.10	36.60	71.90	83.50	61.30	82.80	66.00
Dihedral angle ($PdCNX_2$/NSHC)	87.50	–	86.00	82.70	86.70	82.40	81.70	86.30	80.30

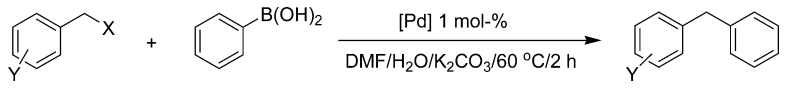
Table 3. Cross-coupling of benzyl bromide and arylboronic acid[a] catalyzed by **6** in different solvents with Cs_2CO_3 as base.



Entry	Solvent	Yield [%]
1	thf	27
2	CH_3CN	55
3	dmf	92
4	dioxane	34
5	H_2O	67
6	thf/H_2O (1:1)	37
7	CH_3CN/H_2O (1:1)	87
8	dmf/H_2O (1:1)	100
9	dioxane/H_2O (1:1)	84
10	dmf/H_2O (1:1)[b]	100
11	dmf/H_2O (1:1)[c]	99

[a] 0.8 mmol of ArX, 1.2 mmol of Cs_2CO_3, 0.8 mmol of $PhB(OH)_2$. [b] K_2CO_3 as base. [c] NaOH as base.

Table 4. Cross-coupling reactions catalyzed by complexes **1**–**7**.



Run	Precatalyst	Substrate[a]	Yield [%]
1	**1**	benzyl bromide	100
2	**2**	benzyl bromide	100
3	**3**	benzyl bromide	100
4	**4**	benzyl bromide	100
5	**5**	benzyl bromide	100
6	**6**	benzyl bromide	100
7	**7**	benzyl bromide	100
8	**1**	2-fluorobenzyl bromide	100
9	**2**	2-fluorobenzyl bromide	99
10	**3**	2-fluorobenzyl bromide	100
11	**4**	2-fluorobenzyl bromide	99
12	**5**	2-fluorobenzyl bromide	99
13	**6**	2-fluorobenzyl bromide	98
14	**7**	2-fluorobenzyl bromide	98
15	**1**	2,4-difluorobenzyl bromide	100
16	**2**	2,4-difluorobenzyl bromide	99
17	**3**	2,4-difluorobenzyl bromide	100
18	**4**	2,4-difluorobenzyl bromide	98
19	**5**	2,4-difluorobenzyl bromide	99
20	**6**	2,4-difluorobenzyl bromide	97
21	**7**	2,4-difluorobenzyl bromide	98
22	**1**	2,6-difluorobenzyl bromide	99
23	**2**	2,6-difluorobenzyl bromide	96
24	**3**	2,6-difluorobenzyl bromide	100
25	**4**	2,6-difluorobenzyl bromide	98
26	**5**	2,6-difluorobenzyl bromide	97
27	**6**	2,6-difluorobenzyl bromide	98
28	**7**	2,6-difluorobenzyl bromide	97
29	**1**	2-(trifluoromethyl)benzyl bromide	98
30	**2**	2-(trifluoromethyl)benzyl bromide	88
31	**3**	2-(trifluoromethyl)benzyl bromide	95
32	**4**	2-(trifluoromethyl)benzyl bromide	94
33	**5**	2-(trifluoromethyl)benzyl bromide	95
34	**6**	2-(trifluoromethyl)benzyl bromide	89
35	**7**	2-(trifluoromethyl)benzyl bromide	91
36	**1**	2,3,4,5,6-pentafluorobenzyl bromide	73
37	**2**	2,3,4,5,6-pentafluorobenzyl bromide	92
38	**3**	2,3,4,5,6-pentafluorobenzyl bromide	95
39	**4**	2,3,4,5,6-pentafluorobenzyl bromide	83
40	**5**	2,3,4,5,6-pentafluorobenzyl bromide	84
41	**6**	2,3,4,5,6-pentafluorobenzyl bromide	90
42	**7**	2,3,4,5,6-pentafluorobenzyl bromide	87
43	**1**	benzyl chloride	62
44	**2**	benzyl chloride	89
45	**3**	benzyl chloride	76

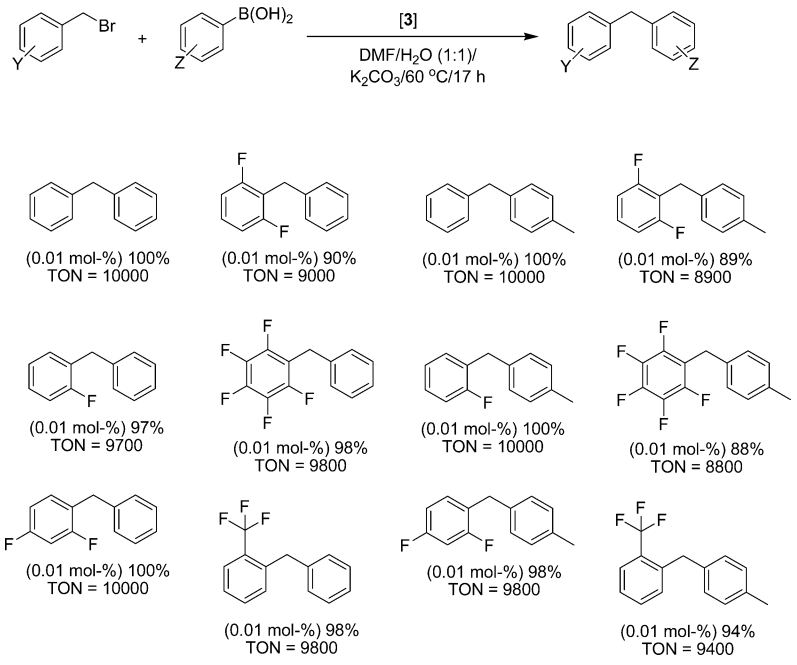
[a] 0.8 mmol of ArX, 1.2 mmol of K_2CO_3, 0.8 mmol of $PhB(OH)_2$.

Conclusions

The carbene hybrid system presented here utilizes azole as a neutral nitrogen donor and its deprotonated form as a heterocyclic carbene ligand. In principle, this synthetic methodology and the structural motifs can be extended to different types of heterocyclic carbenes and azoles. These heterocycle-stabilised heterocyclic carbene complexes are air-stable and easily prepared, and their efficacy toward benzylic coupling has prompted us to examine similar complexes for other catalytic applications. These results will be reported in due course.

Experimental Section

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. Imidazole, benzimidazole, benzoxazole and $Pd(OAc)_2$ were purchased from Sigma–Aldrich and used as received. 1-(2,4,6-Trimethylphenyl)-1*H*-imidazole was prepared as reported previously.[22] ^1H and ^{13}C NMR spectra were recorded with a Bruker AMX 500 spectrometer by using Me_4Si as an internal standard. ^{19}F NMR spectra were recorded with a Bruker ACF 300 spectrometer by using CF_3CO_2H as an external standard. ESI mass spectra were obtained



Scheme 2. Cross-coupling of different fluorobenzyl bromides and arylboronic acid promoted by **3** at a 0.01 mol-% catalyst loading.

with a Finnigan MAT 731 LCQ spectrometer. The yield of the hetero-coupling products was determined with a Hewlett–Packard Series 6890 GC (Santa Clara, CA, USA) coupled to a Hewlett–Packard 5973 MS detector. Elemental analyses were performed with a Perkin–Elmer PE 2400 elemental analyzer at the Department of Chemistry, National University of Singapore.

***trans*-(Imidazole-κ*N*)diiodo(3-isopropylbenzothiazolin-2-ylidene)palladium(II) (1):** Complex **1** was prepared by suspending the dinuclear Pd^{II} precursor $[Pd(\mu\text{-}I)(NSHC)]_2$ [NSHC = 3-isopropylbenzothiazolin-2-ylidene] (97 mg, 0.09 mmol) and imidazole (13 mg, 0.18 mmol) in CH_2Cl_2 (5 mL) and stirring the mixture at room temp. overnight. The precipitate thus obtained was washed several times with Et_2O to give a yellow solid. Yellow single crystals of **1** were obtained upon diffusion of Et_2O into a concentrated CH_2Cl_2 solution. Yield: 97 mg (0.16 mmol, 89%). ^1H NMR (500 MHz, $CDCl_3$): δ = 9.47 (s, 1 H, NH), 8.41 (s, 1 H, NCHN), 7.88 (d, $^3J_{H,H}$ = 8.85 Hz, 1 H, Ar-H), 7.56 (d, $^3J_{H,H}$ = 10.08 Hz, 1 H, Ar-H), 7.48–7.34 (m, 2 H, Ar-H), 6.98 (s, 2 H, NCH=), 6.57 [m, $^3J_{H,H}$ = 7.15 Hz, 1 H, $CH(CH_3)_2$], 1.90 [d, $^3J_{H,H}$ = 6.95 Hz, 6 H, $CH(CH_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 191.0 (s, NCS), 141.4 (s, NCHN), 140.7, 138.9, 134.9, 132.1, 125.9, 124.5, 121.8, 115.8 (s, Ar-C), 63.1 [s, $CH(CH_3)_2$], 19.1 [s, $CH(CH_3)_2$] ppm. MS (ESI, positive mode): *m*/*z* (%) = 546 (100) [M – I + imidazole]$^+$. $C_{13}H_{15}I_2N_3PdS{\cdot}Et_2O{\cdot}H_2O$ (697.71): calcd. C 29.26, H 3.90, N 6.02, S 4.60; found C 29.06, H 3.11, N 5.61, S 5.74. The elemental analysis remained unsatisfactory despite repeated purification and analysis, possibly due to solvation.

***trans*-Diiodo(3-isopropylbenzothiazolin-2-ylidene)[1-(2,4,6-trimethylphenyl)-1*H*-imidazole-κ*N*]palladium(II) (2):** Complex **2** was prepared as a yellow solid in analogy to **1** from the dinuclear Pd^{II} precursor (108 mg, 0.10 mmol) and 1-(2,4,6-trimethylphenyl)-1*H*-imidazole (37 mg, 0.2 mmol). Yellow single crystals of **2** were obtained upon diffusion of Et_2O into a concentrated CH_2Cl_2 solution. Yield: 76 mg (0.105 mmol, 53%). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.27 (s, 1 H, NCHN), 7.89 (s, 1 H, Ar-H), 7.88 (s, 1 H, Ar-H), 7.75 (d, $^3J_{H,H}$ = 8.15 Hz, 1 H, Ar-H), 7.42 (t, $^3J_{H,H}$ = 7.88 Hz, 1 H, Ar-H), 7.35 (t, $^3J_{H,H}$ = 7.58 Hz, 1 H, Ar-H), 6.97 (s, 2 H, NCH=), 6.81 (s, 1 H, Ar-H), 6.58 [m, $^3J_{H,H}$ = 7.09 Hz, 1 H, $CH(CH_3)_2$], 2.34 (s, 3 H, CH_3), 2.17 (s, 3 H, CH_3), 2.02 (s, 3 H, CH_3), 1.91 [d, $^3J_{H,H}$ = 7.55 Hz, 6 H, $CH(CH_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 190.3 (s, NCS), 143.5 (s, NCHN), 141.4, 139.6, 138.9, 135.1, 133.3, 132.5, 129.2, 125.9, 124.4, 122.1, 120.1, 115.8 (s, Ar-C), 63.1 [s, $CH(CH_3)_2$], 21.1 (s, CH_3), 19.1 [s, $CH(CH_3)_2$], 17.6 (s, CH_3) ppm. MS (ESI, positive mode): *m*/*z* (%) = 1136 (100) [M – I + 2 $C_{12}H_{14}N_2$ + CH_3CN]$^+$. $C_{22}H_{25}I_2N_3PdS{\cdot}Et_2O{\cdot}CH_2Cl_2$ (882.80): calcd. C 36.73, H 4.22, N 4.76, S 3.63; found C 36.92, H 4.72, N 4.59, S 3.92.

***trans*-(Benzimidazole-κ*N*)diiodo(3-isopropylbenzothiazolin-2-ylidene)-palladium(II) (3):** Complex **3** was obtained as a yellow solid in analogy to **1** from the dinuclear Pd^{II} precursor (100 mg, 0.093 mmol) and benzimidazole (22 mg, 0.186 mmol). Yellow single crystals of **3** were obtained upon diffusion of Et_2O into a concentrated CH_2Cl_2 solution. Yield: 100 mg (0.15 mmol, 82%). ^1H NMR (500 MHz, [D_6]DMSO): δ = 13.33 (s, 1 H, NH), 8.78 (s, 1 H, NCHN), 8.25 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H, Ar-H), 8.11 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, Ar-H), 7.60–7.55 (m, 2 H, Ar-H), 7.50 (t, $^3J_{H,H}$ = 7.6 Hz, 1 H, Ar-H), 7.40–7.34 (m, 2 H, Ar-H), 6.58 [m, $^3J_{H,H}$ = 6.6 Hz, 1 H, $CH(CH_3)_2$], 1.90 [d, $^3J_{H,H}$ = 7.0 Hz, 6 H, $CH(CH_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (125 MHz, [D_6]DMSO): δ = 192.8 (s, NCS), 144.9 (s, NCHN), 141.2, 140.5, 138.0, 132.5, 127.2, 125.4, 124.1, 123.2, 122.9, 122.3, 120.7, 116.8, 113.0 (s, Ar-C), 62.9 [s, $CH(CH_3)_2$], 19.1 [s, $CH(CH_3)_2$] ppm. MS (ESI, positive mode): *m*/*z* (%) = 645 (100) [M – I + benzimidazole]$^+$, 527 (60) [M – I]$^+$. $C_{17}H_{17}I_2N_3PdS$ (655.63): calcd. C 31.14, H 2.61, N 6.41, S 4.89; found C 31.27, H 2.81, N 6.32, S 4.43.

***trans*-(Benzothiazole-κ*N*)diiodo(3-isopropylbenzothiazolin-2-ylidene)-palladium(II) (4):** Complex **4** was prepared as a yellow solid in analogy to **1** from the dinuclear Pd^{II} precursor (193 mg, 0.18 mmol) and benzothiazole (49 mg, 0.36 mmol). Yellow single crystals of **4** were obtained upon diffusion of Et_2O into a concentrated CH_2Cl_2 solution. Yield: 155 mg (0.23 mmol, 64%). ^1H NMR (500 MHz, $CDCl_3$): δ = 9.46 (s, 1 H, NCHS), 8.88 (d, $^3J_{H,H}$ = 8.20 Hz, 1 H, Ar-H), 7.92 (d, $^3J_{H,H}$ = 8.20 Hz, 2 H, Ar-H), 7.80 (d, $^3J_{H,H}$ = 7.55 Hz, 1 H, Ar-H), 7.69 (t, $^3J_{H,H}$ = 7.88 Hz, 1 H, Ar-H), 7.55 (t,

$^3J_{H,H}$ = 7.25 Hz, 1 H, Ar-H), 7.46 (t, $^3J_{H,H}$ = 7.25 Hz, 1 H, Ar-H), 7.39 (t, $^3J_{H,H}$ = 7.25 Hz, 1 H, Ar-H), 6.68 [m, $^3J_{H,H}$ = 7.15 Hz, 1 H, $CH(CH_3)_2$], 1.98 [d, $^3J_{H,H}$ = 6.95 Hz, 6 H, $CH(CH_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 189.9 (s, NCS), 158.8 (s, NCHS), 150.2, 141.3, 138.9, 131.7 (s, Ar-C), 126.8 (d, $^{2/3}J_{C,C}$ = 20.95 Hz, Ar-C), 126.1, 125.7, 124.7 (s, Ar-C), 122.2 (d, $^{2/3}J_{C,C}$ = 17.30 Hz, Ar-C), 115.9 (s, Ar-C), 63.7 [s, $CH(CH_3)_2$], 19.5 [s, $CH(CH_3)_2$] ppm. MS (ESI, positive mode): *m*/*z* (%) = 586 (90) [M – I + CH_3CN]$^+$. $C_{17}H_{16}I_2N_2PdS_2$ (672.68): calcd. C 30.35, H 2.40, N 4.16, S 9.53; found C 29.96, H 2.25, N 3.89, S 8.96.

***trans*-(Benzoxazole-κ*N*)diiodo(3-isopropylbenzothiazolin-2-ylidene)-palladium(II) (5):** Complex **5** was obtained as a yellow solid in analogy to **1** from the dinuclear Pd^{II} precursor (100 mg, 0.093 mmol) and benzoxazole (22 mg, 0.186 mmol). Yellow single crystals of **5** were obtained upon diffusion of Et_2O into a concentrated CH_2Cl_2 solution. Yield: 98 mg (0.15 mmol, 81%). ^1H NMR (500 MHz, [D_6]-DMSO): δ = 8.74 (s, 1 H, NCHO), 8.39 (d, $^3J_{H,H}$ = 6.9 Hz, 1 H, Ar-H), 7.91 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H, Ar-H), 7.79 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, Ar-H), 7.61 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, Ar-H), 7.52–7.39 (m, 4 H, Ar-H), 6.62 [m, $^3J_{H,H}$ = 7.1 Hz, 1 H, $CH(CH_3)_2$], 1.96 [d, $^3J_{H,H}$ = 7.0 Hz, 6 H, $CH(CH_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (125 MHz, [D_6]-DMSO): δ = 189.0 (s, NCS), 156.2, 149.4, 141.3, 138.8, 137.2, 127.0, 126.2, 125.5, 124.7, 122.8, 122.2, 115.9, 111.5 (s, Ar-C), 63.4 [s, $CH(CH_3)_2$], 19.1 [s, $CH(CH_3)_2$] ppm. MS (ESI, positive mode): *m*/*z* (%) = 656 (100) [M + H]$^+$. $C_{17}H_{16}I_2N_2OPdS$ (656.62): calcd. C 31.10, H 2.46, N 4.27, S 4.88; found C 31.34, H 2.78, N 4.31, S 5.15.

***trans*-(Benzothiazole-κ*N*)(3-benzylbenzothiazolin-2-ylidene)dibromidopalladium(II) (6):** Complex **6** was prepared in analogy to **1** from the dinuclear Pd^{II} precursor [PdBr(μ-Br)(NSHC)]$_2$ [NSHC = 3-benzylbenzothiazolin-2-ylidene; 88 mg, 0.09 mmol] and benzothiazole (24 mg, 0.18 mmol). Yellow single crystals of **6** were obtained upon diffusion of Et_2O into a concentrated CH_2Cl_2 solution. Yield: 94 mg (0.15 mmol, 83%). ^1H NMR (500 MHz, $CDCl_3$): δ = 9.41 (s, 1 H, NCHS), 8.90 (d, $^3J_{H,H}$ = 8.15 Hz, 2 H, Ar-H), 7.89 (d, $^3J_{H,H}$ = 8.20 Hz, 1 H, Ar-H), 7.63 (d, $^3J_{H,H}$ = 6.90 Hz, 4 H, Ar-H), 7.51–7.47 (m, 2 H, Ar-H), 7.42–7.33 (m, 4 H, Ar-H), 6.62 (s, 2 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 195.9 (s, NCS), 158.8 (s, NCHS), 149.7, 142.8, 136.7, 135.4, 133.8, 133.6, 131.8, 129.2, 128.6, 127.7 (s, Ar-C), 127.2 (d, $^{2/3}J_{C,C}$ = 10.03 Hz, Ar-C), 127.0 (s, Ar-C), 126.8 (d, $^{2/3}J_{C,C}$ = 11.84 Hz, Ar-C), 125.2 (d, $^{2/3}J_{C,C}$ = 14.58 Hz, Ar-C), 121.9 (d, $^{2/3}J_{C,C}$ = 25.51 Hz, Ar-C), 115.1 (s, Ar-C), 60.1 (s, C2) ppm. MS (ESI, positive mode): *m*/*z* (%) = 589 (90) [M – Br + CH_3CN]$^+$. $C_{21}H_{16}Br_2N_2PdS_2$ (626.72): calcd. C 40.24, H 2.54, N 4.47, S 10.23; found C 39.02, H 2.56, N 4.18, S 9.37.

***trans*-(Benzothiazole-κ*N*)dibromido(3-propylbenzothiazolin-2-ylidene)-palladium(II) (7):** Complex **7** was prepared as a yellow solid in analogy to **1** from the dinuclear Pd^{II} precursor [PdBr(μ-Br)(NSHC)$_2$] [NSHC = 3-propylbenzothiazolin-2-ylidene; 79 mg, 0.089 mmol] and benzothiazole (24 mg, 0.178 mmol). Yellow single crystals of **7** were obtained upon diffusion of Et_2O into a concentrated CH_2Cl_2 solution. Yield: 82 mg (0.142 mmol, 80%). ^1H NMR (500 MHz, $CDCl_3$): δ = 9.44 (s, 1 H, NCHS), 8.99 (d, $^3J_{H,H}$ = 8.20 Hz, 1 H, Ar-H), 7.93 (d, $^3J_{H,H}$ = 8.20 Hz, 1 H, Ar-H), 7.85 (d, $^3J_{H,H}$ = 7.55 Hz, 1 H, Ar-H), 7.72 (d, $^3J_{H,H}$ = 8.20 Hz, 1 H, Ar-H), 7.69 (t, $^3J_{H,H}$ = 7.88 Hz, 1 H, Ar-H), 7.55 (t, $^3J_{H,H}$ = 7.88 Hz, 2 H, Ar-H), 7.46 (t, $^3J_{H,H}$ = 7.60 Hz, 1 H, Ar-H), 5.25 (t, $^3J_{H,H}$ = 8.18 Hz, 2 H, $CH_2CH_2CH_3$), 2.44 (p. sext, $^3J_{H,H}$ = 7.82 Hz, 2 H, $CH_2CH_2CH_3$), 1.30 (t, $^3J_{H,H}$ = 7.58 Hz, 3 H, $CH_2CH_2CH_3$) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 193.6 (s, NCS), 158.8 (s, NCHS), 149.7, 142.9, 136.7, 131.9, 127.0 (s, Ar-C), 126.8 (d, $^{2/3}J_{C,C}$ = 10.00 Hz, Ar-C), 125.1 (d, $^{2/3}J_{C,C}$ = 29.32 Hz, Ar-C), 122.1 (d, $^{2/3}J_{C,C}$ = 12.84 Hz, Ar-C), 113.7 (s, Ar-C), 57.1 (s, $CH_2CH_2CH_3$), 22.1 (s, $CH_2CH_2CH_3$), 11.8 (s, $CH_2CH_2CH_3$) ppm. MS (ESI, positive mode): *m*/*z* (%) = 541 (40) [M – Br + CH_3CN]$^+$. $C_{17}H_{16}Br_2N_2PdS_2$ (578.68): calcd. C 35.28, H 2.79, N 4.84, S 11.08; found C 35.18, H 2.56, N 4.79, S 10.35.

General Procedure for the Suzuki–Miyaura Reaction: K_2CO_3 (1.2 mmol), benzyl halide (0.8 mmol), phenylboronic acid (0.8 mmol) and dodecane (0.8 mmol as internal standard) were placed in a reaction flask equipped with a stirring bar. An aliquot of solvent (5 mL) was introduced, and the resulting suspension was stirred at room temp. or 60 °C for 10 min before addition of the catalyst. After the desired reaction time, the reaction mixture was cooled to room temp., water was added and the product extracted with CH_2Cl_2 (3 × 4 mL). The combined organic extracts were dried with $MgSO_4$, filtered and the products analyzed by GC/MS. The organic products were purified by TLC chromatography using CH_2Cl_2 as eluent. The characterisation data of these products are given below.

1-Benzylbenzene: The data are similar to those reported previously.[21]

1-Benzyl-2-fluorobenzene: ^1H NMR (500 MHz, $CDCl_3$): δ = 7.31–7.28 (m, 2 H, Ar-H), 7.23–7.14 (m, 5 H, Ar-H), 7.07–7.02 (m, 2 H, Ar-H), 4.01 (s, 2 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 161.0 (d, $^1J_{C,F}$ = 243.20 Hz, Ar-C), 139.9 (s, Ar-C), 131.0 (d, $^{4/5}J_{C,F}$ = 4.55 Hz, Ar-C), 128.7 (d, $^2J_{C,F}$ = 36.44 Hz, Ar-C), 128.1 (s, Ar-C), 127.9 (d, $^{3/4}J_{C,F}$ = 8.20 Hz, Ar-C), 126.2 (s, Ar-C), 124.1 (d, $^{4/5}J_{C,F}$ = 3.60 Hz, Ar-C), 115.3 (d, $^2J_{C,F}$ = 21.86 Hz, Ar-C), 111.2 (s, Ar-C), 34.8 (d, $^{4/5}J_{C,F}$ = 2.74 Hz, CH_2) ppm. $^{19}F\{^1H\}$ NMR (282.28 MHz, $CDCl_3$): δ = –41.9 (s, 1 F, Ar-F) ppm. GC/MS analysis: *m*/*z* = 186 [M]$^+$.

1-Benzyl-2,4-difluorobenzene: ^1H NMR (500 MHz, $CDCl_3$): δ = 7.31–7.28 (m, 3 H, Ar-H), 7.23–7.18 (m, 3 H, Ar-H), 7.11–7.07 (m, 1 H, Ar-H), 6.82–6.77 (m, 1 H, Ar-H), 3.96 (s, 2 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 139.6 (s, Ar-C), 131.5 (d, $^{4/5}J_{C,F}$ = 3.65 Hz, Ar-C), 131.4 (d, $^3J_{C,F}$ = 15.49 Hz, Ar-C), 128.6 (d, $^3J_{C,F}$ = 16.40 Hz, Ar-C), 126.4 (s, Ar-C), 111.2 (d, $^{4/5}J_{C,F}$ = 3.63 Hz, Ar-C), 111.0 (d, $^{4/5}J_{C,F}$ = 4.56 Hz, Ar-C), 104.9 (s, Ar-C), 103.7 (t, $^2J_{C,F}$ = 25.50 Hz, Ar-C), 34.3 (d, $^{4/5}J_{C,F}$ = 1.83 Hz, CH_2) ppm. $^{19}F\{^1H\}$ NMR (282.28 MHz, $CDCl_3$): δ = –37.2 (d, $J_{C,F}$ = 8.27 Hz, 1 F, Ar-F), –37.6 (d, $J_{C,F}$ = 8.24 Hz, 1 F, Ar-F) ppm. GC/MS analysis: *m*/*z* = 204 [M]$^+$.

1-Benzyl-2,6-difluorobenzene: ^1H NMR (500 MHz, $CDCl_3$): δ = 7.29–7.25 (m, 4 H, Ar-H), 7.21–7.12 (m, 2 H, Ar-H), 6.89–6.85 (m, 2 H, Ar-H), 4.01 (s, 2 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 161.4 (d, $^1J_{C,F}$ = 250.00 Hz, Ar-C), 139.2, 128.8 (s, Ar-C), 128.5 (d, $^{4/5}J_{C,F}$ = 6.38 Hz, Ar-C), 127.9 (t, $^{3/4}J_{C,F}$ = 10.48 Hz, Ar-C), 127.2 (d, $^{3/4}J_{C,F}$ = 10.01 Hz, Ar-C), 126.3, 116.9 (s, Ar-C), 111.2 (dd, $^{3/4}J_{C,F}$ = 20.04, $^{4/5}J_{C,F}$ = 6.38 Hz, Ar-C), 28.2 (d, $^{4/5}J_{C,F}$ = 2.72 Hz, CH_2) ppm. $^{19}F\{^1H\}$ NMR (282.28 MHz, $CDCl_3$): δ = –39.0 (s, 2 F, Ar-F) ppm. GC/MS analysis: *m*/*z* = 204 [M]$^+$.

1-Benzyl-2-(trifluoromethyl)benzene: ^1H NMR (500 MHz, $CDCl_3$): δ = 7.69–7.61 (m, 1 H, Ar-H), 7.47–7.35 (m, 1 H, Ar-H), 7.33–7.30 (m, 3 H, Ar-H), 7.25–7.22 (m, 1 H, Ar-H), 7.19–7.15 (m, 3 H, Ar-H), 4.20 (s, 2 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 141.3, 139.9, 139.5, 131.8, 131.7, 129.2, 128.8, 128.6 (s, Ar-C), 127.2 (d, $^{3/4}J_{C,F}$ = 10.93 Hz, Ar-C), 126.3 (d, $^{3/4}J_{C,F}$ = 13.66 Hz, Ar-C), 125.9 (q, $^{4/5}J_{C,F}$ = 5.77 Hz, CF_3), 125.7 (s, Ar-C), 37.8 (d,

$^{4/5}J_{C,F}$ = 1.81 Hz, CH_2) ppm. $^{19}F\{^1H\}$ NMR (282.28 MHz, $CDCl_3$): δ = 16.3 (s, 3 F, CF_3) ppm. GC/MS analysis: *m*/*z* = 236 $[M]^+$.

1-Benzyl-2,3,4,5,6-pentafluorobenzene: ^1H NMR (500 MHz, $CDCl_3$): δ = 7.34–7.29 (m, 2 H, Ar-H), 7.25–7.23 (m, 3 H, Ar-H), 4.04 (s, 2 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 146.0–145.9 (m, Ar-C), 144.1–143.9 (m, Ar-C), 141.3 (s, Ar-C), 140.9–140.8 (m, Ar-C), 139.0–138.8 (m, Ar-C), 138.6–138.4 (m, Ar-C), 137.5 (s, Ar-C), 136.7–136.4 (m, Ar-C), 128.8 (d, $^{3/4}J_{C,F}$ = 8.20 Hz, Ar-C), 128.3 (s, Ar-C), 127.2 (d, $^{3/4}J_{C,F}$ = 10.93 Hz, Ar-C), 126.9 (s, Ar-C), 114.4 (t, $^{2/3}J_{C,F}$ = 18.68 Hz, Ar-C), 28.1 (s, CH_2) ppm. $^{19}F\{^1H\}$ NMR (282.28 MHz, $CDCl_3$): δ = –67.3 (d, $J_{C,F}$ = 8.24 Hz, 1 F, Ar-F), –67.4 (d, $J_{C,F}$ = 8.24 Hz, 1 F, Ar-F), –81.1 (t, $J_{C,F}$ = 20.61 Hz, 1 F, Ar-F), –86.3 (d, $J_{C,F}$ = 8.24 Hz, 1 F, Ar-F), –86.4 (d, $J_{C,F}$ = 8.24 Hz, 1 F, Ar-F) ppm. GC/MS analysis: *m*/*z* = 258 $[M]^+$.

1-Benzyl-4-methylbenzene: ^1H NMR (500 MHz, $CDCl_3$): δ = 7.48 (d, $^3J_{H,H}$ = 8.20 Hz, 5 H, Ar-H), 7.23 (d, $^3J_{H,H}$ = 8.20 Hz, 2 H, Ar-H), 7.09 (d, $^5J_{H,H}$ = 1.90 Hz, 1 H, Ar-H), 3.99 (s, 2 H, CH_2), 2.38 (s, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 138.3, 136.7, 129.4, 129.1, 128.9, 128.8, 128.4, 126.8, 125.9 (s, Ar-C), 53.4 (s, CH_2), 21.1 (s, CH_3) ppm. GC/MS analysis: *m*/*z* = 182 $[M]^+$.

2-(Fluorobenzyl)-4-methylbenzene: ^1H NMR (500 MHz, $CDCl_3$): δ = 7.21–7.09 (m, 6 H, Ar-H), 7.06–7.01 (m, 2 H, Ar-H), 3.97 (s, 2 H, CH_2), 2.32 (s, 2 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 160.9 (d, $^1J_{C,F}$ = 244.13 Hz, Ar-C), 136.8, 136.7 (s, Ar-C), 131.0 (d, $^{4/5}J_{C,F}$ = 4.55 Hz, Ar-C), 129.4, 129.2, 128.7 (s, Ar-C), 128.4 (d, $^{3/4}J_{C,F}$ = 15.49 Hz, Ar-C), 127.8 (d, $^{4/5}J_{C,F}$ = 8.20 Hz, Ar-C), 126.8 (s, Ar-C), 124.0 (d, $^{4/5}J_{C,F}$ = 3.65 Hz, Ar-C), 115.3 (d, $^{2/3}J_{C,F}$ = 21.86 Hz, Ar-C), 34.4 (d, $^{4/5}J_{C,F}$ = 3.65 Hz, CH_2), 21.0 (s, CH_3) ppm. $^{19}F\{^1H\}$ NMR (282.28 MHz, $CDCl_3$): δ = –42.0 (s, 1 F, Ar-F) ppm. GC/MS analysis: *m*/*z* = 200 $[M]^+$.

1-(2,4-Difluorobenzyl)-4-methylbenzene: ^1H NMR (500 MHz, $CDCl_3$): δ = 7.14–7.08 (m, 5 H, Ar-H), 6.83–8.78 (m, 2 H, Ar-H), 3.93 (s, 2 H, CH_2), 2.34 (s, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 161.6 (dd, $^1J_{C,F}$ = 246.25, $^{3/4}J_{C,F}$ = 12.75 and 12.36 Hz, Ar-C), 160.8 (dd, $^1J_{C,F}$ = 246.25, $^{3/4}J_{C,F}$ = 10.90 and 11.85 Hz, Ar-C), 138.3, 136.7, 136.5, 135.9 (s, Ar-C), 131.5 (d, $^{4/5}J_{C,F}$ = 6.39 Hz, Ar-C), 131.4 (d, $^{4/5}J_{C,F}$ = 6.38 Hz, Ar-C), 129.5, 128.3, 128.6 126.8 (s, Ar-C), 124.3 (d, $^{4/5}J_{C,F}$ = 4.56 Hz, Ar-C), 124.2 (d, $^{4/5}J_{C,F}$ = 3.64 Hz, Ar-C), 111.1 (d, $^{4/5}J_{C,F}$ = 3.65 Hz, Ar-C), 110.9 (d, $^{4/5}J_{C,F}$ = 4.55 Hz, Ar-C), 103.7 (t, $^{2/3}J_{C,F}$ = 25.51 Hz, Ar-C), 33.8 (d, $^{4/5}J_{C,F}$ = 2.74 Hz, CH_2), 21.0 (d, $^{4/5}J_{C,F}$ = 9.11 Hz, CH_3) ppm. $^{19}F\{^1H\}$ NMR (282.28 MHz, $CDCl_3$): δ = –37.4 (d, $J_{C,F}$ = 8.24 Hz, 1 F, Ar-F), –38.7 (d, $J_{C,F}$ = 8.24 Hz, 1 F, Ar-F) ppm. GC/MS analysis: *m*/*z* = 218 $[M]^+$.

1-(2,6-Difluorobenzyl)-4-methylbenzene: ^1H NMR (500 MHz, $CDCl_3$): δ = 7.49 (d, $^3J_{H,H}$ = 8.20 Hz, 1 H, Ar-H), 7.18–7.09 (m, 4 H, Ar-H), 6.87 (t, $^3J_{H,H}$ = 7.58 Hz, 2 H, Ar-H), 3.99 (s, 2 H, CH_2), 2.31 (s, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 161.4 (dd, $^1J_{C,F}$ = 250, $^{4/5}J_{C,F}$ = 9.11 and 8.20 Hz, Ar-C), 138.3, 136.7, 136.2, 135.8, 129.4, 129.2, 128.3 (s, Ar-C), 127.7 (t, $^{3/4}J_{C,F}$ = 10.0 Hz, Ar-C), 126.8 (s, Ar-C), 111.3 (d, $^{4/5}J_{C,F}$ = 6.34 Hz, Ar-C), 111.1 (d, $^{4/5}J_{C,F}$ = 6.38 Hz, Ar-C), 27.8 (s, CH_2), 21.0 (s, $^{4/5}J_{C,F}$ = 9.10 Hz, CH_3) ppm. $^{19}F\{^1H\}$ NMR (282.28 MHz, $CDCl_3$): δ = –39.1 (s, 1 F, Ar-F), –40.3 (s, 1 F, Ar-F) ppm. GC/MS analysis: *m*/*z* = 218 $[M]^+$.

4-Methyl-2-(trifluorobenzyl)benzene: ^1H NMR (500 MHz, $CDCl_3$): δ = 7.37–7.28 (m, 2 H, Ar-H), 7.25 (d, $^3J_{H,H}$ = 8.20 Hz, Ar-H), 7.18 (d, $^3J_{H,H}$ = 8.20 Hz, Ar-H), 7.12 (d, $^3J_{H,H}$ = 8.15 Hz, Ar-H), 7.05 (d, $^3J_{H,H}$ = 8.20 Hz, Ar-H), 4.16 (s, 2 H, CH_2), 2.34 (s, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 140.0 (d, $^2J_{C,F}$ = 31.89 Hz, Ar-C), 138.3 (s, Ar-C), 136.8 (d, $^{3/4}J_{C,F}$ = 12.75 Hz, Ar-C), 135.8 (s, Ar-C), 131.9 (s, Ar-C), 131.7 (d, $^{3/4}J_{C,F}$ = 9.11 Hz, Ar-C), 131.4, 129.4 (s, Ar-C), 129.1 (d, $^{2/3}J_{C,F}$ = 22.76 Hz, Ar-C),

Table 5. Selected crystallographic data for complexes **1**–**7**.

	1	**2**	**3**	**4**	**5**	**6**	**7**
Empirical formula	$C_{13}H_{15}I_2N_3S_1$ Pd	$C_{22}H_{25}I_2N_3SPd$	$C_{17}H_{17}I_2N_3SPd$	$C_{18}H_{17.25}Cl_{2.75}I_2N_2S_2Pd$	$C_{17}H_{16}I_2N_2SO$ Pd	$C_{21}H_{16}Br_2N_2S_2Pd$	$C_{17}H_{16}Br_2N_2S_2Pd$
Formula mass	605.54	723.71	655.60	783.40	656.58	626.70	578.66
Color, habit	orange, block	orange, needle	orange, block	orange, block	orange, block	yellow, needle	white, block
Crystal size [mm]	0.32×0.10×0.05	0.36×0.06×0.02	0.16×0.16×0.10	0.18×0.14×0.06	0.26×0.12×0.02	0.20×0.10×0.06	0.30×0.10×0.10
Temperature [K]	223(2) K	295(2) K	223(2) K	293(2) K	223(2) K	223(2) K	223(2) K
Crystal system	monoclinic	orthorhombic	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	*Pbca*	$P2_1/c$	*Pbca*	$P2_1/c$	$P2_1/n$	$P2_1/c$
a [Å]	19.6046(7)	9.1240(6)	15.1785(9)	17.9597(15)	9.1743(5)	5.824(4)	9.3539(5)
b [Å]	15.1707(6)	15.7419(11)	8.1886(5)	9.8547(9)	10.8697(6)	19.560(11)	18.6679(10)
c [Å]	12.3633(5)	35.431(2)	16.8322(10)	27.837(3)	20.8718(11)	18.648(11)	10.7483(6)
α [°]	90	90	90	90	90	90	90
β [°]	107.4560(10)	90	101.7340(10)	90	102.3720(10)	94.899(14)	95.6270(10)
γ [°]	90	90	90	90	90	90	90
V [Å^3]	3507.7(2)	5088.9(6)	2048.4(2)	4926.7(8)	2033.04(19)	2117(2)	1867.80(18)
Z	8	8	4	8	4	4	4
D_c [g cm^{-3}]	2.293	1.889	2.126	2.112	2.145	1.967	2.058
Radiation	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α
μ [mm^{-1}]	4.691	3.251	4.026	3.736	4.059	4.859	5.497
θ range [°]	1.72–27.50	1.15–27.50	1.37–27.50	1.46–27.50	2.00–27.49	1.51–27.50	2.18–27.50
Unique data	24526	34166	13991	32984	14161	14854	13133
$R_{(int)}$	0.0284	0.0627	0.0317	0.0929	0.0347	0.0386	0.0291
Max., min transmission	0.7993, 0.3152	0.9378, 0.3874	0.6889, 0.5652	0.8069, 0.5528	0.9232, 0.4184	0.7592, 0.4432	0.6094, 0.2894
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0342, *wR*2 = 0.0755	*R*1 = 0.0547, *wR*2 = 0.1237	*R*1 = 0.0386, *wR*2 = 0.0873	*R*1 = 0.0762, *wR*2 = 0.1541	*R*1 = 0.0343, *wR*2 = 0.0745	*R*1 = 0.0339, *wR*2 = 0.0782	*R*1 = 0.0322, *wR*2 = 0.0800
R indices (all data)	*R*1 = 0.0404, *wR*2 = 0.0783	*R*1 = 0.0806, *wR*2 = 0.1401	*R*1 = 0.0493, *wR*2 = 0.0974	*R*1 = 0.1084, *wR*2 = 0.1659	*R*1 = 0.0440, *wR*2 = 0.0790	*R*1 = 0.0481, *wR*2 = 0.0926	*R*1 = 0.0417, *wR*2 = 0.0834
Goodness-of-fit on F^2	1.072	1.163	1.042	1.132	1.035	1.054	1.074
Peak/hole [e Å^{-3}]	1.219/–0.580	1.026/–1.050	1.893/–1.361	1.558/–0.996	1.109/–0.884	0.670/–0.631	1.072/–0.430

128.8, 128.6 (s, Ar-C), 126.8, 126.3, 126.1 (s, Ar-C), 126.0 (d, $^{4/5}J_{C,F}$ = 6.38 Hz, Ar-C), 125.8 (q, $^{4/5}J_{C,F}$ = 5.77 Hz, CF_3), 123.5 (s, Ar-C), 37.4 (d, $^{4/5}J_{C,F}$ = 1.83 Hz, CH_2), 21.0 (d, $^{4/5}J_{C,F}$ = 7.29 Hz, CH_3) ppm. $^{19}F\{^1H\}$ NMR (282.28 MHz, $CDCl_3$): δ = 16.4 (s, 3 F, CF_3) ppm. GC/MS analysis: m/z = 250 $[M]^+$.

4-Methyl-(2,3,4,5,6-pentafluorobenzyl)benzene: ^1H NMR (500 MHz, $CDCl_3$): δ = 7.15–7.11 (m, 4 H, Ar-H), 3.99 (s, 2 H, CH_2), 2.33 (s, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 144.1–143.9 (m, Ar-C), 140.9–140.8 (m, Ar-C), 138.9–138.7 (m, Ar-C), 138.6–138.4 (m, Ar-C), 138.3 (s, Ar-C), 136.7–136.4 (m, Ar-C), 134.4 (s, Ar-C), 129.5 (d, $^{4/5}J_{C,F}$ = 6.38 Hz, Ar-C), 128.2, 126.8 (s, Ar-C), 114.7 (t, $^{2/3}J_{C,F}$ = 18.22 Hz, Ar-C), 27.7 (s, CH_2), 20.9 (s, CH_3) ppm. $^{19}F\{^1H\}$ NMR (282.28 MHz, $CDCl_3$): δ = –67.4 (d, $J_{C,F}$ = 8.24 Hz, 1 F, Ar-F), –67.5 (d, $J_{C,F}$ = 8.24 Hz, 1 F, Ar-F), –81.4 (t, $J_{C,F}$ = 20.61 Hz, 1 F, Ar-F), –86.4 (d, $J_{C,F}$ = 8.24 Hz, 1 F, Ar-F), –86.5 (d, $J_{C,F}$ = 8.24 Hz, 1 F, Ar-F) ppm. GC/MS analysis: m/z = 272 $[M]^+$.

X-ray Diffraction Studies: Single crystals of complexes **1**–**7** were obtained by diffusion of Et_2O into CH_2Cl_2 solutions. The crystal of **1** contained two independent molecules in the asymmetric unit of the cell. Suitable crystals were mounted on quartz fibres and X-ray data collected with a Bruker AXS APEX diffractometer equipped with a CCD detector and a graphite-monochromated Mo-K_α radiation source (λ = 0.71073 Å). Data collection, reflection indexing and determination of the lattice parameters and polarization effects were performed with the SMART program suite.[23] Integration of reflection intensities and scaling were performed with SAINT. Empirical absorption correction was performed with SADABS.[24] Space group determination, structure solution and least-squares refinements on $|F|^2$ were carried out with SHELXTL.[25] 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, with hydrogen atoms placed in their ideal positions. The structures of **1** and **2** are shown in Figures 2 and 3, respectively, whereas the other structures (of **3**–**7**) are available as Supporting Information. Selected crystal data for complexes **1**–**7** are given in Tables 2 and 5. CCDC-742911 (**1**), -743693 (**2**), -743695 (**4**), -743696 (**5**) and -743698 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Crystal structures of complexes **3**–**7**.

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